NONEQUILIBRIUM GENERATING FUNCTIONAL AND DYNAMICS OF COARSE-GRAINED VARIABLES

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Abstract

A generating functional formalism is developed to facilitate the derivation of coarse-grained dynamics of macroscopically relevant variables in various types of many-body problems. The relevant variables can be found either by using symmetry analysis of the action or experimental data. The outcome of the coarse-graining process is a set of coupled partial differential equations for the expectation values of the relevant observables. The set of the macroscopically important observables consists typically of conserved variables and order operators, which are related to the broken symmetries of the system. Symmetry breaking (spontaneous or explicit) in the formalism can be dynamically induced by coupling the system to a generalized heat bath.

The nonequilibrium generating functional formalism is applied to coarse-graining of generalized hydrodynamics of macroscopic quantum phenomena such as Bose fluids and superconductors, and finally classical fluids. The method is by no means restricted to fluids, but can be applied to condensed matter problems as well. High density systems are in general more problematic and it remains to be seen if one can come up with more powerful approximation methods within the current formalism in the future.

The generating functional formalism is shown to reproduce in the specific limits the well-known ground state, finite temperature and time-dependent density functional theories in the quantum regime. We enlarge the set of relevant variables to include also non-conserved order-operators and show how to form generalized density functional theories, which can be by construction linked to the phase-transition behaviour of the system. They are extensions of the traditional density functional theories that were not developed to describe phase changes but only facilitated the expression of the system's (free) energy in terms of the conserved density variable (e.g. number density of electrons).

We develop a generalized density functional theory (effective action of the generating functional) for superconductors and superfluids. For superconductors it is shown by simple symmetry analysis that the relevant order parameter is the pair field of two electrons. Coarse-graining out the phononic degrees of freedom is shown to lead to a retarded effective interaction between the electrons. In the local static limit (effective interaction between electrons static) the theory reduces to the time-dependent Ginzburg-Landau theory. Similarly, by symmetry arguments, the order parameter of a weakly interacting Bose fluid is identified and its dynamics in the tree level approximation is shown to follow the Gross-Pitaevskii equation. Higher order corrections can be systematically produced.

Classical molecular dynamics and stochastic cellular automata types of higher level descriptions can be mapped into the same formalism using commonly known techniques. It is also shown how to connect the static and dynamic density functionals to phase-field models (models of critical dynamics), which are commonly used in materials science modelling. A specific example is provided for a liquid-gas-solid system. The phase-field modelling is then

applied to the derivation of dynamics of the liquid-gas phase boundaries and triple lines for which a new projection operator technique is developed. We explain in detail how to go from microscopics to macroscopics and relate the effective parameters on each level to each other. For example, we express the macroscopic surface tensions from the phase-field model in terms of the molecular dynamics simulation parameters. We also discuss how to extract the relevant cross-over time and length scales from the theoretical description and relate them to the experimentally measurable ones. It is shown how the coupling of the triple line and the liquid-gas boundary leads to emergence of memory effects. For confined geometry we also derive a new form for the restoring force acting on the contact line. The phase-field model of the liquid-gas-solid system is first discussed without explicit hydrodynamics from the point of view of diffuse mass transfer and then hydrodynamic effects (momentum conservation) are added.

Evolution equations are derived for the mass, momentum and energy densities representing the proper set of macro variables of simple fluids. The derivation is based on a macroscopic Poisson bracket formulation of phase-field dynamics. Navier-Stokes equations are obtained with extra force terms arising from wall-fluid interactions and capillary stresses. It is also shown how the hydrodynamics boundary conditions for stress tensor can be derived from the bulk fields alone in the sharp interface limit. Some mechanisms for generation of the no-slip boundary condition are also hypothesized. These results are important because they show how in general boundary conditions and corrections to them can be derived and how the numerical implementation can benefit from such a formulation of hydrodynamics, where all boundary conditions are expressed in terms of bulk fields alone. Again, these results have wider applicability than the setting where they have been derived.

The advantage of a systematic coarse-graining procedure enables us to clarify the role of the order parameter concept in the phase-field description of one and two component fluids. We also consider different ways of including gravitational effects and apply dimensional analysis to obtain a condition for the onset of capillary turbulence.

Finally, we present some new formalism for stochastic processes, where the relevant field variables are embedded in an environment characterized by quenched disorder. Whenever some lower dimensional (e.g. defect) structures are projected out of the bulk field evolution equations containing either frozen of coarse-graining generated noise fields, a more complicated effective stochastic noise component will appear in the projected equation of motion of the defect. In particular, the effective noise can be long-ranged even if the quenched background disorder is not. Several condensed matter and hydrodynamical examples describing dynamics of interfaces and line-like objects such as polymers and domain wall defects are considered.

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Colleagues, friends and family,
Thank you.

Helsinki, 19.4.2004
Sami

Author's contribution specified

This section provides a specification of author's original contributions. It is meant to complement Sect. 1.3.1, which contains more explanation on the technical facts. Original work in each chapter is explained below.

Chap. 2 (Non-equilibrium generating functional formalism). Author extends the concept of η-ensemble to cover more general situations than the superfluid [1] example (Sect. 2.1.2). Author shows how the standard quantum mechanical density functional descriptions both for equilibrium and non-equilibrium systems can be derived from a unified formalism (Sect. 2.3.1 and Sect. 2.3.2). These have been been treated as separate issues in the past. Author also extends the meaning of the density functional theory to cover not only the densities of the conserved variables but also those of non-conserved order parameters. Generating functional of similar to used in this work has been suggested in Ref. [2] but as discussed in Sect. 1.3.1, the author approaches the subject from different direction stressing the phase transition aspect. In Sect. 2.4 the author shows how one can extend the formalism to cover more macroscopic starting points. The basic techniques are well known but some generalizations to dissipative systems are presented in Sect. 2.4.1, which have not been combined before in the context of the generating functional formalism. Also the example considered in Sect. 2.4.2 is a new one.

Chap. 3 (Symmetry principles). Many new ideas are suggested to formalise the search of relevant variables. In Sect. 3.1.2 the author applies the ideas presented in Ref. [2] to the justification of the form of the equations of motion of classical fluids. Sect. 3.2 explains how the dynamic symmetry group concept can be useful for more systematic isolation process of relevant degrees of freedom. Even though group theoretical means are commonly utilized in various fields of physics, the author is not aware of systematic application of such techniques within the present nonequilibrium framework. Discussion on dynamic symmetry restoration is also presented.

Chap. 4 (Related approaches). Author shows how the generating functional formalism is related to the different formalisms. More specifically, Sect. 4.1.1 explains some of the mappings between the Peletminskii & Yatsenko & Bogolubov approach and the coarse-grained density matrix theory. Sect. 4.2.1 covers analogs between the Peletminskii & Yatsenko work and Zubarev's formalism. Finally, the similarities between Zubarev's formalism and the non-equilibrium generating functional method are discussed in Sect. 4.2.2.

Chap. 5 (Hydrodynamics of macroscopic quantum systems). Some new ideas, which supplement the symmetry based approach advocated in the thesis, about nuclear density functional theory are discussed by the author in Sect. 5.2. A new type of phonon mediated time-dependent interaction between the electrons is derived by author in Sect. 5.3. Not much effort is used for its detailed analysis given the crudeness of the initial assumptions in its derivation. Based solely on the symmetry principles, the order parameter is isolated in Sect. 5.5: Knowing its microscopic representation, its interpretation becomes unambiguous. The same procedure is also illustrated for superfluids in Sect. 5.7.2. Thus, even though the representation and equations of motions of the order parameters for conventional superconductors and superfluids are well-known, they are derived by new technique, which also allows for straightforward extension of the old results. Also, the identification process of the order parameter as presented by the author is different from the standard exposures to the subject and it is by no means restricted to the examples studied in this chapter.

Chap. 6 (Density Functional Theory). The author proposes a new way of constructing classical density functional theories in Sect. 6.1.3: It is just a straightforward combination of the effective action (of the generating functional) and Doi's [3] techniques. The author presents some analogs between different formulations of non-equilibrium thermodynamics in Sect. 6.5.

Chap. 7 (Phase-field models and density functionals). The new result of Sect. 7.3 is the mapping of the density functional of the liquid-gas-solid system to the phase-field free energy, a simplified form of which has been utilized in the previous work of the author [4]. Both the mapping and the phase-field model used are new ones. In addition, the author is not aware of any systematic attempts to relate phase-field models to (dynamic) density functional theories.

Chap. 8 (Phase boundary dynamics in liquid-gas-solid system). Sect. 8.2.1 contains introductory material derived in the sources mentioned in references therein. Apart from the phase-field surface tensions presented in Sect. 8.2.2 (first derived by M. Dubé) and the dissipative terms of sessile droplet contact line mentioned in Sect. 8.9, all other results are author's own.

Chap. 9 (The route to classical hydrodynamics). Based on macroscopic Poisson brackets, the author derives classical hydrodynamics from first principles. The results are reflected in appearance of novel bulk force terms of capillary stresses and wall-fluid interaction term. The form of the former has been postulated before, but the derivation here contains some new elements. The author systematises the change of macro-variable basis of two-component fluids in Sect. 9.5.3 and shows what kind of complications are imposed by the velocity representation on the fluctuation-dissipation theorem in Sect. 9.5.2. As a new important result the author shows that when dissipation is present, the definition of macroscopic velocity field in terms of the momentum density field leads to contradictory results as far as the equations of motion go. The momentum density field should be considered more fundamental than velocity as the density of conserved quantity.

Chap. 10 (Bulk forces). In Sect. 10.1 the author shows that the pressure term is fixed by the equation of state in the Poisson bracket derivation. The implementation of gravitational effects on fluids are considered in Sect. 10.2. Sect. 10.4 is meant to clarify the choice of the unit systems for dimensional analysis.

Chap. 11 (Emergence of boundary conditions). A systematic derivation of the hydrodynamic boundary conditions on the jump conditions of the stress tensor based on the electromagnetic analogue in Sect. 11.2.2. In Sect. 11.3.1 the author shows what is the microscopic origin of the zero normal velocity condition at solid walls. The derivation of zero tangential velocity at solid-fluid interfaces is harder and some explanations based on diverging viscosity are presented in Sect. 11.3.2. An attempt to clarify the emergence of dissipative phenomena in the vicinity of the solid-fluid boundary based on the in-equivalence of the velocity and momentum representations are pondered in Sect. 11.4.

Chap. 12 (Stochastic properties of interfaces and lines). Some examples of quenched noise processes are presented. The author develops the concept of effective noise correlator, and explains how it can be computed in practice. As the main example serves the domain boundary motion in the continuum version of Random Field Ising model. Different scaling regimes of structure function are studied and results for slow driving are shown to compare favourably with simulations.

Part III (Appendices). Except for App. D.4 (which is based on Ref. [5] with more details and intermediate steps added by author) all material is author's own.

Contents

Part I

Formalism

Chapter 1

Introduction

1.1 Emergence and coarse-graining

More is different. Take a system with the just two constituent objects: Be they men, or mice or elementary particles. Studying experimentally what a single specimen does, when left in an isolated laboratory on its own devices, does not really tell for sure what two specimen would do together. Not to mention ten specimen, or a million. If they were atoms, they might form molecules, which would form bigger structures such as polymers, micelles and finally complex forms of inanimate or living matter. If the specimen were men they would probably form alliances, trade unions, political parties and different schools of thinking about the complex appearance of the world around them. Some of the men would become philosophers and some physicists. And the latter would not be very popular among the former due to their oversimplified reductionist attitude towards the deep concept of emergence.

The reductionist approach to understanding of nature requires that one first specifies the starting level, i.e a microscopic model, which is equivalent to identification of the constituent objects, which make up the system, and interactions (forces) between them. Based on this information, one tries to come up with explanations concerning the collective behaviour of the constituent objects. Collective phenomena are usually detectable only on scales larger than those characteristic of the microscopic model. Therefore one refers to them also as macroscopic phenomena. Reductionist tries to understand the macroscopic phenomena using macroscopic laws derivable (in principle, at least) from a microscopic starting point. Even though he recognizes the fact that more is different from few, he believes that it is possible to say something about the world on a more macroscopic level given the *entire* microscopic model. This approach only makes sense if the microscopic model contains only simple interactions between not too many constituent objects.

Since the concepts of microscopic and macroscopic are not strictly defined, we would like to be able to construct an entire chain of effective models, starting from the one defined on the finest scale and moving on up to larger and larger scales. The process of constructing effective models is called coarse-graining. The aim is to filter out the microscopic degrees of freedom which are not essential to the more macroscopic questions we ask about the system. If the system is correctly chosen, which in technical terms translates to requirement of clear separation of time scales involved in description of phenomena at different coarse-graining levels, we should be able to produce a relatively simple model of the system on a more macroscopic level. For example, if we want to know whether there will be some overspill from a glass of water experiencing a sudden disturbance of a shaky hand, we do not have to solve 10^{23} Newton's equations of motion for all the water molecules, which make up the microscopic model. Instead it suffices to study just a handful (five!) of equations of motion (Navier-Stokes equations) in the coarse-grained macro model, which comprises evolution equations for relevant macro variables, i.e. the mass, momentum and energy densities. The relevant variables are also called coarse-grained variables, or slow variables, because the time scales where they experience considerable changes are much larger than the time scales of the more microscopic degrees of freedom, which have been coarse-grained away. As far as the spilling of water goes, we can reduce the number of macro variables even further owing to the fact that we are only interested in the movement of the liquid-gas phase boundary. Defining a new collective coordinate, which specifies the position of the water-air interface, we can integrate out the bulk degrees of freedom of the Navier-Stokes equations and obtain a further coarse-grained model for the collective interface coordinate alone. This represents another stage of coarse-graining chain and is precisely something we will be doing in this book later on.

Technically the process of coarse-graining consists of three stages. The first stage, identification of the microscopic starting point, is usually the easiest in natural sciences (physics especially) since basic constituent particles and the forces between them can be found. In other fields of science this is more difficult: What is the force between two living cells or two investors in the stock market, are much harder questions. The next step of coarse-graining consists of identification of the relevant variables in our large scale description. In other words, how can we characterize a complicated microscopic many-body system with the smallest possible number of macroscopic variables, which still allow us to sensibly answer the macroscopic questions we are interested in. How do we find the best possible 'collective coordinate basis'? In practice, one usually has to rely on intuition and experimental data at this stage. It is justified, though, to ask how far can we go by using only the information of the microscopic starting point. This question haunts the reductionist mind of the physicist: We would like to be able deduce the relevant variables from microscopics in principle at least and avoid any recourse to emergent arguments. Then again, because the relevant variables by definition have to do with the macroscopic description, it can very well be that not all of them can be isolated without the use of higher level (more coarse-grained) information, which is needed for there recognition. Certainly we can never replace intuition with a mechanical machinery, but it does not hurt to try to develop a technique that can guide the creative thinking. As is clear from the glass-of-water example, the relevant coarse-grained variables can take rather different forms like the hydrodynamic fields of the Navier-Stokes equation and the collective phase boundary coordinate. It turns out that these types of variables are in principle naturally arrived at using symmetry analysis. Unfortunately, there is no systematic and *practical* way of revealing the invariances of the action or symmetries of the density matrix but in the simplest cases. Yet, we believe that it is possible to go beyond the mean-field level in many cases of interest with proper combination of present techniques, if one wants to be able to find the relevant variables from first principles.

The third stage of coarse-graining process produces the equations of motion of the relevant variables. There exist several techniques in the literature for this stage. Classification of them can be made in many ways depending on the basic postulates of each approach. For example, Non-equilibrium Thermodynamics [6, 7, 8], Rational thermodynamics [9] Generalized Thermodynamics [10] and Nonlinear Thermodynamics of irreversible processes [11] start from given set of macro variables. Some approaches such as local space average methods [12] and Generalized Irreversible-Reversible Coupling [13] formulations of continuum thermodynamics have a more microscopic starting point and especially the latter allows for a more systematic development of the coarse-graining chain. The method of producing the evolution equation presented in this work is based on the concept of *nonequilibrium generating functional*, which contains the full microscopic information and the possibility of producing the evolution equations at chosen level of coarse-graining. Owing to the use of the microscopic information in the derivation, our approach is closer the powerful projection operator technique [14] formulations of kinetic equations than the traditional macroscopic theories of nonequilibrium thermodynamics. Of course, in this context we cannot forget the great amount of work that has been put in derivation of transport equations of gases and plasmas (Boltzmann, Vlasov, Balescu-Lenard etc.) in classical [15] and quantum systems [16]. Especially the derivation of hydrodynamic Navier-Stokes equations starting from the Boltzmann equation is analogous to the philosophy advocated with the nonequilibrium generating functional formalism: Invariance analysis of the collision operator (which is already an effective coarse-grained object) reveals the conserved quantities (mass, momentum and energy observables) in the same way as the invariance analysis of the (coarse-grained or microscopic) action yields the relevant variables generating functional formalism.

The outcome of the successfull coarse-graining process is a set of coupled Langevin equations of motion for the relevant variables $\phi_i(\mathbf{x}, t)$. Schematically,

$$\partial_t \phi_i = f(\phi_i) + \eta_i \; . \tag{1.1}$$

Coarse-graining process gives rise to a stochastic force terms denoted by η_i. Here we have written it as additive type of noise for simplicity (in many applications to be considered the noise is actually of multiplicative type). The noise contains contributions from three different sources. First, the effect of the fast degrees of freedom, which have been removed by coarse-graining, on the relevant slow variables can be modelled by a rapidly oscillating noise term. Second, our knowledge of the system is not usually perfect, which results in the appearance of random fields (e.g. impurity fields) in the equation of motion. Finally, the nonlinearities of the theory can be modelled approximately by adding a stochastic component to the linearized deterministic part of the equation. In case the system is fully self-averaging (relative fluctuations vanish in the large scale limit), our knowledge of the microscopic starting point is perfect, and nonlinearities are allowed, the noise term will not be present in Eq. (1.1). One of the advantages of the nonequilibrium generating functional formalism is that the properties of the noise term can be derived, they do not have to be put in by hand.

An ultimate theory of coarse-graining would not only tell which variables are relevant but it also gives means to climb up the coarse-graining ladder from one effective theory to the next describing a whole hierarchy of models. How to do these things in practice (or how to explain them at the level of principle at least) is one of the important open problems of contemporary science. Our goal is more modest: We test our ideas of finding the relevant variables based on symmetry arguments on a few well-known classical and quantum mechanical examples and show that the principles we have put forward really work in these cases. As what comes to the construction of the whole chain of effective models, we typically settle for a two-step chain: We go from an interacting many-body problem to a dynamic density functional theory and from there on to dynamics of lower dimensional structures such as phase-boundaries and lines. Since the formulation of the theory (generating functional) is well-suited for renormalization group (RG) analysis, there is a possibility of constructing a whole (continuous) set of effective theories. In its traditional form, though, the field-theoretic momentum shell renormalization group is too 'democratic' for this purpose: An ultimate coarse-graining technique would have to use a selective type of RG guided by the symmetry analysis performed at each effective level of description.

As an example of a hierarchical chain of models let us consider modelling the dynamics of a set of adatoms on a crystal substrate. The macroscopic problem we are interested in is the behaviour of the center of the mass of the adatoms in the course of time. It is known to be described by a diffusion equation on the large scales [17]. The microscopic starting point could be the quantum mechanical many body description of the substrate + adatoms complex. Via first principles calculations of the adiabatic potential energy surface seen by the adatoms, we can infer their jump rates, which can be used as input parameter of of higher level lattice-gas cellular automata model, which can be further coarse-grained using the methods presented in this work to finally yield the diffusion equation, which gives the hydrodynamic continuum level description of the whole problem. In this way we can integrate the formalism presented in this work with the existing coarse-graining and simulation methods suitable for multi-scale modelling of materials science [18, 19]. We also consider applications of the nonequilibrium generating functional to a direct coarse-graining of density functional representation of quantum and classical many-body systems, without introduction of intermediate coarse-graining levels.

1.2 Goals of this work

This book is intended to communicate to the reader that the idea of coarse-graining can be formulated in a way, which truly encompasses many fields and helps in their conceptual understanding by building bridges between seemingly unrelated things at first sight. On a theoretical side the advantage is more coherent presentation of the subjects. On the practical (computational) side the benefits are that the current formulation is able to connect techniques designed for different effective levels of description. For example, deriving a continuum field theory out of a lattice-gas or molecular dynamics simulation is straightforward. Not all transitions are that easy to describe, though. We are not claiming to be able to unambiguously cross the quantum-classical boundary by deriving Newton's equations of motion for coarse-grained point particles whose quantum mechanical description is given by complicated electron-nucleon wavefunction. Of course, these effects are included in the theory, but one has to come up with more power approximation schemes to obtain practically calculable higher level models. For example, decoupling the nucleons from electrons and treating the former classically results in a classical many-body interaction potential between the classical 'atoms' (nuclear ions), which are not of simple two-body or three-body form, but formally N-body form (where N is a large number). Systems with these types of potentials are difficult to coarse-grain further just by mechanical application of the formalism. If one is able to show that actually the classical atoms really interact only via few-body potentials then one can make some progress.

The main formal message of the generating functional formalism can be condensed into the following relation:

$$\text{effective action } \mathcal{A} = \text{generalized density functional} \rightarrow \text{free energy F} \ . \tag{1.2}$$

This relation provides the connection between the quantum field theoretical effective action (generating functional) and the density functional theories commonly used in electronic structure calculations and classical many-body statistical mechanics. The effective action is a time dependent quantity: Taking variations with respect to its argument fields, which are the relevant variables, we generate their equations of motion. If the system equilibrates in the limit $t \rightarrow \infty$ the effective action gives the static thermodynamic free energy of the system and the equations of motion reduce to equations of state. The last statement is very difficult to prove because of the complicated nonlinear structure of the theory, but at least it can be made plausible in the perturbative sense.

The effective action is also called a generalized density functional, because it not only generates the density functionals of conserved variables (such as number, mass or electron density), but it can also contain order parameters of the theory. This is a point which was missed in the traditional derivations of density functional theory: The generating functional formalism takes into account possible phase transitions, if one is able to find the relevant order operators using first principles or experimental information. It also provides a direct link to important materials science simulation technique called phase-field modelling. The free energy which is used in phase-field models can in principle (and, as our examples will show, in practice, too) be obtained from the density functional, which contains both conserved variables, and order parameters, and their couplings. At this point we have to point out that much of the usefulness of the generating functional formalism for practical calculations depends crucially on the determination of the effective action. Usually this is not an easy task, especially for systems having high densities. However, for many interesting problems, especially critical phenomena related, the precise form of the free energy is not so important and the interesting phenomena will manifest themselves already in the lowest level approximations.

In addition to the generating functional itself, another unifying principle utilized in this work is the use of symmetry principles in *recognition* of the important degrees of freedom. This works both for bulk macro degrees of freedom and for lower dimensional structures such as defects of the order parameter fields [20, 21, 22]. We only concentrate on simple types of defects: Domain walls (phase-boundaries and triple lines), whose projected dynamics is studied in the Applications part. As for bulk dynamics, we discuss how to find the important macro variables based on the symmetries of the action or the density matrix of the system. The non-relativistic generalization of Goldstone's theorem is an important tool for this.

The generating functional formalism and the symmetry principles hopefully provide a more homogeneous picture of the different fields we will be discussing. We show how different starting points for the coarse-graining process, such as classical molecular dynamics level or stochastic cellular automata level can be described using the same language as used on the genuinely quantum mechanical level. This allows the use of the same symmetry principles for different level phenomena. Seeing the symmetries from Newton's equations of motion, or from transition rules of the cellular automata could be very difficult otherwise. Being able to isolate the relevant variables from first principles naturally allows their correct interpretation in simple enough cases where this is possible. This is not always obvious at the macro level. Similarly, it is not always clear from the macroscopic point of view, how to include more microscopic effects in the coarse-grained description. For example, how to include the solid-fluid interaction in the free energy of the density functional formalism. Questions like this can be clarified using the information obtainable from density functional theory.

Finally, we wish not to overestimate the power of the generating functional formalism. The fact is that in its generality the nonequilibrium generating functional formalism is not the best possible tool to be used at each level of the hierarchy of effective models. More specific techniques work better in cases they have been developed for. However, the generating funtional method can be used to complement and unify the specific techniques.

1.3 Contents explained

1.3.1 What is new, what is old and what is in-between

The main difference to traditional formulations of quantum field theoretical models familiar from particle physics is the choice of the time integration contour. There have been many formulations which combine the equilibrium and nonequilibrium processes by a suitable choice of the time-path (Kadanoff-Baym, Keldysh). Historically, the stress has been on the Green's functions and the generating functional has received less attention. The nonequilibrium generating functional formalism presented in this work is identical to the closed-time path Green's function (CTPGF) formalism as presented in Ref. [2]. Chou et al. pointed out the important feature that composite operators can be used in the generating functional including conserved charges and order parameters. What the authors did not mention is the important relation to the density functional theories (quantum and classical, equilibrium and nonequilibrium), which we have explained in this work. Moreover, we have tried to develop a systematic scheme to *identify the order parameters* based on the symmetries of the action and the density matrix. Chou et al. only discussed how to find the conserved variables in addition to showing how to obtain the equations of motion for both conserved variables and order parameters. We have also used an explicit bath in many cases unlike Chou et al.

We are certainly not the first to suggest the use of symmetry principles, either. Those have been successfully applied in great variety of forms to statistical physics and condensed matter problems throughout the history of modern physics. Landau and co-workers explained how the macroscopic free energy can be constructed through symmetry principles as far as critical phenomena are considered.

To put it concisely, almost all of the material in the part Formalism of the book, is well known in one form or another in different areas of physics. Since we have arrived at the generating functional formalism from a little bit different direction than Chou et al., we have stressed more the phase transition aspects. In part Applications the dynamic symmetry group analysis of density matrix and identification of relevant variables has not been discussed in the literature to the extent we present the subject and apply it to macroscopic quantum phenomena in Sect. 5.5. We also derive the equation of motion for the superconductor, which contains a retarded interaction between the the electrons. In the static limit the theory reduces to the time-dependent Ginzburg-Landau model. Similarly, we show that the lowest order order parameter dynamics of a weakly coupled Bose fluid is given by the Gross-Pitaevskii equation. In part Applications we also use the fact (shown in Sect. 2.3) that the generating functional reproduces three different density functional formalisms (Sect. 2.3.1 and Sect. 2.3.2). The ground state and finite temperature formalisms based on effective action technique has been recently derived in Ref. [23] and the dynamic density functional in Ref. [24]. We merely combined these works. In Chap. 7 we clarify the connection of the phase-field free energy to the density functional. Traditionally, the phase field free energies are justified using either macroscopic symmetry arguments or using coarse-grained equilibrium partition function. Chap. 8 contains almost entirely new results. Especially, a new projection formalism capable of attacking dynamic problems is developed for domain walls and triple lines. In applications to classical hydrodynamics starting from Chap. 9 we systematically apply the generating functional formalism to derivation of equations of motion of simple fluids. The outcome is the well-known Navier-Stokes set of equations for relevant variables. There are new force terms in the equations of motion, though, which are not present in the traditional equations. These result from the capillary stresses and interaction with the solid wall. The capillary stress aspect has been discussed before using the phase-field language, e.g. Ref. [25]. We also show the danger of using nonlinear transformations from one set of relevant variables to another. These effects have not to our knowledge been thoroughly discussed. Finally, in Sect. 12.3 we discuss how to replace the complicated quenched noise seen by a moving phase-boundary by an equivalent stochastic process, which makes understanding of the non-equilibrium critical dynamics of collective field coordinates more transparent.

1.3.2 How to read this book

The main formalism has been presented in part Formalism. In part Applications the nonequilibrium generating functional formalism is applied to coarse-graining of hydrodynamics of macroscopic quantum phenomena such as Bose fluids and superconductors, and finally classical fluids. The nasty details have been collected in the appendices. Many of the appendices are actually formulated in a self-consistent manner, so they can be read on individual basis, too. The largest set of appended material is related to the dynamics of liquid-gas phase boundaries (App. C) and classical hydrodynamics (App. D).

The idea of the Applications part of the book is to start from the quantum mechanical systems (Chap. 5), then introduce the reader to the traditional quantum mechanical density functional theory and show its similarity to the classical density functional theory via the Legendre transformation method in Chap. 6 Then, in Chap. 7 we show how to connect the static and dynamic density functionals to phase-field models. The phase-field modelling is then applied to the derivation of the dynamics of liquid-gas phase boundaries and triple lines in Chap. 8. This chapter explains in detail how to go from microscopics to macroscopics and relate the effective parameters on each level to each other. It also discusses how to extract the relevant parameters, time and length scales, from the theoretical description and relate them to the experimentally measurable ones. The phase-field model is first discussed without explicit hydrodynamics from the point of view of diffuse mass transfer in Chap. 8 and the hydrodynamic effects (momentum conservation) are considered in Chap. 9, Chap. 10 and Chap. 11. Finally, Chap. 12 deals with quenched stochasticity abundant in effective interfacial description of various processes.

Chapter 2

Nonequilibrium generating functional formalism

2.1 An intuitive approach to nonequilibrium thermodynamics

To get to the nonequilibrium thermodynamics we should start off by considering to which extent we can extend some concepts of equilibrium thermodynamics. There are many equivalent formulations of equilibrium thermodynamics. We prefer the partition function approach, which establishes a direct link to microscopic world. Partition function Z acts as a generating functional of macroscopically relevant variables such as pressure, internal energy, chemical potential, and so on. Equivalently, we can take some of the thermodynamic potentials such as Helmholz free energy F as the fundamental object as it is defined through $F = -\beta^{-1} \ln Z$, where $\beta \equiv (k_B T)^{-1}$, k_B is the Boltzmann's constant and T is the temperature. Typically, partition function depends on the parameters, which somehow constrain the evolution of the microscopic degrees of freedom in phase space. It will be a function of temperature since T determines the mean energy in canonical ensemble. The partition function will depend on pressure p when the system is confined in volume V. In addition, different types of fields can be coupled to the system biasing its behaviour in the phase space. There is a kind of a duality buried in equilibrium thermodynamics which allows us to express it either in terms of the constraint parameters (say magnetic field h and inverse temperature β) or in terms of the expectation values of the observables that are being constrained (in this case, magnetization $\langle \sum_i s_i \rangle$ and the average exchange energy $\langle H \rangle = \langle \sum_{\langle i,j \rangle} s_i s_j \rangle$) in case of an Ising ferromagnet, for example. The duality can be mathematically expressed through a Legendre transformation, which can be performed on all variables or just on a chosen subset of variables. In case of the Ising model, choosing the latter option relates the Gibb's free energy $G(h, T)$ and Helmholtz free energy F(M, T) via the partial Legendre transform

$$G(h, T) = F(M(h, T)) - h\, M(h, T) \ , \tag{2.1}$$

where the expectation value $\langle \sum_i s_i \rangle \equiv M$ is the magnetization order parameter. Thus, going from constraints (or generalized displacements) to expectation values of constrained observables (or generalized forces) produces a thermodynamic potential, which in the field theoretic language is called effective action. Usual thermodynamics deals with homogeneous variables with no spatial resolution, but it is not difficult to generalize it for spatially inhomogeneous situations, where the observables become $\mathbf{x}$-dependent fields. For instance, the generalization of the relation (2.1) to inhomogeneous external magnetic field $h(\mathbf{x})$ can be written as

$$G[h,T] \equiv F[M[h]] - \int d\mathbf{x}\, h(\mathbf{x})\, M(\mathbf{x}) \ , \tag{2.2}$$

where $M(\mathbf{x})$ is the smoothed version of the block spin magnetization in cell whose center point lies at $\mathbf{x}$. Since the fields have acquired spatial dependence, the free energy functions F and G have to replaced by functionals $F[M]$ and $G[h]$. The generating functional $Z[h]$, whose logarithm gives rise to the free energy $G = -\beta^{-1} \ln Z[h]$, we can be written as

$$Z[h] = \langle e^{\int d\mathbf{x}\, h(\mathbf{x}) \hat{M}(\mathbf{x})} \rangle_{eq} \ , \tag{2.3}$$

where $\langle \cdot \rangle_{eq}$ means average over equilibrium ensemble defined microscopically via the density matrix $\rho_{eq} = e^{-\beta H}$. The operator $\hat{M}(\mathbf{x})$ is the unaveraged magnetization, which by definition is a random variable, whose expectation value $\langle \hat{M}(\mathbf{x}) \rangle_{eq} \equiv M(\mathbf{x})$. It will become clear later on how to define the operator character of observables properly and how to technically include the spatial dependence as indicated in Eq. (2.3).

The magnetic field $h(\mathbf{x})$ is just one particular example of a constraining field $J(\mathbf{x})$, which in the field theoretic language can be called a source field. Similarly, the magnetization $\hat{M}(\mathbf{x})$ is one realization of a more general field variable denoted below by $\hat{\psi}(\mathbf{x})$, whose interpretation depends on the situation it is used. As will turn out later, the constrained degree of freedom $\hat{\psi}$ can be called a response field, an order-parameter field or simply a (macroscopically) relevant variable. Thus, in the general situation we can rewrite Eq. (2.3) as

$$Z[J] = \langle e^{\int d\mathbf{x}\, J(\mathbf{x}) \psi(\mathbf{x})} \rangle_{eq} \ . \tag{2.4}$$

The reason why we have dropped the hat above ψ is the averaging in Eq. (2.4) is to be understood in the *path integral sense*: ψ is just a dummy integration variable. The natural question to ask is if it is possible to generalize Eq. (2.4) to non-equilibrium situation. As will be shown in the rest of this chapter, this is can be done with minimal effort:

$$Z[J] = \langle e^{\int d\mathbf{x} \int dt\, J(\mathbf{x},t)\, \psi(\mathbf{x},t)} \rangle_{non-eq} \ , \tag{2.5}$$

The nonequilibrium probability weight is usually assumed to reduce to the equilibrium weight $\langle \cdot \rangle_{eq}$ as initial or final condition. Using a generalized functional Legendre transformation, we can now trade variable $J(\mathbf{x},t)$ for the expectation value $\langle \psi(\mathbf{x},t) \rangle_{non-eq}$ of the field operator in the same way as we traded the value of the external magnetic field h for $M = \langle \hat{M} \rangle_{eq}$ in Eq. (2.2):

$$\mathcal{A}[\langle \psi \rangle_{non-eq}] = -\ln Z[J] \ - \int d\mathbf{x} \int dt\, J(\mathbf{x},t)\, \langle \psi(\mathbf{x},t) \rangle_{non-eq} \ , \tag{2.6}$$

where we have replaced the Gibbs free energy G by the symbol of the effective action $\mathcal{A}$, which can also be called the generating functional of nonequilibrium thermodynamics. The terminology derives from the fact, that $\mathcal{A}$ contains all the information needed to describe macroscopic thermodynamics in terms of the averages $\langle \psi \rangle_{non-eq}$. Requiring the stationarity of the action with respect to variations of these expectation values produces the equations of motion of the relevant variables, that is, the generalized hydrodynamics. As noted in the introduction, the word hydrodynamics here refers in general to dynamics of macroscopically important degrees of freedom being by no means restricted to description of dynamics of fluids alone.

2.1.1 Missing pieces of the puzzle

We begin with a small inventory of the tool box. What kind of means do we have at hand when trying to explain the dynamics of an interacting many-body system? In many occasions we are forced to approach the non-equilibrium properties through the equilibrium ones relying on the assumption that when the deviations from the equilibrium state are small, the equilibrium information can still be made use of. Furthermore, there exist many techniques, which allow us to obtain the dynamics of the macroscopically relevant variables close to equilibrium. Formally one of the most rigorous paths from microscopics to stochastic dynamics of coarse-grained degrees of freedom is offered by projection operator methods. Since the early days of Nakajima [26], Mori [27] and Zwanzig [28] approaches there have been several later developments such as the Robertson [29] projection operator and the Kawasaki-Gunton [30] projection operator. The idea of these methods is to project out the irrelevant degrees of freedom and produce an equation of motion either for the relevant degrees of freedom directly or for the reduced density matrix describing the system. Typically, a reference state (equilibrium state) is assumed and the equations of motion should hold close to the reference state. This is clearly visible for example in the work of Mori, who produced a linear Langevin equation to describe the dynamics of any relevant observable not too far away from thermal equilibrium state described by density matrix ρ_{eq}.

The projection operator methods deserve a special merit being able to perform the coarse-graining process by rigorously filtering out the fast degrees of freedom. Of course, there is a price to be paid: In their bare form the equations of motion contain terms, whose evaluation requires drastic approximations. This is easy to understand as the starting level of the coarse-graining is the N-particle Liouville equation, where N is a very large number (for a generalization of projection operator formalism to a system with stochastic dynamics, instead of deterministic Liouville dynamics, see Ref. [31]). More specialized approaches existed already much before the projection operator methods. A whole lot of work has been devoted to the hydrodynamic description of liquids and gases revolving around the Boltzmann-equation and its modifications [15]. The less we insist on being able to rigorously connect the macroscopic description to the underlying microscopics, the bigger does the selection of different techniques at our disposal become. Leaving out Standard model level description of the matter, we can say that at the bottom of the hierarchy of effective descriptions lies the the many-body quantum Schrödinger equation (or classical Liouville equation). At the macroscopic end, on the other hand, we have theories of nonequilibrium thermodynamics which utilize phenomenological parameters, constitutive equations and so on, to yield the dynamics of the macro variables.

To summarize, we have many successful means of describing dynamics close to equilibrium once we know what the quantities of interest are. One of the biggest questions, which has not been satisfactorily answered so far, has to do with *finding* the relevant variables suitable for coarse-grained (macroscopic) description of the dynamics. If there is a way of deducing them from the underlying microscopic description of the problem, we should clarify their relation to existing classification of hydrodynamic variables, which to large extent still relies on equilibrium concepts. In other words, if relevant variables can be defined far a way from equilibrium, do they really reduce to their equilibrium counterparts and if so, under what conditions. For example, can the kinetic pressure or local temperature really be related to the variables p and T appearing in the (equilibrium) equation of state? Moreover, can we derive the constitutive laws, which express the currents in terms of the hydrodynamic variables? What are the general properties which make certain systems coarse-grainable?

There are many questions and few general answers. We summarize below a few things, which one has the possibility of shedding some light on using the generating functional formalism to be presented in this chapter.

- Existence of nonequilibrium generating functional (far away from equilibrium).
- Choice of relevant variables (symmetry principles and selective Renormalization Group).
- Form of the equations of motion of relevant variables.
- Stochastic properties of coarse-grained description.

Not to promise too much, let us comment a few things in the list. First, contrary to usual claims in the literature, we feel that the generating functional $Z[J]$ deserves to be called a nonequilibrium partition function as it generates the equations of motion the same way as taking derivatives of ordinary partition function generates equations of state. In the construction there is nothing that would exclude arbitrarily large values of the driving source field J, which implies that the formalism should work for far-from-equilibrium situations as well. Of course, many practical methods of evaluation of the equations of motion or the search methods of relevant variables utilize the fact that the deviation from equilibrium is not too large. In principle the formalism yields the the coupling terms binding together the evolution of the different components of the order parameter, as well as the nonlinear self-interaction terms, which may not always be so easy to fix based on shear symmetry principles of the type used typically in the construction of Landau free energy [32]. Then again, for dense systems we cannot use only the lowest order terms but have to work very hard to generate the relevant higher order corrections. As what comes to the search of the relevant variables, we can only offer a partial answer, which concentrates around identification of conserved and broken-symmetry variables. Here we slightly modify the usual rhetoric, which only mentions the conserved variables and symmetries related to the Hamiltonian of the system. Instead, we identify the symmetries of the density matrix (or the effective action $\mathcal{A}$) and thereby pin down the relevant macro degrees of freedom. Unfortunately, we have very little to offer to systematize the search of relevant variables using improved Renormalization Group (RG) techniques, but we want to point out the importance and potential of new schemes [33, 34], which seem offer some possibilities in this direction and can be readily used within the current framework. Finally, we point out the relevance of the nonequilibrium generating functional method for the deriving the properties of the noise fields which will typically emerge in Langevin type of equations of motion of the relevant variables due to the removal of fast degrees of freedom. The generating functional facilitates the determination of the noise properties (correlation functions) from the first principles.

2.1.2 The idea of generalized η-ensembles

To motivate the generating functional formalism, we will discuss how the idea of spontaneous symmetry breaking naturally leads to construction of probability weights, which we call generalized η-ensembles. In turn, the phase transition picture present the η-ensemble can be formalized and studied by functional Legendre transformation, which relates the effective action $\mathcal{A}$ to the nonequilibrium generating functional. Let us begin by considering the familiar Ising model of a ferromagnet. The equilibrium partition function can be written as

$$Z(T) = \mathrm{Tr}\, e^{-\beta \sum_{\langle i,j \rangle} s_i s_j} \equiv \mathrm{Tr}\, \rho^0_{eq} \; . \tag{2.7}$$

Summation over nearest neighbours is implied in the exchange term and trace means the summation over all spin degrees of freedom $s_i = \pm 1$. If one is interested in studying the order-disorder transition, the relevant order parameter is the magnetization M, which is defined as the expectation value of the order operator $\hat{M} = \sum_i s_i$ over the equilibrium density matrix. However, using ρ^0_{eq} defined in Eq. (2.7) produces always the same result, $M = \mathrm{Tr}\{\hat{M}\rho^0_{eq}\} = 0$ due to the reflection symmetry of the microscopic Hamiltonian even if one goes to the thermodynamic limit. To generate a non-zero expectation value signalling the emergence of long range order, one should study the properties of the ensemble, where there is an additional coupling of the spin degrees of freedom to an external magnetic field h:

$$Z(T,h) = \mathrm{Tr}\, e^{-\beta \sum_{\langle i,j \rangle} s_i s_j + h \sum_i s_i} \equiv \mathrm{Tr}\, \rho^h_{eq} \ , \tag{2.8}$$

Unlike $Z(T)$, $Z(T,h)$ does reveal the ordering transition when the number of spins approaches infinity. In the thermodynamic limit the partition function is not anymore analytic in the whole phase space (T,h). This is reflected in the fact that even for infinitesimally small magnetic field h, there can be a finite magnetization in the system. Thus, below the critical temperature, $T < T_c$

$$m = -\lim_{h \to 0} \lim_{N \to \infty} \frac{1}{\beta N} \frac{\partial \ln Z(T,h)}{\partial h} \neq 0 \ , \tag{2.9}$$

where we have defined magnetization per spin $m = M/N$. The essential point is the following: If we take the thermodynamic limit $N \to \infty$ (or volume $V \to \infty$) before h is taken to zero, a non-zero value of the order parameter does reveal the phase transition, whereas inverting the order of the limits does not. In a sense, adding an infinitesimally small magnetic field is just a trick, but an essential one. It was first introduce by Bogolubov under the name of quasi-averaging [35, 36].

More generally, Bogolubov's quasi-averaging scheme has been designed for system's whose Hamiltonian H possesses some symmetry. In order to study the phase transition associated with the spontaneous breakdown of the symmetry, one calculates the expectation value of the order operator over an ensemble, whose Hamilton's operator has been perturbed by an additional term ηH_{pert}, which breaks the symmetry of H. In the thermodynamic limit, when $\eta \to 0$, non-zero expectation values will be generated analogously to the Ising model. In cases where the limit zero limit of η does not exist in the simplest setting described above, auxiliary conditions must be imposed, which facilitate the computation of the quasi-average [37]. Using temperature as the control parameter, we can say that the high temperature phase corresponding to symmetry group G of H does not describe the properties of the system any more in the low temperature $(T < T_c)$ symmetry broken state, where the density matrix is invariant under smaller symmetry group $G' \in G$. We can *approximate* the broken symmetry state by density matrix of the form $\exp(-\beta H + \eta H_{pert})$, where the symmetry group of $-\beta H + \eta H_{pert}$ is G'. In general, the density matrix does not have to have this simple Gibbsian form but it produces in many cases a reasonably good approximation. When the state (ground state or thermal state described via density matrix) of the system does not share the same symmetries as the Hamiltonian H of the system we say that spontaneous symmetry breaking has taken place. As is clear from above, the definition of system Hamiltonian H takes place through the equilibrium density matrix, so it would be more proper to talk about the symmetry of ρ, when evaluating averages of order operators. We will come back to this point later.

Application of Bogolubov's quasi-averaging to Bose superfluids gives rise a restricted ensemble, which is called η-ensemble [1] after the perturbing external field

$$\hat{\rho}^{\eta}_{eq} \equiv e^{-\beta \hat{H}_B + \eta \int d\mathbf{x}\, \hat{\psi}(\mathbf{x}) + h.c.}\ , \tag{2.10}$$

where the field annihilation operator $\hat{\psi}$ plays the role of the order operator $\hat{M}$ of the magnetic example, and *h.c.* stands for hermitean conjugation. The microscopic Hamiltonian of the weakly interacting Bose fluid is $\hat{H}_B$. It is easy to see that $\hat{\rho}^{\eta}_{eq}$ is completely analogous to the density operator ρ^{h}_{eq} defined in Eq. (2.8). The action of infinitesimal η is to induce a phase transition when the control parameter $T < T_c$. Instead of long range spin order we have long range phase order (to be discussed later), which manifests itself in the non-zero expectation value of the order operator $\hat{\psi}$: $\lim_{\eta \to 0} \mathrm{Tr}\{\rho^{\eta}_{eq} \hat{\psi}\} \neq 0$ for $T < T_c$. The crucial difference as compared to the ferromagnetic example is that the constraining field η is not experimentally realizable in the laboratory like the external magnetic field h. This is not something quite unexpected given that also the symmetries which are broken can in general be quite abstract. After all this said and done we are now ready to generalize the concept of the η-ensemble to the general case of many-body system described by a density matrix, which for familiarity's sake is assumed to of Gibbsian form $\hat{\rho}^{0}_{eq} = \exp(-\beta H(\{\hat{a}^{\dagger}_i\}, \{\hat{a}_i\}))$. In the following we will call the basic creation and annihilation operators $\hat{a}^{\dagger}_i$ and $\hat{a}_i$, reserving the symbol $\hat{\psi}(\{\hat{a}^{\dagger}_i\}, \{\hat{a}_i\})$ for the order operator, which is some function of the basic field operators. In the Bose fluid example $\hat{\psi}^{\dagger} = \hat{a}^{\dagger}$ and $\hat{\psi} = a$ If we can find the symmetry generators of $H(\{\hat{a}^{\dagger}\}, \{\hat{a}\})$, the variables $\hat{Q}$ which satisfy $[\hat{Q}, H(\{\hat{a}^{\dagger}_i\}, \{\hat{a}_i\})] = 0$ that is, then we can in principle construct the order operators $\hat{\psi}$. For finite quantum systems with discrete spectrum we can always decompose $\hat{Q} = \hat{\psi}^{\dagger}\hat{\psi}$, which means that the order operators are just the generalized ladder operators. For further arguments, see Sect. 3.3. The decomposition has nothing to do with the system described by H, it is a property of the Hilbert space itself [38]. These arguments have to be reconsidered for scattering states with continuous spectrum and infinite number of constituent particles. For a known set of order operators ψ_{μ} (there can be many symmetries to be broken), the phase diagram can be constructed by tracing over the generalized η-ensemble weight given by

$$\rho^{\boldsymbol{\eta}}_{eq} \equiv \exp\Big(-\beta H(\{\hat{a}^{\dagger}_i\}, \{\hat{a}_i\}) + \sum_{\mu} \eta_{\mu} \psi_{\mu}(\{\hat{a}^{\dagger}_i\}, \{\hat{a}_i\})\Big) \tag{2.11}$$

Thus, from the symmetry analysis of the equilibrium density matrix we can find the order operators associated with the spontaneous breaking of the continuous symmetries generated by $\hat{Q}_{\mu}$. By construction, when the control parameters of the Hamiltonian are such that some subset $\mu \in K_b \subset K$ of symmetries K of H are broken, then

$$\lim_{\boldsymbol{\eta}' \to 0} \mathrm{Tr} \Big\{ \rho^{\boldsymbol{\eta}'}_{eq}\, \hat{\psi}_{\mu}(\{\hat{a}^{\dagger}_i\}, \{\hat{a}_i\}) \Big\} \neq 0\ . \tag{2.12}$$

where $\boldsymbol{\eta}'$ are conjugate the order parameters $\hat{\psi}_{\mu}$, $\mu \in K_b$. As in the case of the superfluid, there is no guarantee that all fields η_{μ} would be experimentally realizable.

The idea of the η-ensembles is naturally connected with the higher order Legendre transformations advertized earlier. All we need to do is to make the the fields η_{μ} dependent on the space coordinate $\mathbf{x}$ (and time coordinate in the non-equilibrium situation). Then the generating partition functional becomes (with η_{μ} replaced by source field J_{μ}):

$$Z[\mathbf{J}] = \mathrm{Tr}\, e^{-\beta H - \int d\mathbf{x}\, \mathbf{J}(\mathbf{x}) \cdot \hat{\boldsymbol{\psi}}(\mathbf{x})}\ , \tag{2.13}$$

where $\boldsymbol{\psi}$ is a vector with components $\hat{\psi}_\mu$. When the generating functional is arrived at via the method of quasi-averaging, the constrained fields (operators $\hat{\psi}$) have a natural interpretation as order operators. However, the Legendre transformation, which will be discussed more thoroughly in Sect. 2.1.3, only relates the constraining field (J) to its conjugate variable ($\langle \hat{\psi} \rangle$). It does not care if the conjugate variable is an order operator or some other operator, the transformation is completely general in that sense. Therefore, one can also consider Legendre transformation of conserved charges (symmetry generators) $\hat{Q}$, not just the order operators, which in the simplest cases are related to the former via $\hat{Q} = \hat{\psi}^\dagger \hat{\psi}$. This generalization turns out to be important when we will come across the concept of density functional theories in later chapters.

2.1.3 How to see the phase transitions within the formalism

The functional Legendre transformation method of which the generalized η-ensemble offers one example, was originally developed for more efficient technique to describe phase transitions by Belyaev [39] and de Dominics and Martin [40, 41] in the equilibrium quantum statistics. De Dominics gave also related variational formulation of equilibrium classical statistical mechanics [42].

These developments utilized diagrammatic and combinatorial methods to express the grand partition function in terms of the one and two-point functions (correlation function). A field theoretic formulation presented by Dahmen and Jona-Lasinio [43] as well as the effective action method of Cornwall, Jackiw and Tomboulis [44] made the formalism more transparent. They considered a generating functional, which looks like Eq. (2.13) except that in addition to the linearly coupled fields ψ there is also a coupling to the two point function:

$$Z[J_1, J_2] = \tag{2.14}$$
$$\int \mathcal{D}\psi \, \exp\left(\frac{\imath}{\hbar} S[\psi] + \frac{\imath}{\hbar} \int d^4x_1 \; J_1(x_1)\psi(x_1) + \frac{\imath}{2\hbar} \int d^4x_1 \int d^4x_2 \; J_2(x_1, x_2)\psi(x_1)\psi(x_2) \right) ,$$

where $S[\psi]$ is the action some general field theory without any couplings to sources J_1 and J_2. This construction can be continued to higher order correlation functions, which yield more precise information on the phase transition. Use of higher order composite operators allows us to study symmetry breaking patterns in cases where we do not posses order operators of lower order or their value is zero as the theory only allows a symmetric solution for them. For example, in the case of superconductors the relevant order parameter is the anomalous Green's function $\langle \hat{T}_+(\psi(x)\psi(x)) \rangle$, which means that we have to introduce a source J_2 as in Eq. (2.14) in the generating functional. The use of higher order couplings, which allow us to express the partition function (generating functional) in terms of the correlation functions $\langle \psi(x_1) \rangle$, $\langle \psi(x_1)\psi(x_2) \rangle$ etc., can also be utilized to improve the approximative construction of the effective action because the presence of higher order operator products of field variables results in automatic resummation of large subsets of terms of perturbation series. Using the correlation functions (expectation values of composite operators) to improve the approximations of $\mathcal{A}$ by including nonlinear features is analogous to Kawasaki's idea of including higher order operator products [45, 46] as relevant variables to be used in the projection operator method. Kawasaki operated at the level of equation of motion directly whereas the field theoretic methods modify first the action and are then reflected in the emerging equations of motion for the field expectation values. Owing to the higher order operator products, one is not ultimately restricted to study only the small variations close to equilibrium anymore, a feature which is desirable in the studies of dynamics of fluctuations in the vicinity of the critical points [45].

In practice, the construction of the effective action is difficult and requires specialized techniques. Several methods exist especially in the traditional setting where the symmetry breaking is approached through effective action expressed in terms of the constant expectation value of the field operator [47]. Despite the ability to formally include nonlinear effects, the practical computation is hard as the propagators of some theories are functionals of the field expectation values [48]. Powerful diagrammatic methods for higher order Legendre transforms of space dependent field operator products have been developed by Vasiliev [49] among others. Below we will describe some of the results on generalized Legendre transformations, which allow us to reach a sufficient level certainty that they offer enough flexibility and rigour to help us in the difficult task of constructing the effective action. The functional Legendre transformation in the most general form can be formulated as follows. First we define the generating functional,

$$Z[J] \equiv e^{W[J]} \equiv const \int \mathcal{D}\psi \; e^{B[J,\psi]} \; ; \tag{2.15}$$

$$B[J,\psi] \equiv \sum_{n=1}^{\infty} \frac{1}{n!} \int dx_1 \ldots dx_n \; J_n(x_1 \ldots x_n) \, \psi(x_1) \ldots \psi(x_n) \; . \tag{2.16}$$

(The abbreviation *const* means a constant factor.) The source fields (or potentials) J_n are arbitrary symmetric functions of their arguments. For finite temperature field theories, the integrals include imaginary time integration as well. Transformation with respect to the first m sources $J' = J_1 \ldots J_m \mapsto \alpha = \{\alpha_1 \ldots \alpha_n\}$ will be called the Legendre transformation of order m [49]:

$$\mathcal{A}[\alpha, J''] = W[J] - \sum_{k=1}^{m} J_k \alpha_k \; ; \tag{2.17}$$

$$\alpha_n(x_1 \ldots x_n) = \frac{\delta W[J]}{\delta J_n(x_1 \ldots x_n)} = \frac{1}{n!} \langle \psi(x_1) \ldots \psi(x_n) \rangle \; , \tag{2.18}$$

where J'' is the set of higher order potentials not involved in the transformation and the expectation value is computed over the weight e^B. Integrals are implied in the product $J_k \alpha_k$. Convexity of the transformation can only be guaranteed for so-called quasi-probabilistic Euclidean theories, where the functional integrals with weight e^B converge and the measure $(\mathcal{D}\psi \, e^B)$ can be treated as positive. Despite the absence of convexity in the most general case (some more restricted forms of the transformation will be convex as we will see) we can still use it for approximate construction of the effective action including anomalous solutions (Green's functions) of the field theory. All presently known anomalous solutions, corresponding to broken symmetry, can be obtained in this way [49]. Moreover, in all cases one only has to use the lowest order approximation of the effective action functional.

Let us now see how the symmetry breaking takes place at operational level using the weakly interacting Bose fluid as an example. In this case, we will not need higher order operator products (first order suffices) since the order parameter is be simply the expectation value of the annihilation order operator $\hat{\psi}$. The symmetry breaking can be understood qualitatively using the η-ensemble concept introduced in Sect. 2.1.2. The equilibrium density matrix is related to the generating functional through $Z[J] = \mathrm{Tr}\{\hat{\rho}^J_{eq}\}$ In the high symmetry phase, $\hat{\rho}^0_{eq} \equiv e^{-\beta \hat{H}_B}$ commutes with the number operator $\hat{N} \equiv \int d\mathbf{x} \; \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x})$ making $\hat{N}$ a symmetry generator of $\hat{H}_B$ (or equivalently $\hat{\rho}^0_{eq}$):

$$e^{\imath\alpha\hat{N}}\hat{H}_B\, e^{-\imath\alpha\hat{N}} = \hat{H}_B \quad ; \quad e^{\imath\alpha\hat{N}}\hat{\rho}^0_{eq}\, e^{-\imath\alpha\hat{N}} = \hat{\rho}^0_{eq} \tag{2.19}$$

where α is the continuous parameter characterizing the transformation. The value of the order parameter in the high symmetry phase is zero:

$$\langle\hat{\psi}\rangle = \mathrm{Tr}\{\hat{\psi}\,\hat{\rho}^0_{eq}\} = \mathrm{Tr}\{[\hat{\psi},\hat{Q}]\,\hat{\rho}^0_{eq}\} = \mathrm{Tr}\{[\hat{Q},\hat{\rho}^0_{eq}]\,\hat{\psi}\} = 0\ , \tag{2.20}$$

because $\hat{Q}$ is a symmetry of the state ρ^0_{eq} (or Hamiltonian $\hat{H}_B$): $[\hat{Q},\hat{\rho}^0_{eq}] = 0$. Upon altering the constraint parameters of the theory (lowering temperature) we hit at some point the low symmetry phase where the appropriate ensemble weight is no longer given by $\hat{\rho}^0_{eq}$ but $\hat{\rho}^J_{eq} = \exp(-\beta\hat{H}_B) + J\hat{\psi}$ (approximately). In this case the order parameter will become non-zero, as it should:

$$\langle\hat{\psi}\rangle = \mathrm{Tr}\{\hat{\psi}\,\hat{\rho}^J_{eq}\} = \mathrm{Tr}\{[\hat{Q},\hat{\rho}^J_{eq}]\,\hat{\psi}\} \neq 0\ , \tag{2.21}$$

In the broken symmetry phase, by definition, $\hat{Q}$ is not any more a symmetry of the state: $[\hat{Q},\hat{\rho}^J_{eq}] \neq 0$. It is easy to see that the symmetry generator $\hat{Q} = \hat{N} = \hat{\psi}^\dagger\hat{\psi}$ does not commute with the term $J\hat{\psi}$ even though it commutes with $\hat{H}_B$. This is basically the static picture of the phase transitions described by the (algebraicly) simplest conceivable order parameter. The dynamic view to phase transitions will be discussed in Chap. 3.

2.2 Ingredients of the formalism

A brief sketch of the most important features of the nonequilibrium generating functional formalism will be given here. As clarified in the following sections, the nonequilibrium partition function suitable for describing the dynamics of phase transitions can be written as

$$\boxed{Z[J_+,J_-,J_\beta] = \mathrm{Tr}\left\{U(t_f,t_i;J_+)\ \rho_0(J_\beta)\ U^{-1}(t_f,t_i;J_-)\right\}\ ,} \tag{2.22}$$

where $U(t_f,t_i;J_+)$ is the time evolution operator, which evolves the states from the initial time t_i to the final time t_f. Explicitly,

$$\boxed{U(t_f,t_i;J_+) = \hat{T}_+ e^{-\frac{\imath}{\hbar}\int_{t_i}^{t_f} dt \int d\mathbf{x}(\hat{H}(\mathbf{x},t)+\sum_n J^Q_n(\mathbf{x},t)\hat{Q}(\mathbf{x})+\sum_m J^\psi_m(\mathbf{x},t)\hat{\psi}_m(\mathbf{x}))}\ .} \tag{2.23}$$

The time ordering operator is $\hat{T}_+$. Hamilton's operator $\hat{H}(\mathbf{x},t) \equiv H(\hat{a}^\dagger(\mathbf{x}),\hat{a}(\mathbf{x}),t)$, may depend on time through external driving fields, for example. The source fields J^Q and J^ψ are reserved for generation of expectation values of the *composite* operators $\hat{Q}(\mathbf{x}) \equiv \hat{Q}(\hat{a}^\dagger(\mathbf{x}),\hat{a}(\mathbf{x}))$ and $\hat{\psi}(\hat{a}^\dagger(\mathbf{x}),\hat{a}(\mathbf{x}))$. The novelty lies in their choice of these operators. In Sect. 2.1.2 we have shown that the order operators appear naturally in the density matrix describing the broken symmetry states. They constitute the set $\{\hat{\psi}_m\}$ and their expectation values will be the order parameters of the theory. It should be noted that when forming the equation of motion for $\langle\hat{\psi}\rangle$, the Legendre multipliers J will be removed. Unlike real external coupling fields, the Legendre transformation does not induce (explicit) symmetry breaking, its only task is to make the broken symmetries visible in the form of the effective action (or expectation values of order operators). Even though the generating functional looks like the density matrix of the broken phase, it is a different entity. For example, if the system is described by a linearly (explicitly) broken symmetry by an external driving field also the symmetry of the Legendre transformed action will stay linearly broken [50]. Operators $\hat{Q}$ are the generators of the symmetries of the steady-state (equilibrium) density matrix the system evolves to for large enough times. Their presence in Eq. (2.23) will be better justified in Sect. 2.3.1, where it is shown that when the conserved densities in the equilibrium, we obtain the familiar density functional results used in first principles calculations [51].

The initial state ρ_0 in Eq. (2.22)is arbitrary: It can be a pure state or a mixture like thermal ensemble, in which case J_β is the source fixed at the imaginary time value β. Together with the other sources J_+ and J_- it acts as the source field, which can be utilized in the functional Legendre transformation. For a pure initial state, e.g. $\rho_0 = |0\rangle\langle 0|$, the generating functional can be written in a more concise form

$$Z[J] = \int \mathcal{D}\phi \; e^{S[\phi]+J^Q_n Q_n[\phi]+J^\phi_m \psi_m[\phi]} \ , \tag{2.24}$$

where S is the action (not the effective action) defined in terms of the Lagrangian of the system as in Eq. 2.14 and integrals are understood in the products $J^Q_n Q_n[\phi]$ and $J^\phi_m \psi_m[\phi]$ as well as summation over repeated indices. The formal similarity with Eq. (2.10) is obvious (trace of the density matrix gives the generating functional *if* we interpret the symmetry breaking field η as source J). However, as pointed out in the previous paragraph, the effective action formed with the aid of the generating functional $Z[J]$ is capable of describing the physics both in broken and unbroken symmetry case. It is not tied to the broken symmetry phase like the density matrix $\hat{\rho}^\eta_{eq}$.

2.2.1 S-matrix and Closed-time-path

S-matrix is one of the fundamental objects in particle physics. It relates the infinitely past unscattered free particle $|in\rangle$ states to the scattered free particle states $|out\rangle$ at infinitely distant future describing all possible scattering processes. In order to evaluate the probability amplitude for some particular scattering process one needs to compute the scattering matrix elements of the form

$$\langle \mathbf{p}'_1, \mathbf{p}'_2; out \,|\, \mathbf{p}_1, \mathbf{p}_2; in\rangle \equiv \langle \mathbf{p}'_1, \mathbf{p}'_2; in|\hat{S}|\mathbf{p}_1, \mathbf{p}_2; in\rangle \tag{2.25}$$

for a two particle scattering event with incoming free particles ("on the mass shell") with momenta $(\mathbf{p}_1, \mathbf{p}_2)$ and outgoing free particles with momenta $(\mathbf{p}'_1, \mathbf{p}'_2)$. In Eq. (2.25) we have used the fact that the complete set of free in-states is transformed to the complete set of free out-states by the S-operator: $|out\rangle = \hat{S}^\dagger|in\rangle$. Because the particle states can be created by application of field creation operators on the vacuum in-state $|0; in\rangle$, we get

$$|\mathbf{p}_1, \mathbf{p}_2; in\rangle = \hat{a}^\dagger_{in}(\mathbf{p}_1)\hat{a}^\dagger_{in}(\mathbf{p}_2)|0; in\rangle \ . \tag{2.26}$$

where the in and out (creation and annihilation) operators are just unitary transformations of each other: $\hat{a}^\dagger_{out} = \hat{S}^\dagger\hat{a}^\dagger_{in}\hat{S}$. Furthermore, as we can easily express the momentum space creation and annihilation operators in terms of the real space ones $\hat{\phi}(\mathbf{x})$, we see from Eq. (2.25) and Eq. (2.26) that the scattering matrix elements are obtained from computing the expectation values of products of field operators sandwiched between vacuum out-state and vacuum in-state, or between vacuum in-states using the definition of the S-matrix in Eq. (2.25). Reversing the argument, the knowledge of these vacuum expectation values of the time ordered products of field operators (Green's functios) allows us to reconstruct the entire S-matrix. As usual, the Green's functions are most conveniently expressed in terms of the generating functional [47] $Z[J]$ whose relation to S-matrix is given by [52]:

$$\langle 0; out|\hat{T}^{+}_{H}(J)|0; in\rangle = \langle 0; in|\hat{S}\hat{T}^{+}_{H}(J)|0; in\rangle = e^{\imath\theta_S} Z[J] \ , \tag{2.27}$$

where θ_S is a phase shift created generated by the time evolution and and the subscript H refers to Heisenberg representation of the field operators $\hat{\phi}_H$ in the functional ($\hbar = 1$)

$$\hat{T}^{+}_{H}(J) \equiv \hat{T}^{+}_{H}(t_i = -\infty, t_f = +\infty; J) \equiv \hat{T}_{+}\, e^{\imath \int_{-\infty}^{\infty} dt \int d\mathbf{x}\, J(\mathbf{x},t)\hat{\phi}_H(\mathbf{x},t)} \ . \tag{2.28}$$

The origin of the phase factor $\exp(\imath\theta_S)$ in Eq. (2.27) lies in the relation between the vacuum in and out states [52]

$$|0; out\rangle = \hat{S}^{\dagger}|0; in\rangle = e^{\imath\theta_S}|0; in\rangle \ , \tag{2.29}$$

Finally, the explicit operator representation for the S-matrix is expressed in terms of the interaction picture time evolution operator:

$$\hat{S} \equiv U(\infty, -\infty) = \hat{T}_{+}\, e^{-\imath \int_{-\infty}^{\infty} dt\, \hat{H}'_I(t)} \ , \tag{2.30}$$

where $\hat{H}_I$ is the the interaction picture (subscript I) representation of the interaction part $\hat{H}'$of the full Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$, where $\hat{H}_0$ generates the time evolution of the free fields: $H'_I = e^{\imath \hat{H}_0 t} H' e^{-\imath \hat{H}_0 t}$ (H' is in the Schrödinger picture representation).

We will now make some modifications to the traditional formalism presented above. First we note that Eq. (2.27) can be generalized for composite operators coupled to source fields $J_2(x_1, x_2)$, $J_3(x_1, x_2, x_3)$ and so on. For example, the generating functional of both one and two particle Green's functions (correlation functions) can be written as

$$Z[J_1, J_2] = \langle 0; out|\hat{T}^{+}_{H}(J_1, J_2)|0; in\rangle \tag{2.31}$$

$$= \langle 0; out|\hat{T}_{+}\, e^{\imath \int dx_1\, J_1(x_1)\hat{\phi}_H(x_1) + \imath \int dx_1 \int dx_2\, J_2(x_1,x_2)\hat{\phi}_H(x_1)\hat{\phi}_H(x_2)}|0; in\rangle \ , \tag{2.32}$$

where $x_i = (\mathbf{x}_i, t_i)$ ($i = 1, 2$). This starts already looking something like Eq. (2.23), where composite operators $\hat{Q}$ and $\hat{\psi}$ appear. To keep the notation more compact, we do not consider higher than linear couplings $J_1\phi_H$ below.

If we wish to modify the formalism further and make it better suited for description of other type of time evolution more appropriate for condensed matter systems, it is not that a good idea to fix the final state to be that of non-interacting free particles That is, we want to leave out the fixed boundary condition $\langle 0; out|$ and consider only given initial conditions. In other words we wish to consider only matrix elements between in-states (in-in formalism) instead of in and out states (in-out formalism). We cannot use Eq. (2.27) directly even though it obviously converts in-out element into in-in one. The reason is that we have assumed that the time-evolution of the initial condition $|0; in\rangle$ is related to the final state $|0; out\rangle$ by a mere phase factor as shown in Eq. (2.29). If we wish to consider the dynamics of real systems, where the final state can be very different from the initial one (say, phase transitions take place during evolution) there is no guarantee that the vacuum states infinitely far in the past and future are related through a phase factor. As interactions will be switched on and off taking the system out of equilibrium, it future vacuum $|0; out\rangle$ can be unknown to us [53, 54]. To summarize, we leave out the S-operator from Eq. (2.27) and call

$$Z[J] = \langle 0; in|\hat{T}_H^+(J)|0; in\rangle = \int \mathcal{D}\phi \; e^{\imath S[\phi] + \imath J\phi} \tag{2.33}$$

the generating functional of vacuum correlations when Eq. (2.29) holds (path integral representation will be discussed in Sect. 2.2.3). If Eq. (2.29) does not hold, we generalize the concept of the generating functional to include only the initial condition, which leads to the so-called Closed-time-path (CTP) formalism or Keldysh formalism developed by Schwinger [55] and Keldysh [56]:

$$Z[J_+, J_-] \equiv \langle 0|\hat{T}_H^-(J_-)\hat{T}_H^+(J_+)|0\rangle = \int \mathcal{D}(\phi_+, \phi_-) \; e^{\imath S[\phi_+] - \imath S[\phi_-] + \imath J_+\phi_+ - \imath J_-\phi_-} \;, \tag{2.34}$$

where $\int\mathcal{D}(\phi_+, \phi_-) \equiv \int\mathcal{D}\phi_+ \int\mathcal{D}\phi_-$ and the integration paths for ϕ_+ and ϕ_- join at some arbitrary late time t_f, which can be taken to infinity (this can be seen by inserting unit operator $\int \mathcal{D}\psi\, |\psi, t_f\rangle\langle\psi, t_f|$ between $\hat{T}_H^-$ and $\hat{T}_H^+$). We have dropped the 'in'-labels from the state vectors, as we are by definition working with the initial conditions (states) in this formalism. We have also defined a new operator,

$$\hat{T}_H^-(J_-) \equiv \hat{T}_H^-(t_i = -\infty, t_f = +\infty; J_-) \equiv \hat{T}_- \, e^{-\imath \int_{-\infty}^{\infty} dt \int d\mathbf{x}\, J_-(\mathbf{x},t)\hat{\phi}_H(\mathbf{x},t)} \;. \tag{2.35}$$

where $\hat{T}_-$ is the anti-time ordering operator. Comparing Eq. (2.34) with Eq. (2.27) we can say that CPT (in-in) formalism compares the overlap of final states, which result from having two vacua evolving under two different sources J_+ and J_-, whereas the ordinary in-out formalism compares the overlap of the fixed final state with one that results from evolution of initial vacuum under one source field. The doubling of the sources comes naturally given the representation used in Eq. (2.34): If $J_+ = J_-$ then, the operators $\hat{T}_H^+$ and $\hat{T}_H^-$ will cancel each other. Using a different representation, though, as for example in Sect. (2.2.2), we see that sources doubling is not absolutely necessary, but it leads to more symmetric theory. The doubling of the time axis emerges naturally in both cases.

2.2.2 Initial correlations

In the previous section we generalized the usual generating functional formalism in two ways: We allowed for more general sources (though, for notational simplicity we are using just a single particle source) and we introduced a closed-time-path integration. Now it is time to present a third generalization, which allows us to deal with arbitrary initial states, not just vacuum states:

$$Z[J_+, J_-; \rho_0] \equiv \mathrm{Tr}\left\{\rho_0\, \hat{T}_H^-(t_i, t_f, J_-)\hat{T}_H^+(t_i, t_f, J_+)\right\} \tag{2.36}$$

$$= \int \mathcal{D}(\phi_1, \phi_2, \phi_3)\, \langle\phi_1|\rho_0|\phi_2\rangle\langle\phi_2|\hat{T}_H^-(t_i, t_f, J_-)|\phi_3\rangle\langle\phi_3|\hat{T}_H^+(t_i, t_f, J_+)|\phi_1\rangle \tag{2.37}$$

$$= \int \mathcal{D}(\phi_1, \phi_2)\, \langle\phi_2|\rho_0|\phi_1\rangle \int \mathcal{D}\phi_3 \int_{\phi_1}^{\phi_3} \mathcal{D}\phi_+ \int_{\phi_2}^{\phi_3} \mathcal{D}\phi_- \; e^{\imath S[\phi_+] - \imath S[\phi_-] + J_+\phi_+ - J_-\phi_-} \;, \tag{2.38}$$

where the time integrals in the action and coupling terms run from t_i to t_f. The density matrix of the initial state at initial time $t = t_i$ is denoted by ρ_0. Setting $\rho_0 = |0\rangle\langle 0|$ (and $t_i = -\infty$, $t_f = \infty$) reproduces Eq. (2.34). How to obtain the path integral of Eq. (2.38) will become clear in Sect. 2.2.3.

Perhaps an intuitively easier way of understanding how the closed-time-path arises is not to us the definition of Eq. (2.34) but to start off directly with the Green's functions (which can be produced by taking functional derivatives with respect to the sources of the generating functional). The one-particle (temperature) Green's function is defined as

$$G_1(x) \equiv \langle \hat\phi_H(x)\rangle_{\rho_0} = \mathrm{Tr}\{\rho_0 U(t_i,t)\hat\phi_I(x)U(t,t_i)\}\ , \tag{2.39}$$

where the arbitrary initial density matrix is ρ_0 and $x = (\mathbf{x}, t)$. The second equality follows from using the relation between the Heisenberg ($\hat\phi_H$) and interaction representation ($\hat\phi_I$) operators: $\hat\phi_H = U\hat\phi_I U^{-1}$. The interaction picture time evolution operator is defined in Eq. (2.30). It should be kept in mind that it is different from the free field time evolution operator $\exp(\imath \hat H_0 t)$ which appears when Schrödinger picture operators are transformed into interaction representation. Taking the initial time t_i to $-\infty$ we get

$$G_1(x) = \mathrm{Tr}\{\rho_0\, U(-\infty,t)\, \rlap{$\overbrace{}^{\hat 1}$}U(t,\infty)\underbrace{U(\infty,t)\hat\phi_I(x)U(t,-\infty)}_{\hat T_+[\hat S\hat\phi_I(x)]}\} = \mathrm{Tr}\{\rho_0\, \hat S^\dagger \hat T_+[\hat S\hat\phi_I(x)]\}\ . \tag{2.40}$$

We have first inserted a unit operator and then combined the product of the first two time evolution operators into $\hat S^\dagger = U(-\infty,\infty)$. Use of the time ordering operator $\hat T_+$ was justified because the field operator $\hat\phi_I(x)$ is defined at time t. In a similar manner, we obtain the two-point Green's function ($t_1 < t_2$)

$$\begin{aligned}
&\langle\hat\phi_H(x_1)\hat\phi_H(x_2)\rangle_{\rho_0} \\
&\quad= \mathrm{Tr}\{\rho_0\, U(t_i,t_1)\hat\phi_I(x_1)U(t_1,t_i)\, U(t_i,t_2)\hat\phi_I(x_2)U(t_2,t_i)\}|_{t_i=-\infty} && (2.41)\\
&\quad= \mathrm{Tr}\{\rho_0\, U(-\infty,t_1)U(t_1,\infty)\hat T_+[U(\infty,t_1)\hat\phi_I(x_1)U(t_1,t_2)\hat\phi_I(x_2)U(t_2,-\infty)]\} && (2.42)\\
&\quad= \mathrm{Tr}\{\rho_0\, \hat S^\dagger\hat T_+[\hat S\hat\phi_I(x_1)\hat\phi_I(x_2)]\} = \mathrm{Tr}\{\rho_0\, \hat T_P[\hat S^\dagger\hat S\hat\phi_I(x_{1+})\hat\phi_I(x_{2+})]\}\ . && (2.43)
\end{aligned}$$

The complete time path $P = C_+ + C_-$ consists of two contours $C_+ : t_+ \in (-\infty, +\infty)$ and $C_- : t_- \in (+\infty, -\infty)$, which can be imagined form a closed loop around the time axis. In Eq. (2.43) we have defined a time path order operator $\hat T_P$ which sets consecutive time arguments in the countour C_+ before those on the countour C_-. This convention allows us to place the operator $\hat S^\dagger$ to the right hand side of the path ordering operator in Eq. (2.43). Without the the field operators $\hat\phi_I(x_{1+})\hat\phi_I(x_{2+})$ (whose time arguments lie on contour C_+: $x_+ \equiv (\mathbf{x}, t_+)$) we would simply get $\hat S^\dagger\hat S = \hat 1$. Following Ref. [57] we can now define the following *single* source generating functional of the Green's functions

$$Z[J] \equiv \mathrm{Tr}\left\{\rho_0\, \hat T_P\left[\hat S^\dagger\hat S\ e^{\imath\int dx J(x_+)\hat\phi_I(x_+)}\right]\right\}\ . \tag{2.44}$$

To get a more symmetrical expression for the generating functional we can now introduce another source field $J(x_-)$, which is is coupled to field operator $\hat\phi_I(x_-)$. Furthermore, setting $\hat S^\dagger\hat S = \exp(-\imath\int_P dt\, \hat H_I'(t))$ yields

$$Z[J_P] = \mathrm{Tr}\left\{\rho_0\, \hat T_P\left[e^{-\imath\int_P dt\, \hat H_I'(t) + \imath\int_P dx\, J(x_P)\hat\phi_I(x_P)}\right]\right\}\ , \tag{2.45}$$

where the source term $J(x_P) = J(x_+)$ when $t \in C_+$, and $J(x_P) = J(x_-)$ when $t \in C_-$. Hence, the source J_P consists actually of two sources, one defined for the positive contour and one for the negative. For all practical purposes, we can call them by different names J_+ and J_-. The source term can be then written as

$$\int_P dx\, J(x_P)\hat{\phi}_I(x_P) = \int d\mathbf{x} \int_{-\infty}^{\infty} dt \left(J_+(\mathbf{x},t)\hat{\phi}_I(\mathbf{x},t) - J_-(\mathbf{x},t)\hat{\phi}_I(\mathbf{x},t) \right) . \tag{2.46}$$

The negative sign in front of the second term derives from the fact that we have inverted the integration direction of negative times on contour C_- to be the same as on the positive contour. The equivalence of the three different representations (Eq. (2.45), Eq. (2.36) and Eq. (2.22)) of the generating functional will be shown in Sect. 2.2.3.

Let us now briefly discuss some of the effects of the initial density matrix ρ_0 on the physics. With the aid of it we can conveniently model the evolution of pure states or mixtures such as thermal ensembles, which are in equilibrium at $t = t_i$. Several different initial state examples have been considered for instance in Refs. [58, 59]. Let us first consider a case where the equilibrium density matrix $\rho = e^{-\beta H}$ has the same Hamiltonian operator, which appears as the generator of the non-equilibrium dynamics in the time evolution operator U (Eq. (2.23)). In this case we can decompose the time path in three pieces: In addition to the normal contours $C_+ : [t_i \to t_f]$ and $C_- : [t_f \to t_i]$ there is evolution along the imaginary time path denoted by $C_\beta : t \in [t_i, t_i - \imath\beta]$. Typically we set $t_i \to -\infty$ recovering the results of this section. The advantage of setting the initial time infinitely far away is that in the generating functional the contribution from thermal path C_β decouples [60] and can be left out based on Riemann's lemma. It has been shown by direct calculation that leaving out the initial density matrix (more correctly, contribution from the contour C_β) leads to the neglect of initial correlations [61, 62]. When the contribution from the thermal contour is left out, we can say that the system has no direct memory of its initial conditions. Still, it turns out that there is a remnant of the thermal initial conditions in the explicit form of the propagators of the theory in case the system was in Gibb's state to begin with, see Sect. 2.2.3 and Sect. 2.2.4.

In the case of general non-Gibbsian initial conditions at finite t_i, the thermal contour plays no role anymore. Yet, we can represent the matrix elements of the initial density matrix in an exponentiated form as will be shown in Sect. 2.2.3. Cutting off the correlation at two-point level leads to Gaussian initial noise. Higher order corrections are straightforward to include [63, 58]. In addition to more general type of initial correlations, also more complicated path structures have been considered in Refs. [64, 60, 65]. It should be noted [59], though, that the Thermo Field Method of Ref. [64] and the finite temperature field theory of Ref. [65] reduce in the zero temperature limit to the in-out formalism described in Sect. 2.2.1 as the existence of vacuum-out state has to assumed. In contrast the method described in Ref. [60] reduces to in-in formalism and is thus able to deal with genuine nonequilibrium dynamics. There are also exceptional cases where the contour C_β cannot be excluded [64] even if $t_i \to -\infty$.

2.2.3 Different representations of the generating functional

Both the interaction picture and the Heisenberg picture form of the non-equilibrium generating functional can be related simply by leaving out the interaction Hamiltonian $\hat{H}'_I$ from the expression of the generating functional (2.45) and replacing the field operators $\hat{\phi}_I$ by Heisenberg operators $\hat{\phi}_H$. To see how this comes about start with Eq. (2.22) which allow us to present the single source evolution operator in the form (for arbitrary time ordered operators, see e.g. [66])

$$\begin{aligned} U(t_f, t_i, J_+) &= \hat{T}_+ e^{\imath \int_{t_i}^{t_f} dt \int d\mathbf{x}\, H(\hat{\phi}(\mathbf{x})) + J_+(\mathbf{x},t)\hat{\phi}(\mathbf{x})} && (2.47) \\ &= U_0\, \hat{T}_+ e^{\imath \int_{t_i}^{t_f} dt \int d\mathbf{x}\, J_+(\mathbf{x},t)\hat{\phi}_H(\mathbf{x},t)} = U_0 \hat{T}_H^+(J_+)\ , && (2.48) \end{aligned}$$

and $U_0 \equiv \exp(\imath(t_f - t_i)\hat{H})$. A similar decomposition can be applied to the time evolution operator U^{-1}. Due to the anti-time ordering, we obtain

$$U^{-1}(t_f, t_i, J_-) = \hat{T}_- e^{-\imath \int_{t_i}^{t_f} dt \int d\mathbf{x}\, J_-(\mathbf{x},t)\hat{\phi}_H(\mathbf{x},t)}\, U_0^{-1} = \hat{T}_H^-(J_-) U_0^{-1}\ . \qquad (2.49)$$

Using the representations of the time evolution operator given above, the generating functional of Eq. (2.23) now becomes

$$\begin{aligned} Z[J_+, J_-, \rho_0] &= \mathrm{Tr}\left\{U(t_f, t_i, J_+)\rho_0 U^{-1}(t_f, t_i, J_-)\right\} = \mathrm{Tr}\left\{\rho_0 U^{-1}(t_f, t_i, J_-) U(t_f, t_i, J_+)\right\} && (2.50) \\ &= \mathrm{Tr}\rho_0\, \hat{T}_H^-(J_-) U_0^{-1} U_0\, \hat{T}_H^+(J_+) = \mathrm{Tr}\left\{\rho_0\, \hat{T}_P\left[e^{\imath \int_P dt \int d\mathbf{x}\, J(x_P)\hat{\phi}_H(x_P)}\right]\right\}. && (2.51) \end{aligned}$$

As different authors use slightly different language, we mention by passing that the first equality in Eq. (2.50) is consistent with the definitions of Refs. [67, 68], the last in Eq. (2.51) with Refs. [69, 58, 63]. Moreover, if we choose to use a different decomposition in Eq. (2.48), we can easily arrive at the interaction representation discussed in the previous section. Disentangeling only the free (quadratic) part $\hat{H}_0$ of the full Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'$, such that $U_0 = \exp(\imath(t_f - t_i)\hat{H}_0)$ takes us from Eq. (2.51) back to Eq. (2.45).

It is also easy to show how the path integral representation of the generating functional arises using Eq. (2.51). Any time (path) ordered functional of Heisenberg operators can can represented in the path integral form [70] using

$$\begin{aligned} &\langle \psi', t' | \hat{T}_P[\hat{\phi}_H(t_1)\hat{\phi}_H(t_2)\ldots\hat{\phi}_H(t_n)] | \psi'', t'' \rangle \\ &\qquad = \langle \psi' | e^{-\imath(t'-t_1)\hat{H}} \hat{\phi} e^{-\imath(t_1-t_2)\hat{H}} \hat{\phi} e^{-\imath(t_2-t_3)\hat{H}} \ldots \hat{\phi} e^{-\imath(t_n-t'')\hat{H}} | \psi'' \rangle && (2.52) \\ &\qquad = \mathcal{N} \int_{\psi'}^{\psi''} \mathcal{D}\phi \int \mathcal{D}\pi\ \phi(t_1)\phi(t_2)\ldots\phi(t_n)\, e^{\imath S[\phi,\, t',\, t'']}, && (2.53) \end{aligned}$$

where the $\mathcal{N}$ is a normalization constant and the action $S[\phi,\, t',\, t''] = \int_{t''}^{t'} dt \int d\mathbf{x}\, \pi(x)\dot{\phi}(x) - H(\phi)$. Typically, the Hamiltonian can be presented in terms of the momentum ($\pi(x)$) and position ($\phi(x)$) variables in the form $H = (1/2)\pi^2(x) + (1/2)|\nabla\phi|^2 + V(\phi)$. For a general functional F we obtain

$$\langle \psi', t' | \hat{T}_P F[\hat{\phi}_H] | \psi'', t'' \rangle = \mathcal{N} \int_{\psi'}^{\psi''} \mathcal{D}\phi \int \mathcal{D}\pi\ F[\phi]\, e^{\imath S[\phi,\, t',\, t'']}\ . \qquad (2.54)$$

The normalization factor depends on the space-time volume (time interval and space volume to be integrated over) but not on the form of the functional F. The boundary conditions of the ϕ integral satisfy $\phi(\mathbf{x}, t') = \psi'(\mathbf{x})$ and $\phi(\mathbf{x}, t'') = \psi''(\mathbf{x})$. For π-integration there are no boundary conditions (all time slices to be integrated from $-\infty$ to ∞). Finally, all the time arguments of $F[\phi]$ must lie in the interval $[t'', t']$. Treating $\hat{T}_H^{\pm}$ as the functional $F[\hat{\phi}_H]$ it is now easy to see how the path integral representation of Eq. (2.38) comes about.

If the initial density matrix is of the Gibbsian form, $\rho_0 = \exp(-\beta \hat{H})$, we can let it act on the state vector on the left and obtain simply

$$\langle \psi', t' | \rho_0 = \langle \psi', t' - \imath\beta | \ . \tag{2.55}$$

This gives rise to the thermal contour in the complex time plane mentioned in Sect. 2.2.2. In the path integral representation of the generating functional the trace operation the presence of the thermal contour enforces the so-called Martin-Kubo-Schwinger (MKS) boundary condition on the end points of the ϕ-integration:

$$Z[J_+, J_-, \rho_0 = e^{-\beta \hat{H}}] = \mathcal{N} \int \mathcal{D}\phi \int \mathcal{D}\pi \ e^{\imath \int_P [\pi\dot{\phi} - H(\phi) + J\phi]} = \mathcal{N} \int \mathcal{D}\phi \ e^{\imath S + \imath J\phi} \ , \tag{2.56}$$

where the MKS-restriction on ϕ-integral becomes $\phi(\mathbf{x}, t'' - \imath\beta) = \phi(\mathbf{x}, t'')$, and t'' is the initial time. For more general initial states than thermal Gibb's state having the same Hamiltonian as in the time evolution operator, we can use the techniques of Calzetta and Hu [58]. The matrix elements of the initial density matrix in Eq. (2.38) are exponentiable

$$\langle \phi_1, t_i | \rho_o | \phi_2, t_i \rangle = \exp(\imath K[\phi_a]) \ , \tag{2.57}$$

where the functional $K[\phi_a] = K + \int dx \, K_a(x_1)\phi_a(x_1) + K_{ab}(x_1, x_2)\phi_a(x_1)\phi_b(x_2) + \ldots$, and summation over $a, b = +/-$ corresponding to different time contours is implied. The integrals in the expression of $K[\phi_a]$ can be written as four dimensional ones, if one supplements all prefactor functions K_a, K_{ab} and so on, with delta functions of time, which restrict the time moment to the initial time t_i (cf. also [69]). The full generating functional can be conveniently presented as depending on 'new' source fields K_a, K_{ab} etc. in addition to the old ones J_+ and J_-:

$$Z[J_+, J_-, \rho_0] = Z[J_a, K_{ab}, K_{abc}] = \int \mathcal{D}(\phi_a) \, e^{\imath(S[\phi_a] + J_a\phi_a + K_{ab}\phi_a\phi_b + K_{abc}\phi_a\phi_b\phi_c + \ldots)} \ , \tag{2.58}$$

where K_a has been adsorbed into J_a. It should be kept in mind that the K-kernels are only non-zero at initial time. As we will see, a similar looking expansion can be generated for influence functional as well but there the kernel functions are defined for all times. By including the boundary conditions regarding initial times (or in general any fixed time moment) into the definition of the path integral measure, will compactify the path integral representation of the generating functional further. For example, leaving out the initial density matrix ρ from Eq. (2.38) we could write

$$= \int \mathcal{D}\phi_+ \int \mathcal{D}\phi_- \ e^{\imath S[\phi_+] - \imath S[\phi_-] + J_+\phi_+ - J_-\phi_-} \ , \tag{2.59}$$

which would mean that $\phi_+(\mathbf{x}, t_f) = \phi_-(\mathbf{x}, t_f) = \phi_3(\mathbf{x})$, where ϕ_3 is just a dummy field to be integrated over and the initial condition is given (vacuum boundary). This notation [48, 71] can be traced back to Ref. [72]. This can still be made shorter by not separating the time contours or by going over to a doublet field (ϕ_+, ϕ_-) vector representation [73].

2.2.4 Heat bath and the influence functional

In general, we can divide the degrees of freedom under study into two groups: the system degrees of freedom which are directly relevant to us and the degrees of freedom, which we are not directly interested in but which nevertheless have to be taken into account somehow to get the correct description of the physics involved. The latter degrees of freedom are called (heat) bath variables or just bath for short.

We introduce the field b for bath variables and ϕ for system variables. Using Eq. (2.50) we can write the generating functional

$$Z[J_+,J_-,\rho_0] = \mathrm{Tr}\left\{\rho_0 U^{-1}(t_f,t_i,J_-)U(t_f,t_i,J_+)\right\} \ , \tag{2.60}$$

where the initial density matrix has been assumed to be separable into two thermal Gibbs states: $\rho_0 = \rho_{b0}\otimes\rho_{s0}$ (b for bath and s for system). More general initial state preparations have been considered e.g. in Ref. [74]. Assuming that the equilibrium Hamiltonians of the initial density matrices are the same in the time-evolution operators, we can conveniently cast ρ_{0b} and ρ_{0s} into the form of imaginary time evolution operators. From Eq. (2.48) we obtain

$$\begin{aligned} U_{s0}(t_i - \imath\beta_s, t_i, J_{\beta_s}) &= \hat{T}_P\, e^{\imath\int_{t_i}^{t_i-\imath\beta_s} dt \int d\mathbf{x}\, H_s(\hat{\phi}(\mathbf{x})) + J_{\beta_s}(\mathbf{x},t)\hat{\phi}(\mathbf{x})} && (2.61)\\ U_{b0}(t_i - \imath\beta_b, t_i, 0) &= \hat{T}_P\, e^{\imath\int_{t_i}^{t_i-\imath\beta_b} dt \int d\mathbf{x}\, H_b(\hat{b}(\mathbf{x}))} \quad = \quad e^{-\beta_b\int d\mathbf{x}\, H(\hat{b}(\mathbf{x}))} \ . && (2.62)\end{aligned}$$

Initially, the temperatures of the system and the bath have been the same. Choosing them differently allows us to model situations where the system starts off from some non-equilibrium temperature with respect to bath and evolves towards a new equilibrium state characterized by the bath temperature β_b. No source has been assigned to to equilibrium bath functional because we will not be interested in the bath dynamics. The same applies to the evolution operator U of the system-bath complex:

$$U(t_f,t_i,J_+) = \hat{T}_P\, e^{\imath\int_{t_i}^{t_f} dt\int d\mathbf{x}\, H_s(\hat{\phi}(\mathbf{x})) + H_b(\hat{b}(\mathbf{x})) + H_{int}(\hat{\phi}(\mathbf{x}),\hat{b}(\mathbf{x})) + J_+(\mathbf{x},t)\hat{\phi}(\mathbf{x})} \tag{2.63}$$

The interaction Hamiltonian between the system and the bath is denoted by H_{int}. Insertion of three unit operators of the form $\hat{1} = \int \mathcal{D}\phi_i \int \mathcal{D}b_i\, |\phi, b\rangle\langle b,\phi|$ $(i = 1,2,3)$ into the expression of the generating functional (2.60) gives (cf. Eq. (2.37))

$$\begin{aligned} Z[J_+,J_-,J_{\beta_s}] = &\int\mathcal{D}(\phi_1,\phi_2,\phi_3)\int\mathcal{D}(b_1,b_2,b_3)\ \{\langle\phi_1,b_1|U_{s0}(t_i-\imath\beta_s,t_i,J_{\beta_s})U_{b0}(t_i-\imath\beta_b,t_i)\\ &\times\ |\phi_2,b_2\rangle\langle b_2,\phi_2|U^{-1}(t_f,t_i,J_-)|\phi_3,b_3\rangle\langle b_3,\phi_3|U(t_f,t_i,J_+)|\phi_1,b_1\rangle\Big\} \ . \end{aligned} \tag{2.64}$$

We can now (at least formally) eliminate the bath variables in terms of a so-called influence functional $I[\phi_+,\phi_-]$ defined as [75, 76]

$$I[\phi_+,\phi_-] \equiv \int\mathcal{D}(b_1,b_2,b_3)\int\mathcal{D}(b_+,b_-,b_\beta)\ e^{\imath(S_b[b_+]-S_b[b_-]+S_{int}[\phi_+,b_+]-S_{int}[\phi_-,b_-])}\ e^{\imath S_b[b_\beta]} \ . \tag{2.65}$$

The time limits of the actions in the previous result are given in terms of the corresponding Lagrangian densities as follows:

$$S_b[b_\pm] = \int_{t_i}^{t_f} L_b[b_\pm] \ \ ; \ \ S_{int}[\phi_\pm,b_\pm] = \int_{t_i}^{t_f} L_{int}[\phi_\pm,b_\pm] \ \ ; \ \ S_b[b_\beta] = \int_{t_i}^{t_i-\imath\beta_b} L_b[b_\beta] \ . \tag{2.66}$$

The boundary conditions for the fields can be read off from the matrix elements of Eq. (2.64). Specifically, $b_1 = b_+(t_i) = b_\beta(t_i - \imath\beta_b)$, $b_2 = b_-(t_i) = b_\beta(t_i)$ and $b_3 = b_+(t_f) = b_-(t_f)$. For a general initial condition ρ_{b0} we would obtain [76],

$$I[\phi_+, \phi_-] \equiv \int \mathcal{D}(b_+, b_-)\; e^{\imath(S_b[b_+] - S_b[b_-] + S_{int}[\phi_+, b_+] - S_{int}[\phi_-, b_-])}\, \langle b_+(\mathbf{x}), t_i | \rho_{b0} | b_-(\mathbf{x}), t_i \rangle \;, \quad (2.67)$$

where we have used Jordan's notation (Eq. (2.59)) the end point integration being included in the path integral measure. Using the expression (2.65) of the influence functional, we can now express the nonequilibrium generating functional as

$$\begin{aligned} Z[J_+, J_-, J_{\beta_s}] \equiv \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.68)\\ \int \mathcal{D}(\phi_1, \phi_2, \phi_3) \int \mathcal{D}(\phi_+, \phi_-, \phi_\beta)\; e^{\imath(S_s[\phi_+] + J_+\phi_+ - S_s[\phi_-] - J_-\phi_-)}\; e^{\imath(S_s[\phi_\beta] + J_{\beta_s}\phi_\beta)}\; I[\phi_+, \phi_-] \;. \end{aligned}$$

The path integral representation of Z is almost the same as the expression of I but bath fields b replaced with the system field ϕ. The action terms are defined as

$$S_s[\phi_\pm] = \int_{t_i}^{t_f} dt\, L_s[\phi_\pm] \quad ; \quad S_s[\phi_\beta] = \int_{t_i}^{t_i - \imath\beta_s} L_s[\phi_\beta] \;. \quad (2.69)$$

Similarly to the influence functional, the boundary conditions for ϕ-integrals are: $\phi_1 = \phi_+(t_i) = \phi_\beta(t_i - \imath\beta_s)$, $\phi_2 = \phi_-(t_i) = \phi_\beta(t_i)$ and $\phi_3 = \phi_+(t_f) = \phi_-(t_f)$.

The influence functional has played major role in many of the modern approaches to dissipative quantum systems [74]. Some of the ideas leading to the effective action description and thereby to influence functionals, can be traced back to the seminal paper by Onsager and Machlup [77], where they considered the probability distribution(s) of linear classical Langevin equations (point particles moving under stochastic force). In the semi-classical approximation this is nothing but the transition probability for a quantum particle (field theoretic transition probability can be formulated in the same way, see Ref. [60]). However, in this analogue there are no noise sources (bath) in the quantum level, only the classical equation can be seen to contain (bath generated) noise. In the quantum context both quadratic and more complicated heat baths were considered by Feynman and Vernon [78]. Instead of the generating functional one can also consider the time evolution of the reduced density matrix of the system. For suitable coupling Hamiltonian Caldeira and Leggett [79] showed that it obeys a Fokker-Planck equation. This piece of information becomes relevant for us, too, as it offers another possibility to study the dynamics of phase transitions: The relevant variables can be read off from the symmetries of the density matrix or the effective action. Because the reduced density matrix changes in time, it is possible that its symmetries at two different times differ from each other (initial symmetries can be different from the final ones).

We will now see, how one can reduce the generating functional to a form suitable for perturbative calculations. In case the coupling term $L_{int} = -gb\phi$ is linear in the bath and system variables, the influence functional can be computed perturbatively as described by Niemi [60]. The system and bath Lagrangians are of the general form $L = L_0 - V$, where L_0 is the quadratic free part ($L_0 = -(1/2)\phi(\Box + m_s^2)\phi$ and correspondingly for the bath) and V contains the nonlinear self-interactions. Assuming that the initial time is taken to $t_i \to -\infty$, the thermal contour decouples and the influence functional simplifies to

$$I[\phi_+, \phi_-] \;=\; \int \mathcal{D}(b_+, b_-)\; \exp\left(\imath \int \frac{1}{2}\phi_a D_{ab}^{-1}\phi_b + V(\phi_-) + b_-\phi_- - V(\phi_+) - b_+\phi_+\right)$$

$$= \exp\left(-\imath\int V[-\imath\delta/\delta\phi_+] + \imath\int V[+\imath\delta/\delta\phi_-]\right)\exp\left(\frac{\imath g^2}{2}\int\int \phi_a D_{ab}\,\phi_b\right) \quad (2.70)$$

$$= \exp\left(-\imath\int_P V[\imath\delta/\delta\phi]\right)\exp\left(\frac{\imath g^2}{2}\int_P\int_P \phi\, D\,\phi\right) \quad (2.71)$$

Time integrals are running from $-\infty$ to ∞ and $a, b = \pm$. In the last equation (2.71) we have not separated the contours to point out the contour propagators can be extracted from the Green's function of the free field [69, 65] satisfying $(\Box + m_b^2)D = -\imath\delta_P(x_1 - x_2)$ satisfying the Kubo-Martin-Schwinger periodicity condition (2.55). The solution can be presented compactly in terms of the contour ordered theta function θ_P: $D(x_1, x_2) = \theta_P(t_1, t_2)D_>(x_1, x_2) + \theta_P(t_2, t_1)D_<(x_1, x_2)$, where

$$\theta_P \equiv \begin{cases} \theta(t_1 - t_2) & \text{for } t_1 \text{ and } t_2 \text{ both on } C_+ \ ; \\ \theta(t_2 - t_1) & \text{for } t_1 \text{ and } t_2 \text{ both on } C_- \ ; \\ 1 & \text{for } t_1 \text{ on } C_+ \text{ and } t_2 \text{ on } C_- \ ; \\ 0 & \text{for } t_1 \text{ on } C_- \text{ and } t_2 \text{ on } C_+ \ . \end{cases} \quad (2.72)$$

The contour ordering extends in the intuitive manner to the thermal contour as well, but as we have dropped it from the generating functional when taking $t_i \to -\infty$, we do not need to specify the imaginary time ordering at this point. Going back to ± contour representation, the Green's functions D_{ab} are now expressible as

$$\begin{aligned} D_{++}(x_1, x_2) &= \theta(t_1 - t_2)D_>(x_1, x_2) + \theta(t_2 - t_1)D_<(x_1, x_2) \ ; && (2.73)\\ D_{--}(x_1, x_2) &= \theta(t_2 - t_1)D_>(x_1, x_2) + \theta(t_1 - t_2)D_<(x_1, x_2) \ ; && (2.74)\\ D_{+-}(x_1, x_2) &= -D_<(x_1, x_2) \ ; && (2.75)\\ D_{+-}(x_1, x_2) &= -D_>(x_1, x_2) \ , && (2.76) \end{aligned}$$

where the signs are defined consistent with the direction of time contour integration in Eq. (2.70). The advanced and retarded Green's functions contain traces of the initial thermal state even if we have left out the thermal contour contribution from the generating functional. The Fourier space representation reads:

$$D_>(k, t_1, t_2) = -\frac{\imath}{2\omega_k}[(1 - f(\omega_k))e^{-\imath\omega_k(t_1 - t_2)} + f(\omega_k)e^{\imath\omega_k(t_1 - t_2)}] \ , \quad (2.77)$$

and $D_>(k, t_1, t_2) = D_<(k, t_2, t_1)$. The thermal distribution function $f(\omega_k) \equiv 1/(\exp(\beta_b\omega_k) - 1)$ and $\omega_k \equiv (m_b^2 + k^2)^{1/2}$. Therefore, even if the system forgets about the direct influence of infinitely past initial conditions there will be an indirect contribution always in the propagators.

A considerable simplification occurs for quadratic baths because we can leave out the $V[\imath\delta/\delta\phi]$ term in Eq. (2.71). Now, the influence functional becomes

$$I[\phi_+, \phi_-] = \exp\left(\frac{\imath g^2}{2}\int\int \phi_a D_{ab}\,\phi_b\right) \quad (2.78)$$

$$= \exp\left(\frac{\imath g^2}{2}\int\int (\phi_+ D_{++}\,\phi_+ + \phi_- D_{--}\,\phi_- - \phi_+ D_{+-}\,\phi_- - \phi_- D_{-+}\,\phi_+)\right) \quad (2.79)$$

Thus, for quadratic heat baths (or heat baths which are truncated at quadratic level [80]) the only effect of the bath is that the free field structure of the action of the generating functional is modified. Eq. (2.68) reads now

$$
\begin{aligned}
&Z[J_+, J_-, J_{\beta_s}] \equiv \qquad (2.80)\\
&\int \mathcal{D}(\phi_+, \phi_-, \phi_\beta)\; e^{\imath(S_s^0[\phi_+,\phi_-]+V_s[\phi_+]+J_+\phi_+-V_s[\phi_-]-J_-\phi_-)}\; e^{\imath(S_s[\phi_\beta]+J_{\beta_s}\phi_\beta)} \ .
\end{aligned}
$$

To simplify notation, we have assumed that the integrals over contour end points are included in the integral measure. We have also defined the 'free' action

$$
\begin{aligned}
&S_s^0[\phi_+, \phi_-] \equiv \qquad (2.81)\\
&\frac{1}{2}\int \Big(\phi_+(-\Box - m_s^2 - \tilde{D}_{++})\,\phi_+ - \phi_-(-\Box - m_s^2 + \tilde{D}_{--})\,\phi_- - \phi_+\tilde{D}_{+-}\phi_- - \phi_-\tilde{D}_{-+}\phi_+\Big) \ ,
\end{aligned}
$$

where $\tilde{D}_{ab} \equiv g^2 D_{ab}$. So, in a sense, even though we have not double the physical degrees of freedom we can now think Z to represent a system, where there is in addition to the quadratic massive self-interaction also a linear coupling between fields ϕ_+ and ϕ_-. This interaction, though, is dissipative as it derives from the bath interaction. To model real systems, however, one needs to use approximations for the bath-system interaction, which means that depending on the approximation the dissipative effects might not be visible for some composite observables (at least not to lowest order) as we will see in Chap. 5. We also point out the full generating functional (2.80) (with quadratic or non-quadratic bath) can be cast into a form similar to Eq. (2.70) for extraction of Feynman diagrams.

2.2.5 Remarks on external baths, internal baths and renormalization

Bath is called external if its degrees of freedom are separable entities from the system variables and do not require the latter for their definition. The external heat bath variables can be for example particles of type A, which are different from the system constituent particles B. If a clearcut distinguishability is not possible, the bath is called internal: The system acts as its own heat bath. For example, the high frequency Fourier modes of the field ϕ_k may constitute the noisy background of the low-lying Goldstone modes, which make up the system relevant in the hydrodynamic limit. Thus, the concept of internal bath is relevant for renormalization process, where the short wavelength (large wave vector) $k_>$ modes act as a heat bath of the long wavelength modes $k_<$. Integrating out the rapidly oscillating components of the field variables produces stochastic damped equations of motion for the macro variables living on the scale $k_<$. The problem, which is always present in this type of approach is that even if we are able to recognize the relevant scales (which might be many even if the number of coupling constants is small [81]) it can be difficult isolate the different components in practice [82].

As an idealization one can imagine knowing the fast external bath degrees of freedom and their coupling to the slow system variables. Postulating simple enough properties for bath, it can be eliminated partially or completely and the effective system equations of motion derived. Making the size of the bath infinite induces genuine decay of correlations and irreversibility. Also, non-dissipative equations of motion can result for some subset of macro variables. Contrary to the internal bath case, which consists only of the system, one does not have to assume the system to be infinitely large to see explicit decay. The use of external bath allows different kinds of macroscopic boundary conditions to be studied, but in its explicity it is also prone to produce only specialized results depending on the particular way the coupling between the system and the bath has been chosen and what the bath properties are [83]. In the Applications part of this thesis we will study the dynamics of superconductors, where we have a phonon bath acting on system consisting of electrons. This bath can be considered as external since we assume to know its properties at Gaussian level without any renormalization effects from the back reaction of the electrons. Of course, this is just the zeroeth order approximation, which can be improved on. We also discuss the Bose fluids, which have an internal phonon-like bath as can be seen from their excitation spectra.

From the point of theoretical formulation, the division to internal and external baths is somewhat artificial, as the generating functionals look the same in both cases, only the variables have to be re-interpreted. However, from the point of view of elimination of the bath modes, there is an important difference: For internal baths, the elimination takes places gradually respecting long range symmetries of the effective action as in the momentum shell RG. For external ones, we can decimate the bath degrees entirely regardless of their k-values. This process does not necessarily respect the original symmetries the action of the system-bath complex possessed before removal of the bath. If we choose to remove only the most rapidly oscillating Fourier modes of the bath, we can not eliminate it entirely from the effective description and we are then in a sense dealing with internal type of bath.

For internal baths the generating functional looks exactly like in the external case, where field only have different names. First, we divide the field variable (Φ) into slow (ϕ) and fast (φ) modes (soft and hard modes in the particle physics jargon) $\Phi = \phi + \varphi$,

$$\phi(x) = \int_{|k|<K} dk\, \Phi_k\, e^{\imath kx} \quad ; \quad \varphi(x) = \int_{K<|k|<\Lambda} dk\, \Phi_k\, e^{\imath kx} \ , \tag{2.82}$$

where K is corresponds to some coarse-graining box size and Λ is the upper cut-off of integration. Thus, $\varphi = b$ if we want to use the external bath language. Of course, the division is quite arbitrary (as compared to external bath case). Moreover, the assumption about the factorizability of the initial state might be even a worse assumption for internal baths than what it is for external ones. The action gets split accordingly: $S[\Phi] = S[\phi, \varphi] = S_s[\phi] + S_b[\varphi] + S_{int}[\phi, \varphi]$. The influence functional reads [84]

$$\begin{aligned} &I[\phi_+, \phi_-] = \\ &\int \mathcal{D}(\varphi_f, \varphi_+^i, \varphi_-^i) \int \mathcal{D}(\varphi_+, \varphi_-)\ e^{\imath(S_b[\varphi_+] - S_b[\varphi_-] + S_{int}[\phi_+, \varphi_+] - S_{int}[\phi_-, \varphi_-])}\ \rho_0(\varphi_+^i, \varphi_-^i, t_i) \ , \end{aligned} \tag{2.83}$$

which is nothing but our earlier result (2.67). Performing a partial trace (see Sect. 6.3.1 and Sect. 6.5) over the hard modes one obtains an effective action $S_{eff}[\phi, K]$ for the soft ones [85, 86]:

$$e^{\imath S_{eff}[\phi, K]} \equiv \int \mathcal{D}\varphi\ e^{\imath S[\phi, \varphi]} \ . \tag{2.84}$$

This, of course, is nothing but Wilson's momentum shell RG [87]. Integrating over all fields produces the generating functional $Z[J]$, which links together the expectation value of the coarse-grained variable $\langle \phi \rangle_J$ and and the source as explained in Sect. 2.1.3:

$$Z[J] \equiv \exp(W[J]) = \int \mathcal{D}\Phi\ e^{\imath(S[\Phi] + J\Phi)} \ , \tag{2.85}$$

and the generating functional (effective action) is given by $\mathcal{A}[\langle \phi \rangle_J] = W[J] - J\langle \phi \rangle_J$ In general, the two actions $\mathcal{A}$ and S_{eff} are not the same (cf. [84])!. We point out that even in the limit $K \to 0$ the identification $S_{eff}[\phi, K = 0] = \mathcal{A}[\langle \phi \rangle_{J=0}]$, requires the equivalence of the ensemble and spatial averages (see Sect. 6.5). This difference should be kept in mind when constructing the equations of motion for relevant variables. Both actions can be said to be coarse-grained: $\mathcal{A}[\langle\phi\rangle]$ contains the ensemble average of a macroscopically relevant observable (slow variable) and $S_{eff}[\phi]$ contains only the Fourier modes of the field Φ, which are relevant on large scales. In fact it is possible to combine these two methods (elimination of high frequency modes directly from $\mathcal{A}[\langle\phi\rangle]$) into a so-called non-perturbative renormalization group method [88, 34] which belongs to a family of exact renormalization group techniques [89, 90]. These methods form an effective action $\mathcal{A}_K$ relevant for momentum scale K and contrary to $S_{eff}[\phi, K]$, in this case it is true that $\lim_{K\to 0}\mathcal{A}_K \to \mathcal{A}[\langle\phi\rangle_{J=0}]$. Though, the extension to composite operators, which is essential for our purposes of describing nonequilibrium thermodynamics, requires still work [91].

The same remarks that we made on the coarse-grained system dynamics apply to soft mode dynamics as well. As we will see in Sect. 2.3.3 below, the dynamics follows from requiring stationarity of the effective action $\mathcal{A}$ with respect to $\langle\phi\rangle$. The dynamics of the soft modes will be stochastic and dissipative with possible non-local features in space and time [92]. Moreover, one expects renormalization of the parameters of the soft mode Lagrangian and appearance of new effective interactions of higher order in field variables. As in ordinary quantum mechanics, the field theoretical models seem to produce Langevin types of equations of motion whose stochastic properties can be determined from the generating functional directly. For example, Arnold et al. [93] and Bödeker have derived Vlasov-Boltzmann equations of motion for the soft modes of the gauge field in non-Abelian plasmas. Their example is relevant for any effective field theory as they coarse-grain an already coarse-grained theory. In other words, there are two energy scales in the theory to begin with. Removing all momentum modes up to energy scale fixed by the temperature T produces a so-called Hard Thermal Loop effective theory of the full quantum field theory (QCD). Then integrating out all momenta to the next cut-off scale $K = g^2T$ (where g is the weak coupling constant) produces a coarse-grained theory for the soft modes. This theory is simpler than the original being characterized just by a single scale g^2T. Moreover, the correlators of the noise term can also be computed from first principles. Another example of elimination of large momentum modes, which in addition utilizes the CPT-formalism, is the dynamic renormalization group application to stochastic differential equations [94] offering an alternative of the more traditional Martin-Siggia-Rose technique [95].

The elimination of hard modes is a powerful approach to coarse-graining. It is clear from the examples given above and many others that it can be applied to a systems of high complexity, both in classical and quantum settings. Its generality is also one of its weaknesses from the point of view of coarse-graining. For it is often the case that removing short scales also removes some degrees of freedom whose presence might be useful at the next level of the hierarchy of the effective models. For example, suppose we want to construct an effective description of the system consisting of atoms of type A and B. Atoms A tend to react with each other forming bound molecules $A-A$, whose whose chemical properties are vastly different from the individual atoms: They can react with the B atoms whereas single atoms A are not likely to do so. Starting with non-equilibrium initial condition where all the atoms are well separated from each other, we observe formation of molecules $A-A$ and their reactions with B particles. A blunt removal of some degrees of freedom, say the A-atoms can result in a very complicated effective interactions between the 'system' degrees of freedom, the B atoms, making the modelling of the effective B system equally hard as the original problem despite the reduction in the number of degrees of freedom. What would make more sense, is to keep the A–A molecules in the effective description of the coarse-grained level (system = A–$A + B$) instead of introducing some complicated force fields between the B atoms alone. This would be possible if the RG procedure would be selective. In other words, it should only remove the degrees of freedom of least importance. There have been attempts to formulate RG approach in this manner [33] (cf. Sect. XI in Ref.[96]) but we are still missing more powerful tools. One way of producing the 'packaging' effect of particles (clustering of several particles) is to use composite operators in the effective action (higher order products of several basic field operators) in the manner we have described in this chapter. This has been discussed by Kleinert in Refs. [97, 98, 99], where he shows the importance of the effective action $\mathcal{A}[\Phi, G, \alpha_3, \alpha_4]$ in modelling effects of clusters up to four particle composites. This is nothing but fourth order Legendre transform discussed in Sect. 2.1.3. An analogous formulation in the sense of the role of the expectation values of the composite (cluster) operators has been formulated in the non-relativistic many-body theory context. These methods, which are not based on effective action directly, but reparametrization of many-body Hilbert space, are collectively known under the name coupled cluster methods [100], whose extensions has been studied by Arponen, Bishop, Pajanne and Robinson [101, 102, 103, 104]. The potential of these techniques has not yet been fully exploited in the general coarse-graining methodology.

2.3 How to use the formalism in and out of equilibrium

The first section is devoted the determination of the equilibrium properties of the generating functional formalism. It is shown how the generating functional formalism reproduces the results of the ground state and finite temperature quantum density functional theories. Sect. 2.3.2 shows that the various time dependent formulations of density functional theory are equivalent to the generating functional formalism. Sect. 2.3.3 concentrates on the (nonlinear) deterministic dynamics. The actual process of going to equilibrium will be addressed in Sect. 2.3.4, where stochastic properties are discussed.

2.3.1 Finite temperature Density Functional Theory

It is important to realize that the nonequilibrium generating functional formalism does not only reproduce the equilibrium thermodynamics of homogeneous systems when the sources J_+ and J_- are set to zero (or time-axis is made unique through $J_+ = J_-$), but it also reproduces the equilibrium thermodynamics of inhomogeneous systems, which usually goes under the name Density Functional theory. In Chap. 6 we discuss more throughly the differences and similarities of classical and quantum density functional theories at finite and zero temperature. Here we concentrate on demonstrating that the zero and finite temperature quantum density functional theories correspond to the equilibrium limit of the generating functional formalism.

When $J_+ = J_-$, the time evolution operators of Z cancel each other out because of the cyclic property of the trace and Eq. (2.22) reduces to the expression of the (initial) equilibrium generating functional

$$Z[J_\beta] = \mathrm{Tr}\left\{\rho_0(J_\beta)\right\} = \mathrm{Tr}\left\{e^{-\beta(\hat{H}+J_\beta\hat{Q})}\right\} \equiv e^{-\beta W[J_\beta]} \ . \tag{2.86}$$

Choosing the general operator $\hat{Q}(\mathbf{x}) = \hat{n}(\mathbf{x}) \equiv \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$, where $\hat{n}$ is the number density operator, leads us to the ordinary (mass/number) density functional theory. This can be most easily seen from the arguments of Sect. 2.1.2: Symmetry broken ensembles (generalized η-ensembles) can be created by adding to the equilibrium Hamiltonian symmetry breaking pieces of the form $\int d\mathbf{x}\, \eta\hat{\psi}(\mathbf{x})$. Their presence is sufficient to give rise to non-zero value of the order parameter $\langle\hat{\psi}\rangle$ in the broken phase as shown in Sect. 2.1.3. Similarly, we can add symmetry preserving pieces of the form $\int d\mathbf{x}\eta\,\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$. Replacing η by $J_\beta(\mathbf{x})$ takes us back to Eq. (2.86). In the classical case one can see that using this trick of adding a conserved charge of the form $\int \mathcal{D}\mathbf{x}\eta\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}) = \eta\hat{N} \to \mu N$, where μ is the chemical potential and N is the particle number, to the classical Hamiltonian H and performing the classical trace over coordinate and momenta, generates the grand potential Ω as will be shown in Sect. 6.3.2. Ω, which is a function of the chemical potential (or fugacity) is related via a Legendre transformation to the Helmholtz free energy F, which is a function of the particle density n. Thus, intuitively, taking logarithm of $Z[J_\beta]$ in Eq. (2.86) should give us the quantum analogue of the free energy, i.e. the density functional (W).

Several implementations of the density functional theory utilizing the concept of effective action (in our case, the effective action of the generating functional) and/or variational principles [42, 105, 106, 23] exist. In Refs. [23, 107] it is shown that W is a convex functional for *finite* system guaranteeing a one-to-one correspondence between the source J_β and the expectation value of the operator $\hat{Q}$ defined as

$$\langle\hat{Q}(\mathbf{x})\rangle = \frac{1}{Z[J_\beta]}\mathrm{Tr}\left\{\hat{Q}(\mathbf{x})\,e^{-\beta(\hat{H}+J_\beta\hat{Q})}\right\} = \frac{\delta W[J_\beta]}{\delta J_\beta(\mathbf{x})}\ . \tag{2.87}$$

For *infinite* systems we can still perform the Legendre transformation (see remarks in Sect. 2.1.3) but the *derivatives* of the transformed functional can become multivalued. Also, as pointed out by Valiev and Fernando [23], by choosing the operator $\hat{Q}$ suitably, it is possible to produce a whole family of different density functional theories:

A) Setting $\hat{Q}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$ one obtains temperature dependent density functional theory [108], which reduces to the zero temperature DFT in the limit $\beta \to \infty$.

B) Setting $\hat{Q}(\mathbf{x}) = \hat{\psi}^\dagger_\alpha(\mathbf{x})\hat{\psi}_{\alpha'}(\mathbf{x})$, where α and α' are spin indices, produces the spin-density functional theory [109].

C) Setting $\hat{Q}(\mathbf{x}) = \frac{\hbar}{2m_e i}\left[\hat{\psi}^\dagger(\mathbf{x})\nabla\hat{\psi}(\mathbf{x}) - (\nabla\hat{\psi}^\dagger(\mathbf{x}))\hat{\psi}(\mathbf{x})\right]$ produces the current density functional theory [110].

D) Setting $\hat{Q}(\mathbf{x}) = \hat{Q}_{gen}(\hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}(\mathbf{x}))$, where $\hat{Q}_{gen}$ is any general density operator, produces generalized density functional theory for the expectation value $\langle\hat{Q}_{gen}\rangle$. Moreover, $\hat{Q}(\mathbf{x})$ does not have to a density of a conserved operator: It can be the density of an order operator (corresponding to a non-conserved order parameter), for example.

The primary quantity people in the density functional theory are interested in is the expectation value of the energy, which is a functional of the density $\langle\hat{Q}\rangle = \langle\hat{n}\rangle$ Energy can be obtained in terms of the effective action $\mathcal{A}$, which is related to the functional W via the functional Legendre transform:

$$\mathcal{A}[Q] = W[J_\beta] - J_\beta Q\ , \tag{2.88}$$

where $Q \equiv \langle \hat{Q} \rangle$ and $J_\beta Q \equiv \int d\mathbf{x}\, J_\beta(\mathbf{x}) Q(\mathbf{x})$. The equilibrium expectation value Q_{eq} is defined through the 'equation of motion' (see Sect. 2.3.3 and Sect. 2.3.4)

$$\left. \frac{\delta \mathcal{A}[Q]}{\delta Q(\mathbf{x})} \right|_{Q_{eq}} = 0 \; . \tag{2.89}$$

When the value of Q_{eq} is substituted back into the effective action functional, and the result is divided by β, we obtain the equilibrium expectation value of the energy:

$$E = -\frac{1}{\beta} \mathcal{A}[Q_{eq}] \; . \tag{2.90}$$

In the limit $\beta \to \infty$ Eq. (2.90) gives the energy of the ground state. It is important to notice the appearance of the factor $1/\beta$. The action must have units of energy times the units of (imaginary) time which is consistent with Eq. (2.90). After all, there can also exist temperature (time) dependent solutions of the variational problem (2.89). After all, we should keep in mind that when forming the functional integral representation of the generating functional $Z[J]$ the coupling term becomes $\int d\mathbf{x} \int dt\, J_\beta(\mathbf{x}) n(\mathbf{x}, t)$. Thus, even if we use time-independent source field, the density field will be time-dependent in the action. Given the non-linearity of Eq. (2.89), it possesses many kinds of solutions but we must pick out the physically correct one. Using a space independent coupling constant Weinberg [111] showed that the extremizing solution is also a minimum solution of the problem. Furthermore, Cornwall et. al [44] proved that even when there are multiple operators $\hat{Q}_n$ in the Legendre transformation, the expectation value of the energy $E[\phi, G] \int dt = \mathcal{A}[\phi, G]|_{stat}$ (expectation values of one ϕ and two point operators G are included here), where the extent of the time interval equals to $\imath\beta$ in our example. Several condensed matter applications utilize these results. For instance, Rebei and Hitchon derived an expression for the correlation energy of electron gas [112]. Polonyi and Sailer [113] derived corrections to the Hartree-Fock and Kohn-Sham [114] schemes using a similar effective action technique. These examples show that the effective action functional can really bring about something new into the old theories. For example, more powerful diagrammatic methods make the explicit construction of the exchange-correlation functional more explicit than before [23]. In other words, explicit expressions for E_{xc} as a function of the density variable n can be derived and improved systematically.

One of the extensions of the effective action method discussed in Ref. [23] is the natural possibility of including a larger number of operators in the Legendre transform instead of a single density as indicated by the general formula (2.23), where one can think of ρ_0 as the imaginary time evolution operator. This is important as nontrivial (nonlinear) couplings will be generated between the expectation values in the expression of the effective action. The operators do not necessarily have to commute with the Hamiltonian, but if they are not order operators, their relevance for hydrodynamic description must be justified otherwise. We also point out that choosing $\hat{Q}$ to be the CSCO (Complete Set of Commuting Observables) of the equilibrium Hamiltonian $\hat{H}$ or some subset of it (say, just the number operator $\hat{N}$) makes sense quantum mechanically in the sense that sensible density functional description is to be expected. In the microcanonical (isolated) classical ensemble the stationary (equilibrium) solutions of the Liouville equation are in principle functions of the system Hamiltonian H and constants of motion I_n in involution with each other and H: $\{H, I_n\} = 0$, so they are the classical equivalent of CSCO. However, the theory of dynamic system's tells us that for an ergodic system all other I_n except the Hamiltonian are non-isolating constants of motion, which means that H alone is sufficient to characterize the stationary measure of a Hamiltonian system in the (finite) phase-space [115]. From the point of view of general coarse-graining scheme it is important to understand what happens if we choose our equilibrium density matrix to be of the form $\exp(-\beta\hat{H} + \sum_n J_n \hat{Q}_n)$ and the in such away that the classical limits of the variables $\hat{Q}_n$ are the integrals of motion I_n. Naively, by coarse-graining the Wigner representation of the density matrix one would expect that the coarse-grained versions I_n of the operators $\hat{Q}_n$ would appear in the classical equilibrium distribution as well. But, how can they, if the system is ergodic? We should keep in mind that direct coarse-graining of equilibrium density matrix may lead us on the wrong track since we should also pay attention to the way the system gets to equilibrium both quantum mechanically and classically. We should ask first, what is the quantum equivalent of an ergodic system. Partial answers exist (see Jancel [116]) but many questions remain still open. We will continue discussion of the concepts of quantum integrability and nonintegrability in Sect. 3.2.3

2.3.2 Time Dependent Density Functional Theory and Berry's phase

Restricting the formulation to ordinary quantum mechanics instead of quantum fields, we show that the nonequilibrium generating functional reproduces the different time dependent generalizations of the static (equilibrium) density functional theory of Sect. 2.3.1. The problem is to transform the solution of the time dependent Schrödinger equation into a variational form by constructing an action functional analogously to the manner we have proceeded above. The subject has a long history going back to Dirac's variational principle [117]. More recent formulations by Eboli et al. [118] in the quantum field theoretical setting and quantum mechanical approach of Rajagopal [24] make it clear that the time-dependent density functional theory [119] follows from the nonequilibrium generating functional formalism naturally. We start by adding a source term to the Schrödinger equation:

$$\imath\hbar\frac{\partial}{\partial t}|\pm, t\rangle = \left[\hat{H} + \int d\mathbf{x}\, J(\mathbf{x}, t)\hat{n}(\mathbf{x})\right]|\pm, t\rangle \ . \tag{2.91}$$

The plus and minus states refer to the initial and final state asymptotics: $\lim_{t\to t_i}|+, t\rangle = |0\rangle$ and $\lim_{t\to t_f}|-, t\rangle = |0\rangle$, where $|0\rangle$ is the ground state (vacuum) of the operator $\hat{H}$. These states correspond to the in and out states of the S-matrix formalism discussed in Sect. 2.2.1. Following Rajagopal [24] we define a functional

$$\mathcal{A}[\phi_+, \phi_-] \equiv \int_{t_i}^{t_f} dt\, \langle\phi_-, t|(\imath\hbar\partial_t - \hat{H})|\phi_+, t\rangle \ . \tag{2.92}$$

Furthermore, it is required that $\mathcal{A}$ is stationary when the states $|\pm, t\rangle$ are varied independently subject to the constraints

$$\langle\phi_-, t|\hat{n}(\mathbf{x})|\phi_+, t\rangle = n_{-+}(\mathbf{x}, t) \quad ; \quad \langle\phi_-, t|\phi_+, t\rangle = 1 \ . \tag{2.93}$$

The extremizing transition density n_{-+} can be related via the Runge-Gross mapping theorem [120] to the densities $n_\pm$

$$n_\pm(\mathbf{x}, t) = \langle\phi_\pm, t|\hat{n}(\mathbf{x})|\phi_\pm, t\rangle / \langle\phi_\pm, t|\phi_\pm, t\rangle \ , \tag{2.94}$$

which in turn are the densities consistent with the solution of the Schrödinger equation (2.91). In other words, $n_{-+} = n_{-+}[n_-, n_+]$. This relation is invertible making it possible to use n_{-+}

as the basic variable, which is related to the external potential J in the familiar manner

$$\frac{\delta \mathcal{A}[n_{-+}]}{\delta n_{-+}(\mathbf{x},t)} = J(\mathbf{x},t) \ , \tag{2.95}$$

Going from the density variable n_{-+} to the source field J requires the introduction of the functional W, which plays the same role as in the more familiar generating functional description of Eq. (2.86):

$$W[J] = \mathcal{A}[n_{-+}] - \int d\mathbf{x} \int_{t_i}^{t_f} dt\, J(\mathbf{x},t) n_{-+}(\mathbf{x},t) \equiv \int_{t_i}^{t_f} dt\, w(t) \ , \tag{2.96}$$

where we have used Eq. (2.92) to define a time-dependent phase variable $w(t)$ [118],

$$w(t) = \langle \phi_-, t | \Big[\imath\hbar\partial_t - \hat{H} - \int d\mathbf{x}\, J(\mathbf{x},t)\hat{n}(\mathbf{x}) \Big] | \phi_+, t\rangle \ . \tag{2.97}$$

Choosing $w = 0$ at time t_i, the expression $\int_{t_i}^{t_f} dt\, w(t) \equiv \gamma'_B(t_i, t_f)$ tells what is the total phase of the generating functional after time $t_f - t_i$ due to the time evolution. This interpretation is a consequence of the fact that we can cast the generating functional into the same form, which was used for the S-matrix in the in-out representation (cf. Eq. (2.27)). From Ref. [24] we get

$$Z[J] = \langle 0 | \hat{T}^+_H(t_i, t_f, J) | 0 \rangle = \exp\Big(\frac{\imath}{\hbar}\gamma'_B(t_i, t_f, J)\Big) \exp\Big(\frac{\imath}{\hbar}E_0(t_i - t_f)\Big) \ , \tag{2.98}$$

where E_0 is the ground state energy. Berry's phase is the phase change of the eigenstate of the H associated with the adiabatic change of parameters of the Hamiltonian around a closed loop in parameter space [121]. Technically speaking, it originates from the imaginary part of the action in phase space representation [122] ($\imath\, dt\, p(t)\dot{x}(t)$ in terms of the overlap of time-slices of single particle path integral) Therefore Berry's phase can be identified as

$$\gamma_B(t, t_i) \equiv \int_{t_i}^{t} dt'\, \langle \phi_-, t' | \imath\hbar \frac{\partial}{\partial t} | \phi_+, t' \rangle = \gamma'_B(t, t_i, J) - \int_{t_i}^{t} dt' \langle \phi_-, t' | \hat{H}(t') | \phi_+, t' \rangle \ , \tag{2.99}$$

where the latter part is the phase change generated by the pure (time-dependent) Hamiltonian action, $\hat{H}(t') \equiv \hat{H} + \int d\mathbf{x}\, J(\mathbf{x}, t')\hat{n}(\mathbf{x})$.

What is the relevance of Berry's phase for coarse-graining? Whenever we are removing the fast degrees of freedom from description and obtain a coarse-grained theory for the slow degrees of freedom, there will be new interaction terms generated in the effective model. For concreteness, think of the Born-Oppenheimer approximation, which is used to decouple the slow nuclear degrees of freedom ($\mathbf{R}$) from the fast electronic ones ($\mathbf{r}$). Later on in Sect. 5.1 we will come across the following Schrödinger equations for the electrons (2.100) and the nucleons (2.101):

$$[\hat{T}_e(\mathbf{r}) + \hat{V}_e(\mathbf{r}) + \hat{V}_{e-N}(\mathbf{r}, \mathbf{R})]\psi_n(\mathbf{r}; \mathbf{R}) = \epsilon_n(\mathbf{R})\psi_n(\mathbf{r}; \mathbf{R}) \tag{2.100}$$

$$[\hat{T}_N(\mathbf{R}) + \hat{V}_N(\mathbf{R}) + \epsilon_k(\mathbf{R}) + \langle \psi_k | \hat{T}_N(\mathbf{R}) | \psi_k \rangle]\chi_{nk}(\mathbf{R}) = E_n \chi_{nk}(\mathbf{R}) \ , \tag{2.101}$$

where $\psi_n(\mathbf{r}, \mathbf{R}) \equiv \langle \mathbf{r}; \mathbf{R} | \psi_n \rangle$ is the nth eigenvector of the electronic Hamiltonian and $\chi_{nk}(\mathbf{R}) \equiv \langle \mathbf{R} | \chi_{nk} \rangle$ is the nth eigenvector of the nuclear Hamiltonian corresponding to kth effective potential term $\langle \psi_k | \hat{T}_N(\mathbf{R}) | \psi_k \rangle$. Since the latter term can also be presented as $\langle \psi_k | \hat{T}_N(\mathbf{R}) | \psi_k \rangle = (\langle \psi_k | \nabla_{\mathbf{R}} | \psi_k \rangle)^2/(2m_N)$, we can rewrite the nuclear Schrödinger equation as

$$[-\frac{1}{2m_N}\Big(\nabla_{\mathbf{R}} + \mathbf{A}(\mathbf{R})\Big)^2 + \epsilon_k(\mathbf{R}) + V_N(\mathbf{R})]\chi_{nk} = E_n \chi_{nk} \ . \tag{2.102}$$

The effect of the removal of the fast degrees of freedom is the appearance of vector potential $\mathbf{A} \equiv \langle\psi_k|\nabla_{\mathbf{R}}|\psi_k\rangle$ and an effective potential term ϵ_k. Nakahara [123] called the emergence of $\mathbf{A}$ spontaneous creation of gauge symmetry. It is indeed remarkable, that integrating out the bath does not always create only dissipative and stochastic effects. Of course, one has to keep in mind the time scale restrictions, possible higher order corrections and also the set of variables under study. The effects of removing the bath might be different for different variables. When solving the time-dependent Schrödinger equation for the bath variables with the effective Hamiltonian given in Eq. (2.100) gives rise to the Berry's phase in the state vector $|\psi_k, t\rangle$ reflecting the adiabatic influence of the slow nuclear degrees of freedom on the faster ones. The components of the vector potential actually defines a connection on the manifold of the slow degrees of freedom whose geometrical structure is reflected in Berry's phase [123].

Recently, geometric approaches have gained ever more popularity in phase transitions studies in different fields. Optimization problems, for example, can be connected with the geometry of the energy landscapes similar to those of spin-glasses [124]. Some recent studies have indicated that geometric analysis of the topology of the phase space may give rise to more powerful tools for deeper understanding of phase transitions. From the coarse-graining point of view an interesting hypothesis was put forward by Casetti, Pettini and Cohen in Ref. [125]. They showed that the perturbed geodesic motion on the manifold, whose metric is determined by the potential energy of the N-body classical Hamiltonian, can be approximated by a Langevin type of evolution equation for the perturbation vector, with multiplicative noise. Thus, from the very high dimensional space of microscopic degrees of freedom one filters out a coarse-grained equation of motion, whose parameters represent average geometric properties of the manifold. Intriguingly, the authors suggest that there is a deeper connection with the global topology change of the manifold and phase transitions, which are reflected in changes of the parameters of the simplified equation of motion. Even though we make no attempt to utilize these methods in this thesis, it should be kept in mind that one possibility (remote at this point) in the search of relevant macro variables is to use suitably averaged geometric information of the microscopic dynamics. Presumably some topological invariants can play the role of slow or conserved variables.

2.3.3 Equations of motion for relevant variables

The closed-time-path formalism is beneficial for deriving equations of motion of the expectation values of relevant macro operators because it generates equations of motion for the expectation values of the relevant variables respecting causality and normalization requirements [2] (for real-valuedness of the expectation values see [59, 94]). In the usual in-out type of generating functional formalism this is not guaranteed. The drawback of the CPT formalism is that at low loop order there can be unstable solutions [59]. There exist several ways of obtaining the equations of motion once the effective action $\mathcal{A}$ is known. Some ways of computing $\mathcal{A}$ have been discussed in Sect. 2.1.3. It is also possible to proceed deriving the dynamics without the construction of the action as we will see below.

Let us first define the 'canonical' way of producing the evolution equations. The most straightforward technique is to take variations of the action (which is determined in terms of the generating functional $Z[J_+, J_-]$) with respect to time-dependent sources [2]

$$\left.\frac{\delta\mathcal{A}[\phi_+, \phi_-]}{\delta\phi_+(\mathbf{x}, t)}\right|_{\phi_+=\phi_-} = -J(\mathbf{x}, t) \ . \tag{2.103}$$

We have put $J_+ = J_- = J(\mathbf{x}, t)$ (unique time axis) from which it follows that $\phi_+ = \phi_- = \phi(\mathbf{x}, t)$. Of course, it is also possible to derive separate (nonphysical) equations of motion for ϕ_+ and ϕ_- by not setting $J_+ = J_-$ in Eq. (2.103) or by taking variations with respect to $J_+(\mathbf{x}, t)$ and $J_-(\mathbf{x}, t)$ of the Legendre transformation of $\mathcal{A}$, $W[J_+, J_-]$ as in the so-called inversion method of Koide [67]. In case of multiple relevant operators coupled equations of motion result. For example, the physical evolution equations for the one point, $\phi = \langle\hat{\phi}\rangle$, and two-point functions, D_{ab} (see Sect. 2.2.4) become [54]

$$\left.\frac{\delta\mathcal{A}[\phi_+, \phi_-, D_{ab}]}{\delta\phi_+(x)}\right|_{\phi_+ = \phi_-} = 0 \quad ; \quad \left.\frac{\delta\mathcal{A}[\phi_+, \phi_-, D_{ab}]}{\delta D_{ab}(x_1; x_2)}\right|_{\phi_+ = \phi_-} = 0 \, , \tag{2.104}$$

where we have set the external fields to zero ($J = 0$) and denoted $x \equiv (\mathbf{x}, t)$. From Eq. (2.104) and Eq, (2.103) we see that the only difference with the equilibrium formalism is that the source fields are kept separate from each other before the variation. Moreover, in the equilibrium case the sources were independent of time (temperature).

Since the effective action is simple to form at tree-level [52], where no quantum corrections are taken into account, let us now see what is the dynamics of a typical ϕ^4-theory. Leaving out initial correlations, we write the generating functional

$$Z[J_+, J_-] = e^{W[J_+, J_-]} = \int \mathcal{D}(\tilde{\phi}_+, \tilde{\phi}_-)\ e^{\imath(S[\tilde{\phi}_+, \tilde{\phi}_-] + J_+\tilde{\phi}_+ - J_-\tilde{\phi}_-)} \, , \tag{2.105}$$

and the action is given by

$$S = \int dx\ \left\{\tfrac{1}{2}\tilde{\phi}_+[-\Box - m^2]\tilde{\phi}_+ + (\lambda/4)\tilde{\phi}_+^4 - \tfrac{1}{2}\tilde{\phi}_-[-\Box - m^2]\tilde{\phi}_- - (\lambda/4)\tilde{\phi}_-^4\right\} \, . \tag{2.106}$$

At the tree level the effective action, which results from the Legendre transformation $\mathcal{A} = \ln Z - J\phi = W - J\phi$, is easy to obtain: One just needs to replace the dummy integration fields $\tilde{\phi}_+$ and $\tilde{\phi}_-$ in the action S with the expectation values of the field operators $\langle\hat{\phi}_+\rangle = \phi_+$ and $\langle\hat{\phi}_-\rangle = \phi_-$. Thus

$$\mathcal{A}_{tree}[\phi_+, \phi_-] = S[\phi_+, \phi_-]. \tag{2.107}$$

Applying now rule (2.103) and setting the source fields $J_+ = J_- = 0$, we obtain the equation of motion for the expectation value of the field:

$$\frac{\delta\mathcal{A}[\phi_+, \phi_-]}{\delta\phi_+(\mathbf{x}, t)} = -(\Box + m^2)\,\phi + \lambda\phi^3 = 0 \, . \tag{2.108}$$

Some comments as regards the form of the action and the equation of motion are in order. First of all, the relativistic form of the of the free part of the Lagrangian density $(1/2)\phi(\Box + m^2)\phi$ reveals that the 'kinetic energy' of the field term $(\pi(\mathbf{x}, t))$ of the canonical action has been integrated out. In other words,

$$\begin{aligned} S_{can} &= \int dt \int d\mathbf{x}\,(\imath\pi(\mathbf{x}, t)\dot{\phi}(\mathbf{x}, t) - H(\pi, \phi)) \; ; && (2.109)\\ H(\pi, \phi) &= \tfrac{1}{2}\pi^2(\mathbf{x}, t) + \tfrac{1}{2}|\nabla\phi|^2(\mathbf{x}, t) + V(\phi) \, , && (2.110)\end{aligned}$$

and $V(\phi) = (m^2/2)\phi^2 + (\lambda/4)\phi^4$. Removing the variable π gives rise to the Alambartian $\Box$. If one goes over to the complex coordinates $(a(\mathbf{x}, t), a^*(\mathbf{x}, t))$ from the pair $(\pi(\mathbf{x}, t), \phi(\mathbf{x}, t))$

one usually does not integrate out a^* from the canonical action (2.110). Therefore, the corresponding action in the non-relativistic case would be written as

$$S_{can} = \int dt \int d\mathbf{x} \left(\imath a^*(\mathbf{x},t)\partial_t a(\mathbf{x},t) - H(a^*,a) \right) , \tag{2.111}$$

where for a quantum problem $H(a^*,a) = \nu a^* \nabla^2 a + V(a^*,a)$ and $\nu = \hbar^2/(2m)$ $(\hbar = 1)$. We also note that it is possible to cast a fully classical stochastic field theoretic [94] problem or a classical deterministic many-body problem (see Sect. (2.4)) into a suitable form for generating functional formalism.

We also note that the path integral representation of the action of a fully classical (stochastic) problem [94] is given by Eq. (2.111) but without the factor of $\imath$ in front of the term $a^*(\mathbf{x},t)\partial_t a(\mathbf{x},t)$. Thus, in the classical case the tree level equation of motion becomes

$$\frac{\delta \mathcal{A}[a_+,a_+^*,a_-,a_-^*]}{\delta a_+^*(\mathbf{x},t)} = \partial_t a - \nu\nabla^2 a - \frac{\partial V(a^*,a)}{\partial a_+^*} = 0 \ . \tag{2.112}$$

For a fourth order polynomial potential this starts looking like the Ginzburg-Landau equation, which we will come back in more detail in Sect. 5.1. When the expectation values are real, we can rewrite Eq. (2.112) in a more suggestive form by defining a 'free energy' function (having units of action, cf. App. D.1) $F[a] \equiv \int dt \int d\mathbf{x}\, \nu |\nabla a(\mathbf{x},t)|^2 + (m^2/2)a(\mathbf{x},t) + (\lambda/4)a^4(\mathbf{x},t)$. Then, the equation of motion for the order parameter a takes the following form

$$\partial_t a(\mathbf{x},t) + \hat{\Xi}\frac{\delta F[a]}{\delta a(\mathbf{x},t)} = 0 \ , \tag{2.113}$$

where the prefactor $\hat{\Xi} = 1$, in the this case. Later on we will see that $\hat{\Xi}$ is actually an operator, which can contain both dissipative and reactive couplings the order parameter and other relevant quantities of the theory. Eq. (2.113) is basically the simplest evolution equation of a non-conserved order parameter field, which is called Model A in the cathegorization scheme [126] for critical dynamics models. They are also called phase-field models, as the order parameter field acts as an indicator field taking a different value in each of the different phases present in the system. Phase-field modelling is discussed in more detail in Chap. 7.

We have now described the canonical scheme of deriving the equations of motion. Depending on the situation this may not always be the most convenient one. For many purposes it is physically motivated to go to the Wigner representation via the transformation

$$\left\{ \begin{array}{rcl} J_c & \equiv & (J_+ + J_-)/2 \ ; \\ J_\Delta & \equiv & J_+ - J_- \ . \end{array} \right. \tag{2.114}$$

Performing this change in the generating functional $Z[J_+,J_-]$ leads to a corresponding change the the effective action [63], which will now be expressed in terms of the expectation values

$$\left\{ \begin{array}{rcl} \phi_c & \equiv & (\phi_+ + \phi_-)/2 \ ; \\ \phi_\Delta & \equiv & \phi_+ - \phi_- \ . \end{array} \right. \tag{2.115}$$

The physical expectation value of the observable is now given by ϕ_c whereas the ϕ_Δ will be responsible for its fluctuations (Sect. 2.3.4). The equations of motion are generated as before, by taking variations with respect to ϕ_c and ϕ_Δ:

$$\frac{\delta \mathcal{A}[\phi_c,\phi_\Delta]}{\delta \phi_\Delta(\mathbf{x},t)} = -J_c(\mathbf{x},t) \ ; \tag{2.116}$$

$$\frac{\delta \mathcal{A}[\phi_c,\phi_\Delta]}{\delta \phi_c(\mathbf{x},t)} = -J_\Delta(\mathbf{x},t) \ . \tag{2.117}$$

The correct source field appearing on the right hand side of the previous equations can be found from the relation $J_+\phi_+ - J_-\phi_- = J_\Delta\phi_c + J_c\phi_\Delta$. When the source field $J_\Delta = 0$, Eq. (2.116) is the physical equation of motion and Eq. (2.117) is automatically satisfied [94] because of the normalization [2]: $Z[J_\Delta = 0, J_c] = 1$. Owing to the normalization condition we also obtain

$$\phi_\Delta(x)|_{J_\Delta=0} = -\imath \left.\frac{\delta \ln Z[J_\Delta, J_c]}{\delta J_c(x)}\right|_{J_\Delta=0} = 0 \ , \tag{2.118}$$

which becomes handy, when simplifying the physical equation of motion (2.116).

A third way of obtaining the equations of motion, which is fully consistent with the approaches presented above, does not require the construction of the effective action. It suffices to study the symmetries of the generating functional. The Ward-Takahashi identities generate equations of motion for the conserved variables as shown in Ref. [2]. We will return to this important idea in Sect. 3.1.2. Another method, which utilizes the generating functional directly was introduced by Greiner and Leupold in Ref. [80]: It uses the identity

$$0 = \int \mathcal{D}\phi \, \frac{\delta}{\imath\delta\phi}\Big(\rho_0 \, e^{\imath(S+J\phi)}\Big) = \int \mathcal{D}\phi \, \rho_0 \, (S' + J) \, e^{\imath(S+J\phi)} \ , \tag{2.119}$$

and produces a closed equation of motion for actions quadratic in ϕ. For actions having higher powers of field ϕ this approach leads to BBGKY type of hierarchy just like direct averaging of Heisenberg equations of motion for field variables, which is of course always an option. It should be noted that even though the construction of effective action is not easy, it gives an equation of motion for the expectation value of the field and the BBGKY hierarchy problem does not appear (it is non-trivially traded for the possibly problematic construction process of $\mathcal{A}$).

Finally, we note that equations of motion obtained from Eq. (2.103) or Eq. (2.116) using the effective action $\mathcal{A}$ are equivalent to the saddle point equation of motion of the original action S at tree level. This will become clearer in the next section where discuss the quasi-classical corrections to equations of motion, which leads naturally to stochastic Langevin type of equations of motion for the relevant variables. In a way, the highly nonlinear *deterministic* equations of this section will be approximated by a stochastic (less nonlinear) equations of motion.

2.3.4 Stochastic dynamics

There are two main sources of stochasticity in the coarse-grained models. First of all, there is structural randomness present in any realistic problem such as distribution of point defects in crystal or pore structure of sandstone [127]. It is a demanding coarse-graining task to try to come up with the least possible number of macroscopic parameters, such as connectivity or internal surface area, which adequately characterize the complicated structure. This type of randomness is quenched or frozen, opposite to the dynamic (time dependent) type of randomness arising from the removal of the non-interesting degrees of freedom. Random fields associated with the decimation of dynamic variables mimic the effect of the fast degrees of freedom on the slower ones. A third type of noise, which is related to the dynamical noise can come about because of the nonlinearities of the effective theory: It is possible to model the effects of nonlinearites by using stochastic terms (deterministic chaos [128]) to simplify the form of the deterministic part of the equation of motion.

In the generating functional formalism it is basically the double time path structure, which gives rise to the possibility of approximating the nonlinear deterministic dynamics using random fields to describe the interaction of the sources on different contours. Following Chou et al. [2] we try to cast the generating functional into a form, which enables us to interpret it as a generalization of Martin-Siggia-Rose [95] type of generating functional of a stochastic process. The generating functional reads

$$Z[J_+,J_-] = e^{\imath W[J_+,J_-]} = \int \mathcal{D}(\phi'_+,\phi'_-)\; e^{\imath(S[\phi'_+,\phi'_-]+J_+\phi'_+-J_-\phi'_-)} \tag{2.120}$$

We have denoted the dummy integration variables of the generating functional with primed variables to separate them from the expectation values of the corresponding operators (observable quantities), $\phi_\pm = \langle\hat{\phi}_\pm\rangle$, which are Legendre conjugate's of the sources $J_\pm$. Previously, we have occasionally denoted also the dummy integration variables by $\phi_\pm$ when there has been no danger of confusion. However, here one must differentiate between primed fields and unprimed fields since we wish to make a change of variables: $(\phi'_+,\phi'_-) \to (\phi_+,\phi_-)$. The reason for this is that when the generating functional Z has been expressed in terms of the new integration variables, its semi-classical limit corresponds to the generating functional of a classical stochastic process with Gaussian noise. The end result will look like

$$Z[J_+,J_-] \approx \int \mathcal{D}(\phi_+,\phi_-)\; e^{\imath(\mathcal{A}_{tree}[\phi_+,\phi_-]+J_+\phi_+-J_-\phi_-)} \tag{2.121}$$

More formally, this can be seen by performing a double Fourier transformation of the generating functional

$$\begin{aligned} Z[J] = e^{-\imath W[J]} &= \int \mathcal{D}I \underbrace{\int \mathcal{D}Q\; e^{\imath\int Q(I-J)}\,\delta(Q_+-Q_-)}_{\delta(I-J)}\; e^{-\imath W[I]} && (2.122)\\ &\propto \int \mathcal{D}Q \underbrace{\int \mathcal{D}I\; e^{\imath\int QI-\imath W[I]}}_{\exp(\imath S_{eff}[Q])}\; e^{-\imath\int JQ}\,\delta(Q_+-Q_-) && (2.123)\end{aligned}$$

We have denoted $Q=(\phi_+,\phi_-)$ and $\delta(Q_+-Q_-)$ connects the integration paths at the initial time moment. At tree level it can be shown [2] that $S_{eff}\approx\mathcal{A}_{tree}$ and Eq. (2.121) follows. Next, we utilize the representation given in Eq. (2.114) and (2.115) and expand the effective action around the physical solution $\phi_\Delta = 0$:

$$Z(J_c,J_\Delta) \approx \int \mathcal{D}(\phi_c,\phi_\Delta)\; \exp\left(\imath\mathcal{A}_{tree}[\phi_c,\phi_c] + \imath\frac{\delta\mathcal{A}_{tree}}{\delta\phi_\Delta}\phi_\Delta + \frac{\imath}{2}\phi_\Delta\frac{\delta^2\mathcal{A}_{tree}}{\delta\phi_\Delta\delta\phi_\Delta}\phi_\Delta + \imath J_\Delta\phi_c + \imath J_c\phi_\Delta\right). \tag{2.124}$$

Expanding the short-hand notation used above, the first derivative term in the argument of the exponential is

$$\frac{\delta\mathcal{A}_{tree}}{\delta\phi_\Delta}\phi_\Delta = \int dx\; \frac{\delta\mathcal{A}_{tree}}{\delta\phi_\Delta(x)}\bigg|_0 \phi_\Delta(x) = \int dx\; \left(\frac{\delta\mathcal{A}_{tree}[\phi_+,\phi_-]}{\delta\phi(x_+)} + \frac{\delta\mathcal{A}_{tree}[\phi_+,\phi_-]}{\delta\phi(x_-)}\right)\bigg|_0 \phi_\Delta(x)\;, \tag{2.125}$$

where $x_\pm \equiv (\mathbf{x},t_\pm)$ and $|_0$ means that the expression should be evaluated at $\phi_\Delta = 0$. Moreover, we have used the fact that $\delta\mathcal{A}/\delta\phi(x_-) = -\delta\mathcal{A}/\phi_-$. The double time path notation is valid for the expression in the parenthesis in Eq. (2.125) before the time axis are made unique through substitution $\phi_\Delta = 0$. Because differentiation of the effective action with respect to

ϕ_Δ produces by definition the physical equation of motion (Eq. (2.113) in the general case), we can rewrite Eq. (2.125),

$$\frac{\delta \mathcal{A}_{tree}}{\delta \phi_\Delta}\phi_\Delta = 2\int dx \left(\partial_t \phi_c(x) + \hat{\Xi}\frac{\delta F[\phi_c]}{\delta \phi_c(x)} \right) \phi_\Delta(x) \tag{2.126}$$

The second order derivative with respect to ϕ_Δ in Eq. (2.124) can be decomposed into four different terms when distributed on the positive and negative time branches:

$$\begin{aligned} \phi_\Delta \frac{\delta^2 \mathcal{A}_{tree}}{\delta \phi_\Delta \delta \phi_\Delta}\phi_\Delta &= \int dx \int dx'\ \phi_\Delta(x) \left\{ \frac{\delta^2 \mathcal{A}_{tree}}{\delta\phi(x_+)\delta\phi(x_+)} + \frac{\delta^2 \mathcal{A}_{tree}}{\delta\phi(x_+)\delta\phi(x_-)} \right. \qquad (2.127) \\ &\qquad \left. + \frac{\delta^2 \mathcal{A}_{tree}}{\delta\phi(x_-)\delta\phi(x_+)} + \frac{\delta^2 \mathcal{A}_{tree}}{\delta\phi(x_-)\delta\phi(x_-)} \right\} \Bigg|_0 \phi_\Delta(x') \\ &\equiv \imath \int dx \int dx'\ \phi_\Delta(x) R(x,x') \phi_\Delta(x')\ . \qquad (2.128) \end{aligned}$$

Taking into account that when time axis is made unique by making the different sources the same, $\mathcal{A}_{tree}[\phi_c, \phi_c] = 0$. The generating functional (2.124) can now be written as

$$Z[J_c, J_\Delta] = \tag{2.129}$$

$$\int \mathcal{D}(\phi_c, \phi_\Delta)\ \exp\left(\int \imath \left[\partial_t \phi_c + \hat{\Xi}\frac{\delta F[\phi_c]}{\delta \phi_c(x)} \right] \phi_\Delta - \frac{1}{2}\int\int \phi_\Delta R(x,x')\phi_\Delta + \int (\imath J_\Delta \phi_c + \imath J_c \phi_\Delta) \right)\ .$$

We can now see that the source J_c correspond to the physical source j of the Martin-Siggia-Rose [95] formalism (Bausch-Janssen-Wagner-de Dominics formalism [129, 130]) and J_Δ is the response source $\tilde{j}$ related to the fictitious field needed in the representation of the functional delta function. Moreover, setting $J_\Delta = 0$ and integrating over ϕ_Δ gives the generating functional of the correlation functions of a stochastic process with zero mean and correlations given by R^{-1}.

The Langevin equation of motion for the expectation value ϕ_c can be derived by defining a Gaussian noise field ξ whose distribution

$$P[\xi] = const\, e^{-\frac{1}{2}\int\int \xi(x) R(x,x') \xi(x')}\ . \tag{2.130}$$

We also define a new generating functional $\tilde{Z}$ through $Z[J_c, J_\Delta] = \int \mathcal{D}\xi\, P[\xi]\, \tilde{Z}[J_c, J_\Delta, \xi]$. Rewriting Eq. (2.129) in terms of $P[\xi]$ gives

$$Z[J_c, J_\Delta] = \tag{2.131}$$

$$\int \mathcal{D}\xi\, P[\xi] \int \mathcal{D}(\phi_c, \phi_\Delta)\ \exp\left(\imath \int \left(\partial_t \phi_c + \hat{\Xi}\frac{\delta F[\phi_c]}{\delta \phi_c(x)} - \xi \right) \phi_\Delta + \imath \int (J_\Delta \phi_c + J_c \phi_\Delta) \right)$$

Thus, for all practical purposes, the argument of the exponential can be called a new effective action $\tilde{\mathcal{A}}$ which contains a stochastic element ξ:

$$\tilde{\mathcal{A}}[\tilde{\phi}_c, \tilde{\phi}_\Delta, \xi] \equiv \int dx \left(\partial_t \tilde{\phi}_c + \hat{\Xi}\frac{\delta F[\tilde{\phi}_c]}{\delta \tilde{\phi}_c(x)} - \xi \right) \tilde{\phi}_\Delta \tag{2.132}$$

We do not use the symbols ϕ_c and ϕ_Δ together with the action $\tilde{\mathcal{A}}$ anymore because they are completely deterministic expectation values. The new fields $\tilde{\phi}_c$ and $\tilde{\phi}_\Delta$ are stochastic approximations to the old variables ϕ_c and ϕ_Δ. We also point out that there is a functional Jacobian determinant related to the association of ξ with $\tilde{\phi}_c$ but it turns out that as long as there are only first order time derivatives involved (which is true for non-relativistic theories) we can leave it out with no harm done on the interpretation of the results [131, 50]. Forming now the equation of motion via the standard recipe gives

$$\left.\frac{\delta\tilde{\mathcal{A}}}{\delta\tilde{\phi}_\Delta(x)}\right|_{\tilde{\phi}_\Delta=0} = 0 \quad\Longrightarrow\quad \partial_t\tilde{\phi}_c(x) = -\hat{\Xi}\frac{\delta F[\tilde{\phi}_c]}{\delta\tilde{\phi}_c(x)} + \xi(x)\ . \tag{2.133}$$

The source $J_c = 0$ when there are no physical external driving fields. We will see later on that in fact the operator $\hat{\Xi}$ can also depend on the fields $\tilde{\phi}_c$ (Sect. 3.1.2, Chap. 7 and Chap. 9). The form of Ξ can be fixed based on general physical assumptions on streaming and equilibration without having to calculate it. We will now briefly comment on the possibility of direct determination of $\hat{\Xi}$ and its role in equilibration of the system.

2.3.5 Remarks on dissipation

In the previous section we did not make use of the external bath but explained the emergence of stochasticity by introducing a linear coupling of the non-physical variable ϕ_Δ to a field ξ. The purpose of ξ is to mimic the effect of non-linearities (higher order self-couplings) on the dynamics of the physical field ϕ_c. The result is approximative in many ways: It does produce sensible dynamics for the one-point function $\langle\hat{\phi}\rangle$ but the dynamics of two-point Green's function on the double time contour $D_{ab} = \langle\hat{\phi}(x_a)\hat{\phi}(x_b)\rangle$ $(a, b = \pm)$ computed in terms of $\langle\tilde{\phi}(x_a)\tilde{\phi}(x_b)\rangle_\xi$ is just an approximation even if there are only second order interactions in the action [80]. To see the emergence of the dynamic noise due to coarse-graining (which we did not perform explicity in Sect. 2.3.4), one should divide the system under study into the system and bath degrees of freedom. When the bath is removed, new kinds of non-linear self couplings of the system field will emerge and these can be modelled via introduction of noise fields ξ as explained above. Similar approach can be applied directly at the level of the non-linear equation of motion as has been discussed by Zwanzig [14] who shows how the exact non-linear Langevin equation can be traded for the linear Langevin equation of Mori's, with different (renormalized or fluctuation corrected) noise and dissipative properties.

By explicitly integrating out the bath degrees of freedom, we will also see the origin of the dissipation in the system, whose microscopic origin was hidden in Sect. 2.3.4). It should be noted, though, that specifying bath is not absolutely necessary but it makes stochastic and dissipative properties of the system more easily visible. These effects are of course present in the general form of the generating functional. In the original presentation of Zhou et al. [63] of critical dynamics in terms of the generating functional the dissipative effects are hidden in the self-energy terms of the Green's functions. In the (condensed matter) Green's function theory the irreversible dynamics [132] is a result from two factors: Infinite system size and (impurity) scattering. Basically, the 'impurities' can represent the frozen type of randomness if they are fixed. If they are mobile, they can be thought of as dynamic bath degrees of freedom the collisions of which with the system variables result in noise and dissipation. Infinite system size is needed in order for there to be enough phase space volume for the energy to vanish into without having it pumped back by the bath in a finite time. Naturally, the bath can also give rise to Landau type of damping (phase decoherence) without any energy transfer.

When explicit bath is used, it is easy to see the emergence of the dissipation and stochasticity. Several examples ranging from classical to many-body quantum mechanical systems have been studied with linear [68, 133, 134] and higher order couplings between the bath and system variables. For linear couplings in non-relativistic systems one can show that the fluctuation-dissipation relation will be obeyed and the system will relax to Gibbs equilibrium. The Poincare recurrence times become extremely long already for small number N of bath variables ($N \geq 20$ oscillators suffices to make it practically infinite [74]). Analogously to equilibrium phase transitions, rigorously the time's arrow can only emerge in the thermodynamic limit when the number of bath variables goes to infinity [135, 136]. The problem with infinite baths is the mathematical formulation of the quantum mechanics, which requires the use of operator algebras (C^*-algebra). However, the traditional finite dimensional Hilbert space approach is sufficient for the study of non-equilibrium dynamics when equipped with a few reasonable phenomenological assumptions about the irreversibility [137].

At the level of quantum field theoretic formulation it is not problematic to establish the irreversible behaviour at least in low loop order. One should remember though, that for relativistic theories one must go to higher order corrections than Gaussian, to see the emergence of terms which can be interpreted as friction [75, 138]. This is because of the presence of the second order time derivative in the equation of motion instead of first order one as in non-relativistic equations of motion. We must also remember that plain loop-wise determination of the noise properties might not be the best way to proceed in cases where non-perturbative effects due to nonlinearities are important. Of course, the ultimate aim would be to show that the exact deterministic equation of motion, $\delta\mathcal{A}[\phi]/\delta\phi(\mathbf{x},t) = -J(\mathbf{x},t)$, truly drives the system to in such a state, which could be described by a stationary distribution, say of Gibb's type. In the limit of large times, we thus expect that the dynamic equation reduces to the equilibrium equation of state:

$$\lim_{t\to\infty}\left(\partial_t\phi_c + \hat{\Xi}\frac{\delta F[\phi_c]}{\delta\phi_c(\mathbf{x},t)} + J_c(\mathbf{x},t)\right) \;\to\; \hat{\Xi}\frac{\delta F[\phi_c^{eq}]}{\delta\phi_c^{eq}(\mathbf{x})} + J_c(\mathbf{x},\infty) = 0\ , \tag{2.134}$$

where $\phi_c^{eq}(\mathbf{x})$ is the time independent equilibrium expectation value of the field and the source field J_c is assumed to become stationary for large enough times. However, due to the high degree of nonlinearity in field variables, this will not be easy to show from first principles as we know from the theory of dynamic systems. By reducing the degree of non-linearity we also have to face the risk of loosing the possibility to study things like multiple steady-states and the related phase transition dynamics, nonlinearity generated instabilities and so on. But in all honesty, even the tree-order non-linearities are challenging enough to keep us busy for the next century or so.

For many purposes, semi-classical level of description leading to Langevin (2.133) equation for the (partially averaged) expectation values of observables is sufficient. Using an external bath it is possible to show that $\hat{\Xi}(\phi_c)$ indeed contains a part which is related to the noise kernel R^{-1} as required by the fluctuation-dissipation theorem. The coefficient $\hat{\Xi}$ contains also some explicit dependence of the field ϕ_c. The origins of $\hat{\Xi}(\phi_c)$ are rooted in the nonlinear self-interactions of the theory. This can be made manifest by looking at the form of the renormalized action (of relativistic ϕ^4-theory [139], for example):

$$\mathcal{A}[\phi_c] = \int dx\left(\tfrac{1}{2}Z_{eff}[\phi_c](\partial\phi_c)^2 - V_{eff}(\phi_c)\right)\ , \tag{2.135}$$

where $Z_{eff}(\phi_c)$ is the wave function renormalization and V_{eff} is the effective potential corresponding to our free energy F. The saddle point equation of motion results immediately in $\Box\phi_c + Z_{eff}^{-1}[\phi_c]\partial V_{eff}/\partial\phi_c = 0$. In the closed time path case the structure is a bit more complicated but analogous. Thus, in principle we know that there will be some field dependence in the coefficient Ξ. In Sect. 3.1.2 we will give some arguments (cf. Ref. [63]) for the following representation

$$\hat{\Xi}(\cdot) \approx \int dx' \, \{\phi_\mu(x), \phi_\nu(x')\}(\cdot) + M\nabla^2(\cdot) \; , \tag{2.136}$$

when there are several conserved fields ϕ_μ present in the problem. The first term on the right hand side of Eq. (2.136) represents dissipationless streaming and the second one dissipative flux, which is responsible for the fulfilment of the fluctuation-dissipation theorem. Even though any direct (renormalization) proof of the suggested form is difficult to give, the form of the operator $\hat{\Xi}$ can fortunately be found (consistent with Eq. (2.136)) entirely based on the assumption that the system will go to Gibb's equilibrium characterized by the free energy F (App. D.4).

Finally, we point out the possibility of generating dissipative behaviour by truncating the BBGKY moment hierarchy of correlation functions. This dissipation derives from the initial correlations present in ρ_0, Thus, it is not generated by bath as in the other examples above. Calzetta and Hu [58, 140] have shown how the stochastic Dyson's equation (Langevin equation) arises due to the truncation process, which corresponds to the classical Boltzmann's molecular chaos assumption. As is known the full BBGKY hierarchy is reversible but the truncated one is not. So, in a sense, this type of dissipation is artificial dissipation because it results from an incorrect mathematical manipulations. However, it gives a reasonable approximation just like Boltzmann's equation does to real dynamics.

2.4 Unified formalism covering different starting points

This section serves to demonstrate who can one continue further coarse-graining of an effective theory, which has already been coarse-grained. We consider two such effective intermediate coarse-graining levels: Classical Hamiltonian dynamics of an interacting many-body system obeying Newton's equations of motion and lattice-gas type of cellular automata models obeying Master equation. We are not trying to pave the way for going from quantum mechanics to classical mechanics in the general case because any rigorous or semi-rigorous justification is beyond the scope of this book and we direct the reader to the references mentioned in Chap. 1. Similarly, references for going from the fully classical Newton's dynamics to lattice-gas description are dealt with in the Introduction.

Our starting point is that the dynamic rules (Newton's equations of motion or transition probabilities) are known. The question is how to obtain evolution equations for quantities of interest such as mass or momentum densities. We will show that despite the shift from quantum to classical world, we can disguise the problem in the same Quantum Field Theoretic (QFT) form as before. So, with minor modifications, we are able to address quantum field theory, ordinary quantum mechanics and classical problems using the same language. The field theoretic representation does not make the explicit calculations easier as using the standard representation but it facilitates the use of certain techniques, such as symmetry analysis of the effective action based on continuum field representation or spectrum generating algebra, which are not (readily at least) available in the traditional formulation.

2.4.1 Classical Molecular Dynamics level

The basic formalism for second quantized representation of classical many-body system has been given in Refs. [3, 141] and subsequently used in several contexts [142, 143, 53]. The idea is to cast the time evolution of the deterministic Liouville equation, $\partial_t P = \imath \hat{L} P$, where $\hat{L}$ is the Liouville operator, into a representation, which looks like second quantized many-body quantum mechanics. So, this is just a different representation of the classical problem, not a coarse-graining act linking the quantum and classical worlds. The central object is the time dependent state vector

$$|\phi(t)\rangle \equiv \sum_{N=0}^{\infty} \int d\mathbf{q}^N \, P_N(\{\mathbf{q}_i\}, t) \, |\mathbf{q}^N\rangle \tag{2.137}$$

where $\mathbf{q}^N$ refers to all phase space coordinates $\{\mathbf{q}_i\} \equiv \{\mathbf{x}_i, \mathbf{p}_i\}$ and $|\mathbf{q}^N\rangle \equiv \prod_{i=1}^N a^\dagger(\mathbf{q}_i)|0\rangle$ is the occupation number representation of a state with N point particles located at sites $\mathbf{q}_i$. The state vectors are symmetrized leading to a bosonic Fock-space description familiar from many-body quantum mechanics. Creation and annihilation operators satisfy the usual algebra

$$[a(\mathbf{q}), a(\mathbf{q}')] = [a^\dagger(\mathbf{q}), a^\dagger(\mathbf{q}')] = 0 \;\; ; \;\; [a(\mathbf{q}), a^\dagger(\mathbf{q}')] = \delta(\mathbf{q} - \mathbf{q}') \; . \tag{2.138}$$

The formalism is general enough to cover chemical reactions, which can lead to non-Hermitean representations of the time evolution operator. Then, the spectral decomposition of operators must differentiate between the left and right eigenvectors:

$$\hat{A} = \sum_p |L_p\rangle \lambda_p \langle R_p| \; , \tag{2.139}$$

where the left and right eiqenvectors are orthogonal. For Hermitean operators the usual symmetric decomposition holds. The vacuum state is special. According to Ref. [3]

$$a(\mathbf{q})|0\rangle = 0 \;\; ; \;\; \langle 0|a^\dagger(\mathbf{q}) = 0 \; . \tag{2.140}$$

This relation holds even though a and $a^\dagger$ are not Hermitean conjugates [144]. There is another difference from usual quantum mechanics related to the expectation values of observables: The mean value (expectation value) of an observable A at time t in state $|\phi(t)\rangle = \exp(-\imath t \hat{L})|\mathbf{q}^N\rangle$ is given by

$$\langle \alpha|\hat{A}|\phi(t)\rangle = \langle 0|e^{\int dq \, a(\mathbf{q})} \, A(a^\dagger, a) \, e^{-\imath t \hat{L}(a^\dagger, a)}|\mathbf{q}^N\rangle \; . \tag{2.141}$$

The coherent state (Glauber state) $\langle \alpha| \equiv \langle 0| \exp \int dq \, a(\mathbf{q})$ is always needed as the bra-state because technically speaking it projects out the physical (probability) content of the state vector $|\phi(t)\rangle$ by collecting contributions from all different N-particle subspaces of the Fock space. The explicit representation of the Liouville operator for a system with pair potential $V(\mathbf{x} - \mathbf{x}')$ is given by [3]

$$\begin{aligned} \hat{L} \;\; = & \int d\mathbf{x} \int d\mathbf{p} \; a^\dagger(\mathbf{x}, \mathbf{p}) \Big(\frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{x}} \Big) a(\mathbf{x}, \mathbf{p}) - \frac{1}{2} \int d\mathbf{x} \int d\mathbf{p} \int d\mathbf{x}' \int d\mathbf{p}' \; \Big\{ a^\dagger(\mathbf{x}, \mathbf{p}) a^\dagger(\mathbf{x}', \mathbf{p}') \\ & \times \Big(\nabla_{\mathbf{x}} V(\mathbf{x} - \mathbf{x}') \Big) \cdot \Big(\nabla_{\mathbf{p}} a(\mathbf{x}, \mathbf{p}) a(\mathbf{x}', \mathbf{p}') - \nabla_{\mathbf{p}'} a(\mathbf{x}', \mathbf{p}') a(\mathbf{x}, \mathbf{p}) \Big) \Big\} \; . \end{aligned} \tag{2.142}$$

It is important to notice that the variables $\mathbf{x}$ and $\mathbf{p}$ are not conjugate variables above but ordinary dummy integration variables. In Eq. (2.141) we chose the simple initial state

$|\mathbf{q}^N\rangle$ with N particles with positions and momenta $\mathbf{q}_i$. Equally well, we could have chosen a thermal initial distribution $\rho_0|0\rangle$, where $\rho_0 \equiv \int d\mathbf{q}^N \exp(-\beta \tilde{H}_N(a^\dagger, a))/Z_N$ and $Z_N \equiv \mathrm{Tr}\{\exp(-\beta \tilde{H}_N(a^\dagger, a))\}$.

It is now time to consider a few generalizations to the basic scheme presented above. First, we note that we can easily form the path integral representation of the generating functional:

$$Z[J] = \tag{2.143}$$
$$\mathrm{Tr}\left\{|0\rangle\langle 0|e^a U^{-1}(t_f, t_i, J)\right\} = \mathrm{Tr}\left\{e^a U^{-1}(t_f, t_i, J)|0\rangle\langle 0|\right\} = \mathrm{Tr}\left\{U^{-1}(t_f, t_i, J)|0\rangle\langle 0|e^a\right\} ,$$

where we have introduced a short-hand notation $\langle\alpha| = \langle 0|\exp(\int d\mathbf{x} \int d\mathbf{p}\, a(\mathbf{x}, \mathbf{p})) \equiv \langle 0|\exp(a)$, and

$$U^{-1}(t_f, t_i, J) = \hat{T}_-\, e^{-\imath \int_{t_i}^{t_f} dt \int d\mathbf{q}\ (L(a^\dagger(\mathbf{q}), a(\mathbf{q})) + J(\mathbf{q},t) a(\mathbf{q}) + h.c.)} . \tag{2.144}$$

This is basically the same formula, which we have been using before but with Hamiltonian replaced by Liouvillean time evolution operator. We have also used the basic field operators coupled with sources for simplicity. In applications there would be additional composite operators corresponding to the relevant slow variables of the system coupled to their own sources. As we can see from Eq. (2.143) things are complicated by the presence of the operators $|0\rangle\langle 0|$ and e^a. One (formal) possibility of making the problem appear more like our genuinely quantum mechanical formulation is to take $|0\rangle\langle 0|$ to the right hand side of U^{-1} and call it ρ_0 (pure initial state). Then we can commute e^a through the time evolution operator as long as we hit the ket-vector of the projector $|0\rangle\langle 0|$: This amounts to replacing $L(a^\dagger, a)$ with $e^a L(a^\dagger, a) e^{-a} = L(a^\dagger + 1, a)$. This is fine for single time path formalism, but it does not work if we want to use CPT formulation. Instead, we can keep e^a on the left of U^{-1} and take $\rho_0 = |0\rangle\langle 0|$ to the right as indicated by the center expression in Eq. (2.143). Then, it is possible to add a term $e^{\imath t\hat{L}}$ to the right hand side of ρ_0 because $|0\rangle\langle 0|e^{\imath t\hat{L}} = |0\rangle\langle 0|$ according to Eq. (2.140). Apart from the operator e^a the representation of the generating functional is then identical to Eq. (2.50) given that we add a source J_-. Of course, we do not have to insist on the closed-time-path implementation because the meaning of the in and out-states is not the same any more as in the real quantum description.

Another possible generalization deals with modelling of dissipative classical systems. The most rigorous way of modelling such a system would be to introduce a bath and coarse-grain directly the Hamiltonian system + bath complex by forming its generalized time dependent density functional representation. That can be straightforwardly done by using Eq. (2.143) with bath and the source term coupled to composite operators such as the number density, $\int d\mathbf{q} \int dt\, J(\mathbf{q}, t) a^\dagger(\mathbf{q}, t) a(\mathbf{q}, t)$. However, we could spare us from extra work if it was possible to directly generalize the treatment for dissipative Liouville equations describing the time evolution of a general non-Hamiltonian set of evolution equations

$$\dot{q}_i = f(\{q_i\}) , \tag{2.145}$$

where f is a given function and $i = 1 \ldots 6N$. The usual assumption in the literature about the form of the evolution equation of the phase space density of the system (2.145) has the form $\partial_t P_N + \nabla_{\mathbf{q}} \cdot (\dot{\mathbf{q}} P_N) = 0$. As pointed out in Refs. [145, 146, 147], in this equation there is no reference to the phase space metric g. In general, Tuckerman et al. [145] claim that one has to allow for a curved space with non-constant phase space metric leading to the evolution equation

$$\partial_t(\sqrt{g} P_N) + \nabla_{\mathbf{q}} \cdot (\dot{\mathbf{q}} \sqrt{g} P_N) = 0 . \tag{2.146}$$

Any nontrivial metric has to be taken into account in the integration measure of Eq. (2.137): instead of integrating over $\int d\mathbf{q}^N P_N$ we have $\int d\mathbf{q}^N(\sqrt{g}P_N)$. Thus, setting $\tilde{P}_N \equiv \sqrt{g}P_N$, we notice that it satisfies the equation $\partial_t\tilde{P}_N + (\nabla_{\mathbf{q}}\cdot\dot{\mathbf{q}} + \dot{\mathbf{q}}\cdot\nabla_{\mathbf{q}})\tilde{P}_N = 0$, or $\partial_t\tilde{P}_N + \imath\tilde{L}\tilde{P}_N = 0$, which can be readily exponentiated to give the time evolution operator. The explicit presence of the metric is important in observables, which contain the distribution function in nonlinear combinations such as the (microscopic) Gibbs entropy. Even though the smoothness and the existence properties of invariant measures are not given a proper account (not to mention the generalization to include chemical reactions) in many of the more practically oriented exposures of the subject [148, 149, 150], as far as the form of the generalized Liouville equation can be represented as $(\partial_t + \imath\hat{L})P_N = 0$, with $\hat{L}$ as linear operator, it is straightforward to use it in the the generating functional coarse-graining formalism. In the next section we see that when approximation the continuous systems by a lattice-gas type of description with stochastic (or deterministic) transition rules we can readily obtain the path integral generating functional and thereby the dynamics of expectation values of relevant observables.

2.4.2 Markov Chain Cellular Automata level

Here we cast the time evolution of the probability density of a given Master equation into the Schrödinger form as we did for the Liouvillean in the previous section. Corresponding to Eq. (2.137) we get in the lattice case

$$|\phi(t)\rangle \equiv \sum_{\{n_i\}} P(\{n_i\}, t)\,|\{n_i\}\rangle \ , \tag{2.147}$$

where $|\{n_i\}\rangle \equiv \prod_i (a_i^\dagger)^{n_i}|0\rangle$ Existence of the lattice is only assumed to facilitate the $\mathbf{x}$-representation of the field operators. To make the discussion more concrete we will consider a model of a directed fermionic world line, which lives on an $L \times L$-lattice, with periodic boundary conditions. The lattice consists of vertices and bonds: If a bond is part of the world line, along that bond there is an arrow pointing from one vertex to the next in such a way that the closed world line comprises of a set of arrows pointing left and down. The line cannot cross itself but it can cross the system boundaries because of periodicity condition. The dynamics is such that first a vertex is pick randomly and the configuration of arrows related to that vertex is checked. If there are no arrows (line does not pass through that vertex) a new vertex is chosen. Only if a combination of arrows having a corner shape (one down arrow and one left arrow) at a vertex is found, we parallel transport both arrows to the next nearest neighbour vertex with probability λ. To make this clear, let us enumerate the arrows instead of the vertices. Let there be a left arrow at lattice site (i, j) and a down arrow at $(i + 1, j + 1)$. If the vertex connecting these two arrows is chosen, with probability λ we parallel transport the down arrow to lattice site $(i - 1, j + 1)$ and the left arrow to site $(i, j + 2)$. The Master equation now takes the following form in the second quantized notation:

$$\frac{d}{dt}|\phi(t)\rangle = \sum_{\{n_i\}} \frac{d}{dt}P(n_1, n_2, \ldots)(a_1^\dagger)^{n_1}(a_2^\dagger)^{n_2}\ldots|0\rangle \equiv \hat{H}_M|\phi(t)\rangle \ . \tag{2.148}$$

To obtain an explicit representation of the Master (Fokker-Planck) operator $\hat{H}_M$ we first have to consider how the occupation probability P changes. We get

$$\frac{d}{dt}P = \lambda\sum_{i,j}\{[n(i+1, j+1) + 1][n(i, j) + 1]P_{in} - n(i+1, j+1)n(i, j)P\} \ , \tag{2.149}$$

where P_{in} is the probability of finding a configuration with one 'extra' particle at sites $(i+1, j+1)$ (down arrow) and (i,j) (left arrow), and a hole (no arrows) at sites $(i-1, j-1)$ and $(i, j+2)$:

$$P_{in} \equiv P\Big(n(i-1,j+1)-1, n(i,j+2)-1, n(i+1,j+1)+1, n(i,j)+1\Big) \ . \tag{2.150}$$

The probability of finding the configuration with unchanged number of particles is naturally

$$P \equiv P\Big(n(i-1,j+1), n(i,j+2), n(i+1,j+1), n(i,j)\Big) \ , \tag{2.151}$$

with only those sites written down whose occupation probability can change as a result of the attempt move. Using now the definitions of the creation and annihilation operators,

$$a_i^\dagger|\ldots, n(i), \ldots\rangle = |\ldots, n(i)+1, \ldots\rangle \ \ ; \ \ a_i|\ldots, n(i), \ldots\rangle = n(i)|\ldots, n(i)-1, \ldots\rangle \ , \tag{2.152}$$

and $[a(i), a^\dagger(j)] = \delta_{ij}$, we obtain the second quantized representation of the Master equation (2.148) with time evolution operator

$$\begin{aligned} \hat{H}_M \ &= \ \lambda \sum_{i,j} \Big\{ a(i+1,j+1)a(i,j)a^\dagger(i-1,j+1)a^\dagger(i,j+2) \\ &\qquad - a^\dagger(i+1,j+1)a(i+1,j+1)a^\dagger(i,j)a(i,j) \Big\} \ . \end{aligned} \tag{2.153}$$

Continuum limit can be easily taken in the path integral representation. What is important to notice is that the theory does not yet include truly fermionic operators. Even though there cannot be but one arrow at each lattice site, the operators a and $a^\dagger$ satisfy the hard core boson (or spin-one-half) anticommutation condition $[a_i, a_i^\dagger]_+ = 0$ but commute for different lattice sites. To make the annihilation and creation operators truly anticommute between different sites, we have to fermionize the theory. This can be done in dimensions $D = 1, 2, 3$ using the Jordan-Wigner transformation [151, 152]. In general, it has been shown by Fradkin [153] that a two-dimensional spin-one-half system can be mapped via Jordan-Wigner transformation into a system of spinless fermions minimally coupled to an Abelian gauge field with a Chern-Simmons term. This is another example (cf. Sect. 2.3.2) of coarse-graining giving rise to gauge fields in the effective description. Here, there is no information loss, though: The gauge fields can be eliminated by changing the commutation relation of the 'matter' fields $(a, a^\dagger)$. The world line model described in this section is one particular representation of a Restricted-Solid-on-Solid crystal growth model, whose Master equation based coarse-graining has been recently studied in Ref. [154]. Through a sequence of mappings it is possible to relate it also to the six-vertex model (whose equilibrium partition function can be found exactly [155]) and to Burger's turbulence [156].

Chapter 3

Symmetry principles

3.1 Coarse-grained dynamics for conserved variables

3.1.1 Exact and approximate symmetries of the action

There are two closely related objects, whose symmetry properties we use to identify the relevant coarse-grained variables: The density matrix and the action of the nonequilibrium generating functional. Their symmetries are related to one another because the latter is the trace of the former, when decorated with the couplings to the source fields. (Source terms are, of course, not included in the symmetry analysis of the action: They are only needed for the formation of the effective action via the Legendre transformation.) Since the initial density matrix appears only as a boundary condition in the functional integral representation of the action, any variational approach for symmetry analysis must be modified appropriately. If there is a bath, it can either be analyzed together with the system or integrated out resulting typically in an effective system action, which shows decoherence or dissipation.

Let us first discuss exact symmetries. Continuous symmetries of the action (Lagrangian) are related to conservation laws of the system according to Noether's theorem, which holds for both relativistic and nonrelativistic systems [157]. Using particle physics language, let us first discuss the concept of gauge invariance, which means that the generating functional of the Green's functions of the theory is invariant under gauge transformations of the matter and gauge fields. This is easy to understand because the value of any (functional) does not depend on the dummy integration variables, which can be freely redefined. Gauge transformation is just a special type of redefinition of the dummy integration variables. The only pieces of the generating functional of the Green's functions, which are not gauge invariant are the source coupling terms and gauge fixing terms. When performing an infinitesimal variation of the fields (gauge transformation), the condition on vanishing source and gauge fixing terms is translated into a form of a balance equation, which reduces to the conservation equation for current density when external sources are set to zero. This identity is called the Ward-Takahashi identity in Abelian and Slavnov-Taylor identity in non-Abelian field theories. In condensed matter systems Zhou et al. [63] and Su [158] et al. have demonstrated the effectiveness of Ward-Takahashi identities in deriving energy and momentum balance equations for a electron-phonon-impurity system. Following their lead, we try to argue in Sect. 3.1.2 the form of the balance equations of classical fluids.

In practice the exact symmetries are hard to find just like the exactly conserved constants of motion as we know from the theory of dynamic systems [116]: The set of known isolating primary integrals of motion of a Hamiltonian system, which is not confined in finite space usually reduce to energy, linear and angular momentum. Exactly integrable systems represent but tiny subclass of all real systems. To extend the program of finding the relevant macro variables, we should really start looking for approximate symmetries [159] (and conservation) laws in addition to (or instead of) exact ones. In practice, we will in any case have to deal with a some sort of effective Lagrangian (action), so there is no point trying to isolate its exact invariants, which is mathematically hard. Spontaneous breaking of a continuous exact symmetry gives rise to low energy excitations called Goldstone bosons. There exists a systematic way of expressing the low energy (coarse-grained) effective Lagrangian of the system in terms of the Goldstone modes [157, 160]. This will be utilized in Sect. 5.8 where the Goldstone mode representation of the order parameter of superfluids and superconductors is discussed (see also Sect. 4.1.3). The simplicity (compared to high energy phenomena) and similarity of the low energy Lagrangians of various systems is one source of universality [161], which could also be formulated using renormalization group arguments as usually done in equilibrium statistical mechanics. Thus, the coarse-grained physics (Lagrangian) is not necessarily as sensitive as one might think, to the various approximations one is bound to make, when trying to simplify the description. The Goldstone bosons related to the approximate symmetries of effective description are called pseudo-Goldstone bosons or (massless) quasi-particles [157, 162] in condensed matter systems. Not all quasi-particles are Goldstone bosons, though. Optical phonons, for example, do have a finite energy for zero wave vectors and cannot be called Goldstone modes [163]. Similarly, plasmons have a finite energy for zero wavevector [1], because of the long range Coulomb forces. It is the long range Coulomb forces which are also responsible for the missing Goldstone mode of the superconductors where the photonic excitations acquire a small mass.

3.1.2 Link to classical hydrodynamics

In Ref. [63] the authors gave some general arguments for derivation of equations of motion for conserved macro variables Q_i based on the symmetry analysis of the action. They gave a specific demonstration for isotropic antiferromagnet (model G of critical dynamics [126]) whose Lie group is finite. Below we try to adapt this method for an infinite dimensional system of classical hydrodynamics. Under the action of the symmetry group,

$$Q_\alpha \to Q'_\alpha = Q_\alpha + \imath f_{\alpha\beta\gamma}\zeta_\beta Q_\gamma \ , \tag{3.1}$$

where $f_{\alpha\beta\gamma}$ are the structure constants of the symmetry group and ζ_β are the infinitesimal parameters of the transformation. If the Lagrangian (action) of the system is invariant under the global symmetry transformation, we obtain the Ward-Takahashi identities for conserved currents j_α:

$$\langle \partial_\mu j^\mu_\alpha \rangle = \langle \partial_0 j^0_\alpha \rangle + \langle \partial_s j^s_\alpha \rangle = \partial_t Q_\alpha + \nabla \cdot \mathbf{j} = \imath f_{\alpha\beta\gamma} J_\beta Q_\gamma = 0 \ . \tag{3.2}$$

The zeroeth component is the time, and index s marks the spatial components. When brackets are not shown, the quantities are assumed averaged. The appearance of the current $J_\beta(x) \equiv \delta\mathcal{A}[Q]/\delta Q_\beta(x)$ is dictated by the Ward-Takahashi identity as the source term of the generating functional is not invariant under the symmetry transformation. The final equality follows in the non-driven case where external sources are set to zero: $J_\beta = 0$.

Suppose now that the system has reached a steady-state: If there is dissipation in the system, it is balanced by introducing an extra current ΔJ_α. Since $\partial_t Q_\alpha = 0$ in the steady-state by definition, Eq. (3.2) gives

$$\nabla \cdot \mathbf{j}' = \imath f_{\alpha\beta\gamma}(\Delta J_\beta) Q_\gamma \ . \tag{3.3}$$

On the other hand, linear response argument suggests that we can write the difference between the conserved currents with and without additional driving (cf. Sect. 4.1.3) as

$$\mathbf{j}' - \mathbf{j} = -M_{\alpha\beta} \nabla(\Delta J_\beta) \ , \tag{3.4}$$

We can relate the extra current ΔJ_β needed to maintain the steady-state to the steady-state form of the action $\mathcal{A}_s$: $\delta \mathcal{A}_s[Q]/\delta Q_\beta = \Delta J_\beta$, which is the general form of the equation of motion. Calling $\mathcal{A}_s[Q] \equiv F[Q]$, 'free energy', we can express ΔJ_β in terms of F and substitute it back Eq. (3.3):

$$\nabla \cdot \left(\mathbf{j} - M_{\alpha\beta} \nabla \frac{\delta F[Q]}{\delta Q_\beta} \right) = \imath f_{\alpha\beta\gamma} \frac{\delta F[Q]}{\delta Q_\beta} Q_\gamma \tag{3.5}$$

We can now add the dissipative effects to the general current balance equation (3.2) by solving for the current $\mathbf{j}$ from Eq. (3.5):

$$\partial_t Q_\alpha = \imath f_{\alpha\beta\gamma} Q_\gamma \frac{\delta F[Q]}{\delta Q_\beta} + M_{\alpha\beta} \nabla^2 \frac{\delta F[Q]}{\delta Q_\beta} \ . \tag{3.6}$$

Rigorously speaking, to justify the use of the free energy, we should accompany the dissipative term $M_{\alpha\beta}\nabla^2(\delta F[Q]/\delta Q_\beta)$ with a proper stochastic field if we want the steady-state to correspond to a Gibb's equilibrium state as discussed in Sect. 2.3.4.

Let us now express the structure factors of the Lie symmetry algebra in a more useful form. In general, the Lie algebra of the symmetry generators is closed by the commutator relations

$$[Q_\alpha, Q_\beta] = \imath f_{\alpha\beta\gamma} Q_\gamma \ . \tag{3.7}$$

Additionally, if there are non-conserved (order) operators ψ_β present, Zhou et al. [63] propose the following commutator relation for them: $[Q_\alpha, \psi_\beta] = \imath f_{\alpha\beta\gamma} Q_\gamma$ for them. This relation bears a great similarity to an early approach of quantum kinetics formulated by Peletminskii and Yatsenko [164]. They proposed encoding the symmetries of the problem in the free part of the system Hamiltonian H_0 satisfying the commutation relation $[H_0, \psi_k] = a_{km}\psi_m$, which reduces to the form suggested by Zhou et al. if one takes H_0 to consist of of a sum of conserved charges $\sum_i Q_i$. Furthermore, our standard assumption of the commutation relation satisfied by the order operator and its associated conserved charge, $[Q, \psi] \propto \psi$, is a special case of the same relation.

In the classical case the commutators have to be replaced by Poisson brackets, and we will show later on in Chap. 9 and App. D.1 that the Poisson brackets of the classical mass ϕ and momentum densities (conserved variables) $\mathbf{j}$ satisfy

$$\begin{aligned} \{\phi(\mathbf{x}), j_i(\mathbf{x}')\} &= \phi(\mathbf{x}')\partial_i \delta(\mathbf{x} - \mathbf{x}') \ ; && (3.8) \\ \{j_s(\mathbf{x}), j_i(\mathbf{x}')\} &= -j_i(\mathbf{x})\partial'_s \delta(\mathbf{x} - \mathbf{x}') + j_s(\mathbf{x}')\partial_i \delta(\mathbf{x} - \mathbf{x}') \ . && (3.9) \end{aligned}$$

Formally, we can cast these equations into the form (3.7) by introducing a vector index $Q_{\gamma,x} \equiv Q_\gamma(\mathbf{x})$, which allows us to write Eq. (3.8) and Eq. (3.9) as

$$\begin{aligned} \{Q_{0,\mathbf{x}}, Q_{i,\mathbf{x}'}\} &= \tilde{f}_i(\mathbf{x}, \mathbf{x}') Q_{0,\mathbf{x}'} \ ; && (3.10) \\ \{Q_{s,\mathbf{x}}, Q_{i,\mathbf{x}'}\} &= \tilde{f}_s(\mathbf{x}, \mathbf{x}') Q_{i,\mathbf{x}} + \tilde{f}_i(\mathbf{x}', \mathbf{x}) Q_{s,\mathbf{x}} && (3.11) \end{aligned}$$

where we have defined $Q_{0,\mathbf{x}} \equiv \phi(\mathbf{x})$ and $Q_{i,\mathbf{x}} \equiv j_i(\mathbf{x})$ and $\tilde{f}_s(\mathbf{x},\mathbf{x}') \equiv \partial_s \delta(\mathbf{x}-\mathbf{x}')$. Thus, we can easily find a function $f_{\alpha,\mathbf{x};\beta,\mathbf{x}';\gamma,\mathbf{x}''}$ such that Eq. (3.10) and Eq. (3.11) are equivalent to

$$\{Q_{\alpha,\mathbf{x}}, Q_{\beta,\mathbf{x}'}\} \;=\; f_{\alpha,\mathbf{x};\beta,\mathbf{x}';\gamma,\mathbf{x}''} Q_{\gamma,\mathbf{x}''} \ , \tag{3.12}$$

where the summation convention is replaced by integration for the $\mathbf{x}''$-index. For more rigorous treatment of Lie-algebra's of spatially extended systems the reader is referred to Refs. [50, 165]. Replacing now the the term $\imath f_{\alpha\beta\gamma}$ in the evolution equation (3.6) by the Poisson bracket given in Eq. (3.12) leads to the following classical type of equation of motion (where no stochastic terms have been taken into account)

$$\partial_t Q_\alpha = \int dx' \, \{Q_\alpha(x), Q_\beta(x')\} \frac{\delta F[Q]}{\delta Q_\beta(x')} + \hat{\Gamma}_{\alpha\beta} \frac{\delta F[Q]}{\delta Q_\beta(x)} \equiv -\hat{\Xi}_{\alpha\beta} \frac{\delta F[Q]}{\delta Q_\beta} \ , \tag{3.13}$$

where we have defined an evolution operator $\hat{\Xi}_{\alpha\beta}$, which consists of a streaming term (reactive couplings) given by the Poisson bracket and a dissipative term, whose prefactor is given by $\hat{\Gamma}_{\alpha\beta} \equiv M_{\alpha\beta}\nabla^2$ consistent with the conservation law for the variable Q. When a suitable stochastic term is added to Eq. (3.13) the Gibb's equilibrium $\exp(-\beta F)$ will be finally reached. The whole form of the evolution equation can be actually justified based on the relaxation argument alone as will be discussed in Chap. 7. In this section we have merely motivated the the form that macroscopic evolution equations take from the microscopics. The other advantage, which is not offered by the direct macroscopic approaches which postulate the form of Eq. (3.13) for time evolution is that here one can try to obtain the transport coefficients from first principles. In phase-field modelling type of macroscopic approaches these have to be fitted from experimental data.

Even from microscopic point of view the derivation presented above leaves many important questions open. Even though, it is possible to derive the transport coefficients such as $M_{\alpha\beta}$ using renormalization group techniques, it requires hard work to give them explicit expressions in terms of the microscopic parameters of the theory. To our knowledge this has not been explicitly done in the current context. The γ-matrix derivation presented in Ref. [63] is illuminating but technically not entirely convincing. We also point out that one does not need to explicitly reveal the commutator structure of the streaming term in Eq. (3.6) ($\imath f_{\alpha\beta\gamma}Q_\gamma$) as the conserved current can be also directly constructed as shown in Ref. [158] freeing one from the burden of thinking the crossing of the quantum-classical border line, which very subtle. In fact, keeping the commutator term in Eq. (3.6) as it appears cannot be correct for scalar operators at least, because inside the commutator there appear expectation values of operators, which are commuting numbers. Writing instead

$$\partial_t Q_\alpha = \langle[\hat{Q}_\alpha, \hat{Q}_\beta]\rangle \frac{\delta F[Q]}{\delta Q_\beta} + M_{\alpha\beta}(\hbar)\nabla^2 \frac{\delta F[Q]}{\delta Q_\beta} \ , \tag{3.14}$$

is more correct if we insist in making a contact with the Lie group structure through the commutator representation. On the other hand, since it is rigorously true [165] that

$$\langle[\hat{Q}_\alpha, \hat{Q}_\beta]\rangle = \{\langle\hat{Q}_\alpha\rangle, \langle\hat{Q}_\beta\rangle\} \ , \tag{3.15}$$

we should indeed be able to replace the expectation value of the commutator by the Poisson bracket of the expectation values without any explicit reference to the canonical quantization recipe: $[\hat{Q}_\alpha, \hat{Q}_\beta] \to \imath\hbar\{Q_\alpha, Q_\beta\}$. However, now the limit $\hbar \to 0$ does not give the correct answer (relaxation to Gibbs equilibrium) if it happens that $M_{\alpha\beta}(\hbar) \to 0$ as $\hbar \to 0$ because then the dissipative term (and the noise term which is not shown) would vanish. If there exists a non-zero limit for the noise kernel (as in the case of damped harmonic oscillator [74]), this is not a problem. All in all, it is better not to call the evolution equation (3.13) classical in the general case, since many of the observables we are interested in do not have a classical partner: order parameter of the superfluid condensate is one example.

3.2 Finding relevant variables in the general case

In the absence of small expansion parameter like density for dilute systems it becomes nearly impossible to extract the different time scales of an interacting many-body system from equations of motion alone [45]. To pin down the slow variables one therefore usually relies on experimental information on symmetry properties or utilizes the (few) microscopical conservation laws such as mass, momentum and energy conservation. In this section we want to discuss a third possibility, which is of first-principles character being based on the group theoretic analysis of the system's density matrix. Our claim is that the slow variables associated with conservation laws and symmetry-broken variables can be found by analysing the dynamic symmetry group (spectrum generating algebra) of the density matrix. In practice, the task is heavy and therefore the best way is usually to utilize experimental techniques to find out the important symmetries and relevant order parameters.

3.2.1 Dynamic symmetry group of the density matrix

Dynamic symmetry group [166] of the Hamiltonian contains all the information of a quantum system concerning the eigenstates of the Hamiltonian and the transition operators between the eigenstates. In other words,

$$H = H(T_i) \quad ; \quad a = a(T_i) \ , \tag{3.16}$$

where the a denotes the transition operators (generalized ladder operators) and T_i are the generators of the dynamic group. For any finite quantum system there is only a finite number of them: $i = 1 \dots n_g$. The generators form a Lie algebra

$$[T_i, T_j] = \sum_{k=1}^{n_g} C_{ijk} T_k \ , \tag{3.17}$$

where the structure constants are C_{ijk}. The dynamic group will play a central role in the determination of the relevant macro variables. In practice it not easier to find the dynamic symmetry group than diagonalize an arbitary many-body Hamiltonian, which means that much of what we say will remain on a formal level. However, just like diagonalization can be done approximately using various techniques, it is also possible to extract information concerning the dynamic group once the system has been reduced by some means to a simple enough form, which is usually a mean-field type of representation where the nonlinear operator products have been simplified by contracting some terms.

Let us now give a couple of examples of dynamic groups. The simplest is perhaps the H_4-group (Heisenberg-Weyl group) of the harmonic oscillator, whose Hamiltonian $H = \hbar\omega(\hat{n} + 1/2)$. It consists of four generators $a^\dagger, a, \hat{n}$ and the identity I satisfying the following algebra

$$[a, a^\dagger] = I \quad ; \quad [\hat{n}, a^\dagger] = a^\dagger \quad ; \quad [\hat{n}, a] = -a \quad ; \quad [\hat{O}, I] = 0 \ , \tag{3.18}$$

where $\hat{O} = a^\dagger, a, \hat{n}$. The group representation theory tells us how to classify the generators of the dynamic group into different subgroup chains, each of which has its own physical meaning. Operators, which commute with all the generators of the dynamic group (subgroup) are called Casimir operators, and they will play an important role in the hunt for relevant macro variables as we will see below. For harmonic oscillator there is the following subgroup chain [167] $H_4 \supset U(1) \otimes U(1)$, and the Casimir operators associated with the chain members are $C_{H_4} = -\frac{1}{2}I$, $C_{U(1)} = I$ and $C_{U(1)} = \hat{n}$. The Casimir operators of a particular group chain will form a complete set of commuting observables (CSCO), which are the relevant quantum numbers labelling the eigenstates of the quantum system. For example, the Hamiltonian eigenstates of the harmonic oscillator are $|n\rangle$, where the label is the eigenvalue of the nontrivial Casimir operator $\hat{n}$ of the group chain. A second example is a spin system [168], whose Hamiltonian is given by $H = aJ^2 + bJ_z$. The dynamic group chain is now $O(3) \supset O(2)$. The generators of the rotation group $O(3)$ are J_+, J_-, J_z and the generator of $O(2)$ is J_z. The Casimirs can be found right away: $C_{O(3)} = J^2$ (total angular momentum) and $C_{O(2)} = J_z$. Consequently, the eigenstates are $|jm\rangle$ labelled by the the eigenvalues of the CSCO generators J^2 and J_z.

Even for the simplest Hamiltonian, there is an infinite number of operators, which commute with it: Take for example all projectors $|n\rangle\langle n|$ of the eigenstates of Hamiltonian and their sums and products. The essence of the Casimir operators is that they will correspond to the conserved macro-observables of any dynamic problem, because they commute with the Hamiltonian. Furhtermore, CSCO gives us the *smallest* number of commuting operators sufficient to span the Hilbert space of the system. They will act as a basis set of any hydrodynamical description. It is important to notice that in principle there is a mechanical way (based on the representation theory of groups) of producing the conserved charges of the problem. However, this is not easy in practice as we know.

The slight modification which we propose to the standard scheme is to consider the dynamic symmetry group of the density matrix instead of the Hamiltonian of the system, which is responsible for the time evolution. The reason for this is that to see the broken symmetry, we need to average the order operator over the broken symmetry ensemble (density matrix). In Gibb's equilibrium the density matrix ρ_{bs} of the broken symmetry ensemble can be approximated by

$$\rho_{bs} \approx \rho_{eq}^{J} = e^{-\beta H_s' + J\psi} \ , \tag{3.19}$$

where J is the conjugate field of the order operator ψ. As we have explained in Sect. 2.1.3, this construction is sufficient to separate between the symmetric and unsymmetric phases. It is also important to separate between the Hamiltonian H_s responsible for the time evolution of the system and the Hamiltonian H_s' appearing in the (final state) equilibrium density matrix. These two do not have to be the same, although for special type of system-bath couplings it can be shown [169] that irrespective of the initial condition the system, whose generator of time evolution is H_s, will go to Gibb's equilibrium described by the Gibb's density $\exp(-\beta H_s)$ in the symmetric case. In general we expect the following to scenario to hold when $t \to \infty$:

$$\rho_s(t) = \mathrm{Tr}_B\{U(t)\rho_0 U^\dagger(t)\} \to \begin{cases} \rho_{eq}^{0} = e^{-\beta H_s'} & \text{for } \mu_i \in S \ ; \\ \rho_{eq}^{J} = e^{-\beta H_s' + \sum_i J_i \psi_i} & \text{for } \mu_i \in U \ . \end{cases} \tag{3.20}$$

The set S represents the values of the the coupling constants μ_i in the symmetric phase. The coupling constants μ_i denote the conjugate variables of symmetry generators, such as β, which is conjugate to energy, or chemical potential μ, which is conjugate to particle number etc. The set U represents the values of the coupling constants for which the symmetries related to order parameters ψ_i have been broken.

3.2.2 Symmetry breaking and restoration

In this section we will consider the operational definitions of symmetry breaking and restoration. First we provide a three item list which shows the analogs between the ground state, finite temperature and dynamic formalisms:

- **Ground state formalism**
  Let Q be the symmetry generator of the system Hamiltonian H_s: $[Q, H_s] = 0$. Let ψ be the order operator and for simplicity assume $Q = \psi^\dagger\psi$ and $[\psi, \psi^\dagger] = 1$. The ground state is denoted by $|G\rangle$. Spontaneous symmetry breaking occurs if

  $$\begin{aligned} \langle G(\mu)|\psi|G(\mu)\rangle &= \mathrm{Tr}\{\psi|G(\mu)\rangle\langle G(\mu)|\} = \mathrm{Tr}\{[\psi, Q]|G(\mu)\rangle\langle G(\mu)|\} && (3.21) \\ &= \mathrm{Tr}\{[Q, |G(\mu)\rangle\langle G(\mu)|]\psi\} \neq 0 \,, && (3.22) \end{aligned}$$

  or equivalently, $[Q, |G(\mu)\rangle\langle G(\mu)|] \neq 0$ for some values of the control parameters μ (conjugate variables of conserved or constrained quantities).

- **Finite temperature formalism**
  Let Q be the symmetry generator of the system Hamiltonian H_s: $[Q, H_s] = 0$. Then, it is a symmetry generator of the equilibrium density matrix $\rho_{eq} = \exp(-\beta H_s)$: $[Q, \rho_{eq}] = 0$. Spontaneous symmetry breaking takes place, if Q is not a symmetry of $\rho_{bs}(\mu)$, which is the relevant ensemble weight in some (broken symmetry) phase: $\langle\psi\rangle = \mathrm{Tr}\{[Q, \rho_{bs}(\mu)]\psi\} \neq 0$, or equivalently, $[Q, \rho_{bs}(\mu)] \neq 0$ for some values of the control parameters μ. In the equilibrium case we can only see the symmetry breaking indirectly via Bogolubov's quasi-averaging or from analytic properties of the partition function.

- **Nonequilibrium formalism**
  Let Q be the symmetry of the initial system density matrix $\rho_s(0, \mu)$, i.e. $[Q, \rho_s(0, \mu)] = 0$. The time dependent density matrix is obtained in the usual manner by tracing out the bath from the Heisenberg representation of the total density matrix. We say that dynamic symmetry breaking occurs if $\langle\psi\rangle = \mathrm{Tr}\{[Q, \rho_s(t, \mu')]\psi\} \neq 0$, or $[Q, \rho_s(t, \mu')] \neq 0$ for some values of the control parameters μ' and time t. In the dynamic case the transition can in principle be seen by observing the change in the form of the system density matrix directly. The transition can be generated by changing some of the bath parameters like temperature: $\mu = \beta_1 < \beta_2 = \mu'$.

It is easy to see that nonequilibrium formalism reduces to the finite temperature one if we have $\rho_s(t, \mu) \to \rho_{bs}(\mu)$ when $t \to \infty$ and $\rho_s(0, \mu) = \rho_{eq}$. Similarly, the finite temperature formalism reduces to the ground state formalism when $T \to 0$ and $\rho_{bs} \to |G(\mu)\rangle\langle G(\mu)|$ The definition of the nonequilibrium formalism presented in the last item of the list is rather narrow in the sense that it does not take into account intermediate symmetry breakings and restorations. Dynamic symmetry breaking and restoration can be defined by saying that if the set of symmetry generators $Q_i(t_1)$, $i \in K$ at time t_1 is not the same as the set of generators at time $t_2 > t_1$, some old generators have vanished and some new have emerged. In a closed system this cannot happen since the number basic observables commuting with the density matrix at some initial time stays the same for all times: They are unitarily related to each other. With a bath we have a richer structure. Unfortunately, the dissipation makes also some of the language related to static dynamic groups obsolete (such as the concept of conserved charge has to be modified, since the system observables become time dependent due to the bath influence). Therefore, in the following we will concentrate on the dynamic group of the final density matrix and Gibb's equilibrium, where we can talk about a stationary Hamiltonian H'_s possessing a well-defined dynamic group structure.

Next, we discuss the important mean-field approach to symmetry breaking. As we have pointed out before, even though we use a density matrix $\rho_{bs} \approx \rho_{eq}^J = \exp(-\beta H + J\Delta)$ to describe the broken symmetry phase, it does not necessarily mean that we would have broken the symmetry *explictly* by adding a coupling term $J\Delta$, where Δ denotes the order parameter. As a concrete example we use the mean-field theory of BCS superconductivity. Suppose first, that the order parameter satisfies

$$[Q_\Delta, \Delta] \propto \Delta \ . \tag{3.23}$$

Here Q_Δ is the symmetry generator of the symmetric equilibrium ensemble The density matrix in the mean-field approximation is given in terms of the mean-field Hamiltonian H_{mf}:

$$\rho_{eq} \approx \exp(-\beta H_{mf}\Big(\langle\Delta\rangle = 0)\Big) \ . \tag{3.24}$$

Order parameter Δ is associated with the symmetry generator of the equilibrium ensemble Q_Δ, which, by definition, satisfies $[Q_\Delta, \rho_{eq}] = 0$. In Sect. 5.5 we will show how Δ and Q_Δ can be constructed from first principles. Below their microscopic representation will pop out of the mean-field treatment. When the expectation value of the order operator $\langle\Delta\rangle = 0$, we obviously have that $[\rho_{eq}, Q_\Delta] = 0$ as shown in item 'Finite temperature formalism' of the list above. On the other hand, in the broken symmetry phase described by weight ρ_{bs} the order parameter becomes non-zero: $\langle\Delta\rangle \neq 0$, which means that Q_Δ is not a symmetry of ρ_{bs}: $[Q_\Delta, \rho_{bs}] \neq 0$. Thus, we can take $\rho_{bs} \approx \exp\Big(-\beta H_{mf}(\langle\Delta\rangle \neq 0)\Big)$. The mean-field Hamiltonian of BCS model can be obtained by choosing to contract creation (annihilation) operators with opposite momenta and spin in the interaction part of the Hamiltonian. Thus,

$$\rho \approx \exp\Big(-\beta H_{mf}(\langle\Delta\rangle)\Big) = \exp\Big(-\beta H_0 + \beta\langle\Delta\rangle \sum_k a^\dagger_{k\uparrow} a^\dagger_{-k\downarrow} + \beta|\langle\Delta\rangle|^2/g + h.c.\Big) \tag{3.25}$$

$$\approx \begin{cases} \exp\Big(-\beta H_0\Big) = \rho_{eq} & \langle\Delta\rangle = 0 \ ; \\ \exp\Big(-\beta H_0 + \beta\langle\Delta\rangle\Delta^\dagger + h.c.\Big) = \rho^J_{eq} = \rho_{bs} & \langle\Delta\rangle \neq 0 \ . \end{cases} \tag{3.26}$$

We have defined $H_0 \equiv \sum_{k\sigma} \epsilon_k a^\dagger_{k\sigma} a_{k\sigma}$, $\Delta \equiv g\sum_k a_{-k\downarrow} a_{k\uparrow}$, g is the contact potential and summation over k is restricted in the vicinity of the Fermi surface. In the lower equation (3.26) we have assumed that Δ is small and dropped the quadratic term $\langle\Delta\rangle^2$. Interpreting $\beta\langle\Delta\rangle = J$, we see that the broken symmetry ensemble is approximatively described by a density matrix ρ^J_{eq}, which we have been using many times. In a way, the mean-field approximation the spontaneous symmetry breaking has masked itself to look like an explicit symmetry breaking in an 'external' field $J = \beta\langle\Delta\rangle$. It should be noted that the analysis above is insufficient to prove the existence of the spontaneous symmetry breaking as long as $\langle\Delta\rangle$ is kept as a free parameter. Its value should be self-consistently fixed by minimizing the free energy with respect to it. This leads to the gap equation and allows the construction of the mean-field phase diagram. Another method of seeing the spontaneous symmetry breaking, which is also convinient for determination of the phase diagram is the coherent state method [170]. It is closely related to our methodology as it makes a direct use of the dynamic symmetry group of the system and has been successfully applied to situations such as high-T$_c$ superconductivity[171]. The close analogy to our Legendre transformation based method comes from the fact that the coherent state parameters appear as conjugate fields of generalized ladder operators (generators of dynamic symmetry group). Therefore, the coherent state parameters can be interpreted as order parameters of the theory [172].

Finally, we will consider the signature of the spontaneous symmetry breaking from the point of view of symmetry transformation and the symmetry of the expectation value of order operator. Let Q be the generator of some symmetry of the symmetric phase and ψ the associated order operator satisfying $[\psi, Q] = \psi$. In the broken symmetry phase the expectation value of the order operator will not be invariant under the continuous symmetry transformation:

$$\lim_{J\to 0} \mathrm{Tr}\left\{ e^{\imath\alpha Q}\psi e^{-\imath\alpha Q}\, e^{-\beta H + J\psi} \right\} = \lim_{J\to 0} \mathrm{Tr}\left\{ \psi\, e^{-\imath\alpha Q} e^{-\beta H + J\psi} e^{\imath\alpha Q} \right\} \tag{3.27}$$

$$= \lim_{J\to 0} \mathrm{Tr}\left\{ \psi e^{-\beta H + \exp(\imath\alpha) J\psi} \right\} = \lim_{J\to 0} \frac{\delta}{\delta(e^{\imath\alpha}J)} \mathrm{Tr}\left\{ e^{-\beta H + \exp(\imath\alpha) J\psi} \right\} \tag{3.28}$$

$$= e^{-\imath\alpha} \lim_{J\to 0} \frac{\delta}{\delta J} \mathrm{Tr}\left\{ e^{-\imath\alpha Q} e^{-\beta H + J\psi} e^{\imath\alpha Q} \right\} = e^{-\imath\alpha}\, \underbrace{\lim_{J\to 0} \frac{\delta}{\delta J} \mathrm{Tr}\left\{ e^{-\beta H + J\psi} \right\}}_{\lim_{J\to 0}\langle\psi\rangle_J} . \tag{3.29}$$

Bogolubov's quasi-average makes the last term non-zero, and we see that an extra phase has been created because the ensemble is non-symmetric. In the symmetric ensemble we have $\mathrm{Tr}\left\{ e^{\imath\alpha Q}\psi e^{-\imath\alpha Q} e^{-\beta H} \right\} = 0$, because $[Q, e^{-\beta H}] = [Q, \rho_{eq}] = 0$. These results will be made use of in Sect. 5.7.2

3.2.3 Can we really predict which symmetries are going to be broken?

The dilemma associated with the spontaneous symmetry breaking is the following. How can we see which symmetry is going to be broken under the dynamics without putting in the answer by hand? First, we have to find the symmetries of the system. In the long time limit this can be achieved (in principle) by isolating the complete set of commuting observables from the dynamic symmetry group of the density matrix. The next question is, based on the known symmetries, can we construct the *equilibrium* phase diagram using already existing formalisms? The answer is yes: In the previous section we mentioned that self-consistent mean-field approach and coherent state method can be used to construct (an approximate) phase-diagram. As what comes to the generating functional formalism, given that a few conditions are fulfilled, the answer is positive, as discussed in Sect. 2.1.2. It suffices to form the effective action (free energy) $\mathcal{A}[\langle\psi_i\rangle]$, which is obtained from the Legendre transformation of the generating functional $Z[\{J_i\}] = \mathrm{Tr}\exp(-\beta H_s + \sum_i J_i\psi_i)$. The condition that should be fulfilled is that the Legendre transformation exists for each particular composite order-operator ψ_i. Secondly, we have assumed that for finite quantum systems we are able to decompose each Hermitean symmetry generator $Q = \psi^\dagger\psi$. If this is not true, more complicated relations between the order parameter and symmetry generator must be considered such as $[Q, A] = \psi$, where A is symmetry restoring variable [1]. In fact, in some applications (e.g. superfluidity) we will be considering later on, the real order parameter will be the phase of the expectation value of ψ. However, it can be computed from $\langle\psi\rangle$ via a nonlinear transformation, which allows us to still formulate much of the discussion in terms of ψ. What we basically expect the Legendre transformation of the generating functional to give us is an effective action whose *pointwise density* allows us to extract the phase diagram from its local minimima. The non-convexity vs. convexity issue is pondered in more detail in App. A. To see phase transitions, we expect a non-convex pointwise action density in the same sense as the concept is used in the critical dynamics (phase-field) community [126]. Another, and more correct way of expressing the same thing is to say that we expect the effective action to give rise to anomalous solutions for various Green's functions, the behaviour of which will aid in the construction of the phase diagram. The existence of anomalous solutions is of course a hall mark of field theories, so we should be careful as we have also assumed the generalized ladder operator presentation of the symmetry generator $Q_i = \psi_i^\dagger \psi_i$, which might not be valid in all cases in infinite space. However, if there are systems for which the effective action behaves the way we have described above, we have basically been able to conctruct the phase diagram based on the use of the symmetrical ensemble! We have not put in any symmetry breaking by hand. The job of the Legendre transformation is not to induce *explicit* symmetry breaking beacuse the field J of the generating functional is just a dummy variable, which will be traded for the expectation value of its conjugate field when going from $Z[J]$ to $\mathcal{A}[\langle\psi\rangle]$. However, the Legendre transformation is capable of *revealing* the phase transition (and the phase diagram) in the form of the anomalous solutions because each $\langle\psi\rangle$ corresponds to some J, which can break the symmetry.

Let us now discuss, whether we can expect to be able to predict *phase transitions taking place in course of the time evolution* of the system. For concreteness sake let us use the simulation of the Heisenberg model as an example. In the symmetric high temperature phase the spins are pointing in random directions resulting in zero value of the magnetization order parameter $\langle\psi\rangle$. Temperature of the system can be changed by changing the temperature of the heat bath. Quenching the bath from high to sufficiently low temperature will result in ordering of the spins and emergence of a non-zero value for the order parameter, if we only use the spatial averaging from a single simulation run. However, if we take an ensemble average over the full initial density matrix, no net magnetization will be generated if there is nothing asymmetric in the initial distribution, bath coupling or time evolution operators. In each run long range order will emerge, but the overall direction of the net magnetization depends on the initial condition we have started from: If there is no bias in the initial conditions (or time evolution), the value of the order parameter will remain zero even though long range ordering takes place. If we were able to take the thermodynamic limit in the simulation, we would guarantee that once the system has chosen some ordering direction, it will keep it. However, in a fully symmetric ensemble (dynamic or static) taking the thermodynamic limit does not yet fix any particular direction, so averaging over the (symmetric) initial distribution would still destroy the emergence of the non-zero value of magnetization. On the other hand, thermodynamic limit combined with an infinitesimally small external field coupled with the *correct order parameter* would not only break the ergodicity but also fix the direction of the net magnetization giving rise to a non-zero value of the order parameter. Another possibility would be to introduce some randomness into the system (e.g. impurities) such that when phase transition temperature is approached, the system 'knows' which way to go and the end result will be biased to produce a non-zero value for the order parameter. But even in this case, one needs to know how to couple the disorder with the correct order parameter.

Our assumption is that the functional Legendre transformation will automatically reveal the symmetry breaking under dynamical conditions in the same way it reveals the equilibrium phase transitions. We introduce the order operators ψ_i associated with all the relevant symmetry generators (Casimir operators) into the time evolution operator as indicated in Sect. 2.2: $Z = \mathrm{Tr}\{U(t_f, t_i, \{(J_i)_+\})\rho_0 U^{-1}(t_f, t_i, \{(J_i)_-\})\}$. If the static analogy holds holds, forming the effective action $\mathcal{A}$ should now contain information on how the symmetry breaking takes place dynamically. Again, we have not broken the symmetry explictly: The source terms $\{J_i\}$ are needed for the Legendre transformation. Computing the equations by requiring stationarity of the action against the variations of $\langle\psi_i(\mathbf{x},t)\rangle$ produces the equations of motion for the order parameters, which will also reveal the order in which the symmetries are broken in different spatial regions.

In general, systems with many simultaneously broken symmetries are not easy to study. These systems are abundant in condensed matter physics where one can have coexistence and competition of phenomena such as superconductivity, structural transitions [173], spin waves, charge density waves [174], ferroelectricity [175], and so on. Even in the equilibrium case, depending on the particular way one contracts the nonlinear operator products to produce a theory quadratic in field operators leads in each case to a different mean-field model. There are several advantages in the generating functional formalism that make it an attractive choice for modeling complicated systems. First, we are able to construct *dynamic* mean-field theories. To our knowledge, the coherent state method has been so far used in static problems, but it should be possible to develop a time-dependent generalization of it, too. Second, by including renormalization effects we wish to go beyond standard mean-field results. For example, one can utilize the non-perturbative renormalization flow of Berges et al. [34] to construct the effective action on a chosen scale $\mathbf{k}$ and then form the dynamic mean-field theory based on $\mathcal{A}_{\mathbf{k}}$. This way one would be able to discuss even the transport coefficients appearing in the mean-field equations of motion on a coarser scale. Third, the couplings between the various order parameters and conserved variables are generated correctly owing to the simultaneous Legendre transformation with respect to several variables.

An important question left open by the formalism is related to the seemingly large (but finite) number of symmetry generators (in a finite quantum system). It will be impractical to write down an equation of motion for each of the symmetery generators and their associated order operators if there is more than a handfull of them. Can we somehow show that there are systems where the number of dynamic symmetry group generators diminishes in the course of time due to the dissipative coupling to the heat bath so that in the end there is just a small number of them left (such as mass, momentum and energy densities)? These systems would then be suitable for coarse-graining treatment, because the number of relevant macrovariables would be small engouh. However, one of the advantages of the generating functional formalism is that it also works for any incomplete set of relevant variables. In other words, it can produce the equations of motion for a subset of symmetry generators or order operators. An interesting possibility, which can perhaps partly explain the apparently small number of relevant variables in some systems like simple fluids, can be loosely formulated in the language of dynamical symmetries. Again we have to be careful not to use blindly the results of ordinary finite quantum systems in the quantum field theory setting. According to the standard terminology, a finite quantum system is said to posess a dynamic symmetry if its Hamiltonian (density matrix in our case) can be expressed as a function of the Casimir opertors (Q_i) of a single subgroup chain. If the *dynamic* symmetry is broken, the system is not integrable any more and (quantum) chaos sets in [167]. In order to break the dynamic symmetry, it suffices to destroy one of the commuting observables or alter the coefficients in the expansion of the system density matrix (or 'time dependent effective Hamiltonian' $\tilde{H}(t)$) in such a way that it is not possible to possible to express it any more in terms of the Casimir operators of a single subgroup chain. Here, $\tilde{H}(t)$ is defined through $\rho_s(t) = \exp(\beta \tilde{H}(t)) \equiv \mathrm{Tr}_B\{U(t)\rho_0 U^{-1}(t)\}$ and Tr_B is the trace over the bath. As we are using the nomenclature of the static equilibrium theory to speculate what might happen in a dissipative dynamic system, everything should be taken with a grain of salt. However, as far as we can really talk about an instantaneous dynamic symmetry group of a dissipative system, then it is possible that there are but few isolating first integrals (good quantum numbers), which are relevant for hydrodynamic description. Analogously to the classical arguments presented in the end of Sect. 2.3.2 the chaotic behaviour resulting from dynamic phase transition of a finite dimensional quantum system are reflected in the topology of the phase space.

Before the story gets too complicated, we must remember that nothing forces us to use 'ab initio' determination of the symmetries to find the relevant macro variables. Physical intuition cannot be replaced by mechanical machinery in practical problems. In most cases, it is far more sensible to use experimental information on the symmetries and their associated order parameters. Using these one can proceed in the familiar manner by substituting them into the generating functional, which will serve to produce the dynamics.

3.2.4 Non-relativistic Goldstone's theorem for ensembles

We will now justify why the dynamic symmetry group of the final steady-state density matrix is on special importance for coarse-grained descripition of any system. It is noted by passing that a more detailed description of the intermediate time-scale phenomena (which can have relatively long but not infinite life time) would be obtained by studying the dynamic group of the time dependent density matrix. The problem is that for finite dimensional isolated Hamiltonian systems the symmetries of the initial density matrix determine the group structure and symmetries for all times leading to less rich structure than in open systems where dissipation gives rise to important effects in the phase transition picture. For example, in an open system, contrary to closed one, the symmetry generator of the density matrix does not necessarily have to be a conserved variable. This can be easily seen by considering Lindblad type of Master eqaution for the reduced density matrix of the system and showing that $[Q(t), \rho_s(t)] = 0$ is not equivalent to $(d/dt)\mathrm{Tr}\{Q(t)\rho_s(t)\} = 0$. Of course, in the case of dissipative system one should strictly speaking use the concept of the symmetry generator of the semigroup, not dynamic symmetry group. These complications will not be important as far as we are concentrating on the hydrodynamic behaviour emerging in the limit $t \to \infty$, where the system density matrix reduces to steady-state, which can in general be assumed to be of the form $\exp(-\beta H_s')$. The exponential form is not essential, all that matters is that there is a well-defined dynamic group structure in steady-state. For system's where Gibbsian equilibrium is reached with $H_s' = H_s$ [169] (the latter being the time evolution Hamiltonian of the system) the study of the dynamic symmetries of the density matrix reduce to the study of the dynamic symmetries of its Hamiltonian.

Below we demonstrate that both conserved symmetry generators and order-operators associated with broken symmetries are relevant hydrodynamic variables as their life time goes to infinity on large enough scales. This result is based on the non-relativistic version of the Goldstone's theorem [176], which is also known as the Bogolubov's $1/q^2$-law [35, 177]. Let $Q = \int d\mathbf{x} Q(x)$ be a conserved charge, and a generator of a continuous symmetry of the final state equilibrium density matrix $[\rho_s(\infty), Q] = 0$ in the symmetric phase. So far we have been assuming that we can relate the conserved variable to the order parameter ψ via $Q = \psi^\dagger \psi$. More generally [1], we are trying to find local variables A and B, which satisfy $[A(\mathbf{x}), Q] = B(\mathbf{x})$. The observable A is a so-called symmetry restoring variable and B is the symmetry breaking variable alias order parameter. So far, we have been using $A = B = \psi$. As before, if the state $\rho_s(\infty)$ is symmetric under Q ($[\rho_s(\infty), Q] = 0$), then $\langle B(\mathbf{x})\rangle = 0$. If the state $\rho_s(\infty)$ breaks the symmetry ($[\rho_s(\infty), Q] \neq 0$), then $\langle B(\mathbf{x})\rangle = \langle B\rangle \neq 0$ assuming translational invariance of the equilibrium state. Following now Ref. [1], we compute the response function χ''_{QA} in the symmetry broken ensemble: $\chi''_{QA} = \int d\mathbf{x}'\,[Q(\mathbf{x}',t), A(\mathbf{x})] = \langle B\rangle$. The important point is the in the previous equation the right hand side does not depend on time because on the left $\int d\mathbf{x}'Q(\mathbf{x}',t)$ is a conserved charge, which is independent of time. Therefore,

$$\chi''_{QA}(k=0,\omega) = \pi\langle B\rangle\delta(\omega)\ . \tag{3.30}$$

Furthermore, based on Eq. (3.30) we assume that there is nothing anomalous in the limiting process $\lim_{k\to 0}\chi''_{QA}(k,\omega) = \pi\langle B\rangle\delta(\omega)$. But this implies the existence of an infinitely long lived mode, whose energy $\omega(k)$ goes to zero, when k goes to zero: A Goldstone mode, that is! This can be seen by writing

$$\chi''_{QA}(k,\omega) = \pi\langle B\rangle\delta(\omega-\omega(k))\ . \tag{3.31}$$

Indeed, plugging Eq. (3.31) into the Bogolubov's inequality we can see that the static susceptiblilty diverges like k^{-2}:

$$\int d\omega\frac{1}{\pi\omega}\chi_{AA}(k,\omega) \equiv \chi_{AA}(k) \geq \frac{|\chi_{QA}(k)|^2}{\chi_{QQ}(k)} \sim \frac{|\langle B\rangle|^2}{k^2}\ . \tag{3.32}$$

The origin of the k^{-2} divergence is in the conservation law of the variable Q. Using projection operator methods [14] one can show in general for a non-conserved variable, which satisfies the equation of motion $\partial_t A + \nabla\cdot j_A = S$, where j_A is a current and S is a source, the correlation function can be written as

$$C_{AA}(k,z) = \frac{\imath\beta^{-1}\chi_{AA}(k)}{z + \imath\sigma_{AA}\chi^{-1}_{AA}(k)}\ , \tag{3.33}$$

where the static susceptibility is given in terms of the Kubo scalar product $\langle C_1|C_2\rangle \equiv \mathrm{Tr}\{\rho_{eq}C_1^\dagger C_2\}$ as $\chi_{AA}(k) = \beta\langle A(k)|A(k)\rangle$. The memory function reads

$$\sigma_{AA}(k,z) = \beta\langle\dot{A}(k)|P_\perp\frac{\imath}{z - P_\perp L P_\perp}P_\perp|\dot{A}(k)\rangle\ , \tag{3.34}$$

where $P_\perp$ is the projection operator into the space orthogonal to relevant slow variables and L is the time evolution operator (Hamiltonian or Liouvillean).

From the denominator or the correlation function given in Eq. (3.33) we can read off the life time τ of the 'quasi-particle': $1/\tau = \sigma_{AA}/\chi_{AA}(k)$. For conserved variables the susceptibility will go to a finite value when $k\to 0$ but the memory function goes like $\sigma \approx \sigma_2 k^2 + \ldots$, where the coefficient functions σ_i are hydrodynamic transport coefficients (diffusion constant in this case). Therefore the life time diverges as k^{-2}. For symmetry broken variables the opposite happens: The susceptibility diverges as least as fast as k^{-2} but the memory function goes to a constant in the small wavevector limit resulting in an infinite life time. Thus, we have shown that indeed it is the dynamic symmetry group of the density matrix, which is important in deriving the generalized hydrodynamics. Namely, in cases where $H'_s \neq H_s$ one needs to define the symmetries of the system based on its density matrix $\rho_s(\infty)$, as all expectation values in the formulae above are calculated with the weight $\rho_s(\infty)$. Most importantly, the static susceptibility is calculated using the broken symmetry ensemble, which reveals the divergence as in static phase transitions. It is interesting to notice that in Zubarev's nonequilibrium formalism, which has many similarites with our nonequilibrium generating functional formalism (Sect. 4), the averages will be performed over time-dependent ensemble weights including the susceptibility. This gives rise to some interesting possibilities concerning a more detailed picture of dynamics and identification of relevant degrees of freedom based on the symmetries of the *time dependent density matrix* when the system has yet not reached the asymptotic regime $t \to \infty$. We also point out the renormalization group methods applied to the effective action of the generating functional may aid in the classification of the relevant variables according to the the speed their life times diverge. In anomalous transport [178] on fractal structures $\sigma \approx \sigma_2 k^\gamma$, where $\gamma \neq 2$ (cf. diffusive fluid flow in a porous disorderd medium modeled by a percolative pipe network). Speculatively, if one refrains from using the standard Gree-Kubo type of close-to-equilibrium ansatz when constructing the transport coefficients some anomalies would probably be avoidable. In general, the existence of the transport coefficients is not a trivial thing. Kinetic extensions of the Green-Kubo relations have been proposed [169, 179] and it remains to be seen if the validity of the 'old laws' of Fick's and Fourier's, for example, will be better understood in the near future.

3.3 Order operators as ladder operators

It is now time to pause for a moment to think about the validity range and pitfalls of our procedure for reckognition of the relevant variables. We have used either a direct symmetry analysis of the action of the generating functional or we have read off the relevant variables from the density matrix. Direct symmetry analysis of action is always possible, though not necessarily easy to perform. It works for both infinite and finite dimensional systems. In zero temperature case infinite volume limit (combined with infinite particle number limit) is necessary to see the spontaneous symmetry breaking rigorously: The vacuum state has to become degenerate to allow the system to choose from different ground states of which not all share the symmetry properties of the Hamiltonian. In the case of ensembles (finite temperature or non-equilibrium situation), we have seen in the previous Sect. 3.2.4 that thermodynamic limit is needed to rigorously see the diverging life time of the quasi-particle excitation, which is a hallmark of a relevant variable. This comes about through the divergence of the susceptibility χ, which goes like k^{-2} when averages are computed over the final state equilibrium (Gibb's) distribution. Thus, the infinite life time can be understood based on familiar arguments from equilibrium thermodynamics. The thermodynamic limit in this case is only something which makes the phase transition phenomenon more easily defineable mathematically. From physics experience we know that phase transitions (spontaneous symmetry breaking) can be seen in finite systems, though the divergences are not as clear (transition peaks are shifted and flattened) as in the infinite system size idealizations. Thus, in a finite size system one can study effective phase transitions and effective ergodicity breaking [180] (restricted ensemble) by considering finite observational time scales. Different signs of spontaneous symmetry breaking (such as effective clustrization property [177]) can be seen for sufficiently large *finite size* quantum systems both at finite and zero temperature.

The mathematics of finite systems is simpler than infinite ones. As usual in quantum many-body theory, we can assume periodic boundary conditions for the second quantized representation of the creation annihilation operators (generalized ladder operators), using standard volume normalization [181]. At the end of the calculation one can take the thermodynamic limit ($N \to \infty$, $V \to \infty$) recovering field theoretic description. If symmetry breaking is defined in the effective sense for finite systems based on sufficiently long return time as compared to relevant observational time scales, we can study the system in symmetry broken and symmetrical phases using different density matrices as described in Sect. 3.2. We can also study symmetry breaking in finite system using an infinite heat bath to get rid of recurrent behaviour. The dynamic symmetry group of the density matrix may then contain different number of symmetry generators at initial time moment and in the final state. Dynamical symmetry of the Hamiltonian has been utilized previously in the study of zero temperature and finite temperature phase transitions of *finite* quantum systems in the context of coherent state analysis [170]. The idea can be easily explained in terms of the ground state formalism. One first computes the expectaton value of the Hamiltonian in the approximate ground state $|\eta\rangle$, which is generated from the physical vacuum through the action of a generalized displacement operator $T(\eta)$: $|\eta\rangle = T(\eta)|0\rangle$, just like in the case of simple harmonic oscillator. The variation of the coherent state expectation value (so-called Q-reprerepresentative [172]),

$$\delta\langle\eta|H|\eta\rangle = 0 \ , \tag{3.35}$$

yields the approximate ground state energy as a function of the symmetry constrained variational parameters $\eta = (\eta_1, \eta_2, \ldots)$. This gives rise to the possibility of plotting energy surfaces of the system as a function of the parameters η_i. Since the variational parameters of $|\eta\rangle$ can be related to the physical order parameters ψ_i, the minimization of $\langle\eta|H|\eta\rangle$ with respect to η_i corresponds to the minimization of the free energy with respect to the order parameters at zero temperature. In this context, the order parameters ψ_i (expectation values of the order operators $\hat{\psi}_i$) are simply related to the field operators, which have been averaged out (contracted) when forming the mean-field Hamiltonian, whose dynamic symmetry group can be found painlessly. Coherent state analysis has also been utilized [170, 182] in crossing the quantum-classical boundary by letting the number of degrees of freedom $N \to \infty$ ($1/N$-expansion).

Above we have presented arguements for using normal finite dimensional operator representation of quantum mechanics for analyzing studying spontaneous symmetry breaking, which strictly speaking is defined in the quantum field theoretical sense only (thermodynamic limit). Let us now comment on the use of the relation

$$[Q, \psi] \propto \psi \ , \tag{3.36}$$

which we have frequently made use of. Eq. (3.36) utilizes the factorization property of self-adjoint observables of Hilbert space of square integrable functions $L^2(V)$, where the volume V is finite. In such a space it is always possible to define adjoint ladder operators ($\psi^\dagger$ and ψ), which shift the eigenvalue of the symmetry generator Q by a finite amount (the ladder spacing does not have to be constant):

$$\psi^\dagger = \sum_{n=0}^{\infty} (q_{n+1} - q_0)^{1/2} |Q_{n+1}\rangle\langle Q_n| \ ; \tag{3.37}$$

$$\psi = \sum_{n=0}^{\infty} (q_{n+1} - q_0)^{1/2} |Q_n\rangle\langle Q_{n+1}| \ , \tag{3.38}$$

where q_0 is the ground state. In general, we expect the spectrum of the Hamiltonian (density matrix) to be parametrizable in terms is mutually commuting operators (symmetry generators Q_i), which for finite V can be factorized as $Q_i = \psi^\dagger\psi = \sum_n (q_n)_i |Q_n\rangle\langle Q_n|$, where $(q_n)_i$ is the nth eigenvalue of the ith generator. Infinite volume limit gives rise to the possibility of having continuous scattering spectrum and the ladder structure is not representable any more in the discrete manner as in Eq. (3.37) and Eq. (3.38). Any degeneracy present in finite volume is assumed to be removed by introduction of different ladder operators for different quantum numbers. Assuming also the existence of a normalizable ground state ket vector, we have in general

$$[Q,\psi] = [\psi^\dagger,\psi]\,\psi \ , \tag{3.39}$$

where the commutator

$$[\psi^\dagger,\psi] = \sum_{n=0}^{\infty}(q_n - q_{n+1})|Q_n\rangle\langle Q_n| \ . \tag{3.40}$$

From the point of view of the symmetry generator Q, the operator $[\psi^\dagger,\psi]$ can be treated as a c-number, since it is diagonal in the eigenstate basis of Q, and

$$[Q,[\psi^\dagger,\psi]] = 0 \ . \tag{3.41}$$

Without the assumption $[\psi^\dagger,\psi] = const$, we have to generalize the discussion on the symmetry breaking presented in Sect. 3.2.2 and Sect. 2.1.3. Writing $[\psi^\dagger,\psi] = a$, where a is a diagonal operator with a well defined inverse, we have from Eq. (3.40) that

$$\psi = a^{-1}[Q,\psi] \ . \tag{3.42}$$

Calculating the expectation value of ψ in the state ρ we get $\langle\psi\rangle = \mathrm{Tr}\{\psi\rho\} = \mathrm{Tr}\{a^{-1}[Q,\psi]\rho\} = \mathrm{Tr}\{[Q,\psi](\rho a^{-1})\} = \mathrm{Tr}\{[(\rho a^{-1}),Q]\psi\} = \mathrm{Tr}\{[\rho,Q]a^{-1}\psi\}$, because $[a^{-1},Q] = 0$. Thus, we can still use the same arguments as before: if Q is the symmetry of the ensemble ($[\rho,Q] = 0$), then $\langle\psi\rangle = 0$. If the symmetry has been broken ($[\rho,Q] \neq 0$), then $\langle\psi\rangle \neq 0$. As discussed in Ref. [38] the ladder operator definition can be generalized in various ways. For example, one can define $[H,L^\pm] = L^\pm f^\pm(H)$, where L^+ is the raising and L^- is the lowering operator, which does not have to be the hermitean conjugate of the former. Also, Ref. [38] presents some simple examples (e.g. hydrogen atom) where the spectrum generating algebra can be found based on construction of the ladder operators. Moreover, the order operator definition based on the commutation relation $[Q,\psi] \propto \psi$ can be generalized to the form $[Q,A] = B$ as discussed in sections 3.1.2, 3.2.3, 3.2.4, and 4.1. In many cases, it suffices, though, to consider the special case $B \propto \psi$ (or $\psi^\dagger$) and $A \propto \psi$ (or $\psi^\dagger$), which is equivalent to saying $[\psi,\psi^\dagger] = const$. Let us now present a list of some cases, where this type of simplification is allowed and useful:

1. In Chap. 5 'macroscopic' creation annihilation operators are introduced, which in the case of superfuilds treat entire Helium atoms as field excitations. Despite their microscopic composite character (atoms consisting of several electrons and nucleons) it is possible to use the simple ansatz $[\psi,\psi^\dagger] = 1$ and $Q = \psi^\dagger\psi$, to discuss symmetry breaking. This example also clearly shows that it is possible to define coarse-grained objects (say, using selective RG, for example) such as atoms, whose field operator algebra is simple enough to facilitate explicit computations. This type of approach should be generalizable to more complicated systems as well.

2. Any mean-field type of theory which is quadratic in field annihilation and creation opereators can be brought via a Bogolubov transformation into a form, which allows one to use the simple relation $[\psi,\psi^\dagger] = const$. In this case the composite operators ψ and $\psi^\dagger$ are linear combinations of the microscopic field operators.

3. All quantum systems, which are isospectral with a system of harmonic oscillators can fall naturally into the category, which can be modeled using the simple commutation relations mentioned above in the rigorouse sense. Of course, this is but a vanishing subset of realistic systems most of which possess an unevenly spaced spectrum of eigenstates. However, some relatively complicated integrable many-body models such as variants of Calogero-Moser model [183, 184] do have a constant gap between successsive eigenenergies.

4. Knowledge of experimentally observed symmetries of complicated systems allows the construction of dynamic symmetry group and transition operator construction, which obeys simple Lie group commutation properties similar to the harmonic oscillator ladder algebra. As in the case of mean-field theories Bogolubov transformation facilitates the quasi-particle description of the theory (see e.g. $SU(5)$-theory of high-temperature superconductivity [171]).

3.4 Remarks on quasi-particle concept

In condensed matter physics quasi-particle is another name for our relevant (macro)variable. By definition, what makes the relevant variable relevant is its long life time. In the hydrodynamic regime all fluctuations except the ones with practically infinite life time have already relaxed. The name quasi-particle refers to the fact, that it is a collective excitation, not a real particle. It is some function of the basic particle field operators, just like the composite operators which we have been using so far. Another name for quasi-particle appropriate due to the composite structure is collective coordinate. By going over to a suitable generalized coordinate frame one can usually present the spectrum of the system in terms of weakly interacting quasi-particle excitations even if in the basis of the original creation and annihilation operators the theory is strongly interacting. This was beautifully shown by Landau's Fermi liquid theory which has been an active field of research ever since. Typically, in the mean-field level, the quadratic many-body Hamiltonians can be diagonalized in terms of Bogoliubov transformation into quasi-particle coordinate basis, in which case they form a free non-interacting gas of excitations whose thermodynamics can be found out easily [173].

Good examples of collective excitations are phonons, which are the normal coordinates of the displacement field of the nuclear positions. Photons are quanta of the electromagnetic field and magnons are quanta of the spin waves, which are low energy excitations of many different types of magnets [185]. Plasmons are the long wavelength excitations of the density field of a gas of charged particles [181] and so on. In fact, the whole basis of modern solid state physics, which has been build up on band structure theory relies on effective single electron description. Of course, the developent of the electronic structure theory has been developed from the static point of view, so calling the effective single electron wavefunctions (which certainly are collective coordinates) as wave functions of quasi-particles is a bit unusual statement and we refrain from doing that. It is just interesting to note that we can formulate the whole electronic structure theory in terms of the static or dynamic density functionals, which can be seen as evolution equations for relevant variables (Chap. 2). In fact, the Hartree-Fock equation and its generalization do resemble the non-linear Schrödinger equation, which typically results from the generating functional analysis as the equation of motion of the relevant variable.

Let us briefly take a look at the traditional way of hunting quasi-particles in solid state physics. Typically, one studies the pole structure of the Green's function of the interacting theory. If one finds that

$$G(\mathbf{k}, t - t') = \langle \hat{T}_+ (a(\mathbf{k}, t) a^\dagger (\mathbf{k}, t')) \rangle \approx e^{-\imath E(\mathbf{k})(t-t')} e^{-\Gamma(k)(t-t')} , \tag{3.43}$$

and $\Gamma \rightarrow 0$ when $k \rightarrow 0$, such that the life time $1/\Gamma \rightarrow \infty$, one can say that there are quasi-particle excitations in the system, since in the long time limit their dispersion relation becomes particle-like. In terms of the Lehmann representation of the Green's function one can state as a general rule the following [181]: "In any many-particle system for which perturbation theory converges, there are quasi-particles in the vicinity of the chemical potential μ". This statement does still not give us any means to construct an operator representation of the quasi-particles in terms of the basic creation and annihilation operators of the interacting theory. Some of the excitations with long life time must be somehow related to the order operators or conserved charges of the theory, and to study the generalized hydrodynamics we would need their (approximate) operator representation. Based on the dynamic symmetry group analysis we argued in Sect. 3.2 that an explicit representation is obtained directly from the generators of the dynamic symmetry group. On that same token, it seems plausible to generalize of the quote above to the form: Quasi-particles can be found in the vicinity of any variable which is conjugate to a symmetry generator of the (steady state) density matrix. After all, in exactly the same way it was shown in Ref. [181] that chemical potential (which is conjugate to particle number charge) has this property, one can use in the Lehmann representation composite ladder operators $\psi^\dagger(a^\dagger, a)$ and $\psi(a^\dagger, a)$, satisfying $\psi^\dagger\psi = Q$, where Q is a good quantum number of the system. In the derivation one also needs to assume that $[\psi^\dagger, \psi] = c$, where c is a number or operator commuting with the rest of the generators. For general composite operators this does not hold whereas special cases where this assumption can be utilized are discussed in Sect. 3.3. Construction of the Lehmann representation with identification $\psi^\dagger\psi = Q$ basically amounts to the replacement of the chemical potential μ with the conjugate variable μ_Q of Q in the derivation of the dispersion relation (3.43). In Sect. 3.2.4 we have shown that these types of collective observables have infinite life times based on the non-relativistic version of the Goldstone's theorem. Another word which characterizes those the quasi-particles which decouple from the energy spectrum in the limit $k \rightarrow 0$ is a (pseudo) Goldstone excitation. As we have mentioned before, the Goldstone's theorem was originally devised for zero temperature relativistic systems, not for finite temperature non-relativistic quasi-particles.

Chapter 4

Related approaches

We will now compare the structure of the formalism to some of the closely related formalisms. There have been many formulations which combine the equilibrium and non-equilibrium processes by a suitable choice of the time-path (Kadanoff-Baym, Keldysh). Historically, the stress has been on the Green's functions and the generating functional has received less attention. The non-equilibrium generating functional formalism presented in this work is identical to the closed-time path Green's function (CTPGF) formalism as presented in Ref. [2]. Chou et al. pointed out the important feature that composite operators can be used in the generating functional including conserved charges and order parameters. What the authors did not mention is the important relation to the density functional theories (quantum and classical, equilibrium and non-equilibrium), which we have explained in this work. Moreover, we have tried to develop a systematic scheme to identify the order parameters. Chou et al. only discussed how to find the conserved variables in addition to showing how to obtain the equations of motion for both conserved variables and non-conserved order parameters once they have been identified by other means. We have also used an explicit bath coupled with the system in many cases unlike Chou et al.

In this section we will show that the generating functional formalism has important connections to the older results derived and utilized by several Russian authors following the ideas of Bogolubov. A particularly powerful formalism for non-equilibrium phenomena, which reduces to many of the known formalisms such as Mori-Zwanzig projection operator approach in appropriate limits, has been developed by Zubarev et al [186, 179]. We should also mention the work of Peletminskii and Yatsenko [164], whose formalism of quantum kinetic equations which appears to have some important common features with Zubarev's approach. Zubarev's non-equilibrium statistical operator again, uses the information theoretical starting point, which was clearly advocated by Jaynes [187] and later on developed by Grandy [188].

Bogolubov's starting point concerning the evolution of the density matrix of an equilibrating system can be simply represented via a general ansatz

$$\rho_s(t) = \rho_{eq} + e^{-t/t_1}\rho_1 + e^{-t/t_2}\rho_2 + \dots \tag{4.1}$$

where ρ_i (i = 1, 2, ...) are non-equilibrium corrections to the equilibrium density matrix ρ_{eq}. Their influence will vanish after the cross-over times t_i have been reached. Thus, the effect of the bath is to change the symmetries of $\rho_s(t)$ in the course of time evolution. By expanding the exponentials and carrying out the trace in the expression of $\rho_s(t) = \mathrm{Tr}_B\{U(t)\rho_0 U^{-1}(t)\}$, we have the formal result

$$\rho_s(t) = e^{-\beta\tilde{H}(t)} = e^{-\beta\sum_n r_n(t) f_n(\{\hat{a}_i^\dagger\},\{\hat{a}_i\})} \ . \tag{4.2}$$

In this section we denote operators with caret symbol ˆ to clearly separate them from their expectation values. The exponential form of the density matrix given in Eq. (4.2) is not necessary, it is just used to remind us of the fact that if the system relaxes to Gibb's equilibrium given by $\rho_s(\infty) = \exp(-\beta' H')$, where

$$\beta' H' \equiv \beta\tilde{H}(\infty) \ , \tag{4.3}$$

studying the symmetries of the Hamiltonian H' is equivalent to studying the symmetries of the density matrix $\rho_s(\infty)$. If one wants to use a non-Gibbsian initial state, one must abandon Eq. (4.3) which in addition assumes the factorizability of the initial bath and system density matrices. Both the bath and the system have been assumed to be at temperature β at the initial time. In the final state, the common factor of all operators in the argument of the exponential having units of inverse of energy defines the final temperature β' according to Eq. (4.3).

Supposing now that we can analyze the algebraic structure of the system density matrix encoded in the effective Hamiltonian $\tilde{H}$, we can group the operators according to the lifetimes of their prefactor functions. Combining the most long lived ones into operators $\hat{Q}$ (which correspond to the conserved variables) we get in the simplest approximation ($t \gg t_1$)

$$\rho_s(t) \approx e^{-\sum_n' s_n(t)\hat{Q}_n - \sum_m' d_m(t)\psi_m)} \ , \tag{4.4}$$

where $\hat{Q}_n = \hat{Q}_n(\{\hat{a}_i^\dagger\},\{\hat{a}_i\})$ and $\hat{\psi}_m = \hat{\psi}_m(\{\hat{a}_i^\dagger\},\{\hat{a}_i\})$ and β has been absorbed into the new numerical coefficients s_n and d_m. The operators $\hat{\psi}_n$ represent (but not necessarily external) symmetry breaking fields, which have emerged due to a dynamical symmetry breaking induced by the heat bath. In general, the conserved operators (hydrodynamically relevant degrees of freedom) do not have to appear as simple linear sum of the form $\sum_n \hat{Q}_n$ as above but nonlinear combinations (e.g. $\sum_{nm} \hat{Q}_n\hat{Q}_m$) occur [170].

There are several advantages of considering the (over)simplified density matrix given in Eq. (4.4). First, $\rho_s(t)$ presents the simplest possible form of the density matrix, which allows us to discuss simplification occurring due to disappearance of 'charges' and the relation of the dynamic group structure of $\tilde{H}$ to spontaneous (and explicit) symmetry breaking. Effectively, we can write instead of Eq. (4.1)

$$\rho_s(t) \approx e^{-\beta' H' + \exp(-t/t_1)\hat{Q}_1 + \exp(-t/t_2)\hat{Q}_2 + \ldots} \tag{4.5}$$

where the number of parameters needed for description of the theory is reduced in the course of the time evolution. In the final state we have $\beta' H' = \lim_{t\to\infty}(\sum_n' s_n(t)\hat{Q}_n + \sum_m' d_m(t)\hat{\psi}_m)$. Second, if the dynamic group is a (semi-simple) Lie algebra, it is convenient to to operate in the Cartan basis, where charges $\hat{Q}_n$ commute with each other and ψ_m can be considered as generalized ladder operators [189, 190]. Therefore, we can assume as further simplification that the operators in Eq. (4.4) satisfy

$$[\hat{Q}_i, \hat{Q}_j] = 0 \ \ ; \ \ [\hat{Q}_i, \hat{\psi}_j] \propto \hat{\psi}_j \ . \tag{4.6}$$

The third advantage of considering the representation (4.4) is that we can see interesting connections with the Zubarev's and Jaynes'es formalisms of non-equilibrium thermodynamics as will become clear in the subsequent sections.

4.1 Kinetic equations from approximate symmetries

Based on the Bogolubov's idea on the relaxation of the density matrix of low density gases Peletminskii and Yatsenko (PY) in Ref. [164] developed a method to derive the transport equations using the known symmetries of the unperturbed Hamiltonian responsible for the time evolution of the system. Equivalently, we can speak of the *approximate* symmetries of the total Hamiltonian including perturbations or *approximate* symmetries of the non-equilibrium density matrix to be defined shortly. Peletminskii and Yatsenko consider a situation where complicated non-equilibrium density matrix reduces to a Gibbsian form after successive reductions of the number of relevant (macroscopic) parameters γ_k occurring at cross-over times t_i as shown in Eq. (4.1). The parameters γ_k are the coupling constants of the theory, and they are related to the prefactor functions r_n (Eq. (4.2)) or to the functions s_n and d_n (Eq. (4.4)) as will be described in Sect. 4.1.1. More specifically, PY assume

$$\rho_s(t) \approx \exp\Big(-\sum_k X_k(\{\gamma_i(t)\})\hat{\gamma}_k\Big) \equiv \rho^{(0)}(\gamma) \ , \tag{4.7}$$

when t is sufficiently large such that all time dependence is buried in the implicit time dependence of the prefactor functions X_k on the expectation values

$$\gamma_i = \mathrm{Tr}\{\hat{\gamma}_k \, \rho^{(0)}(\gamma)\} \ . \tag{4.8}$$

Just as we assumed that the prefactor functions s_n and d_m approach some constant values when $t \to \infty$, it is shown in Ref. [164] that the expectation values of γ_i relax to their equilibrium values making the prefactor functions X_k constant for $t \to \infty$.

By separating out the perturbative part V of the full Hamiltonian, $H = H_0 + V$, we can obtain kinetic equations for the relevant variables γ_k order by order in the perturbation potential. The fundamental kinetic equation obtained by Peletminskii and Yatsenko reads

$$\partial_t \gamma_k = L_k(\gamma(t)) = \mathrm{Tr}\{\hat{\gamma}_k \, \rho(\gamma)\} \ , \tag{4.9}$$

which looks like a typical phase-field evolution equation if one takes e.g. $L_k(\gamma) = \gamma_k - \gamma_k^3$. The derivation of phase-field equations has been discussed in Sect. 3.1.2 and Chap. 7. The operator L_k can be perturbatively expressed in terms of a function f and a time evolution operator $S_\tau^{(0)}\gamma(0) = \gamma(\tau)$ as

$$\begin{aligned} & L_k(\gamma) = \\ & L_k^{(0)}(\gamma(t)) + \underbrace{\imath \mathrm{Tr}\{\rho^0(\gamma(t))[V, \hat{\gamma}_k]\}}_{L_k^{(1)}} + \underbrace{\imath \lim_{\eta \to 0} \int_{-\infty}^{0} d\tau \; e^{\eta\tau} \mathrm{Tr}\{[V, \hat{\gamma}_k] e^{\imath H_0 \tau} f(S_\tau^{(0)}\gamma) e^{-\imath H_0 \tau}\}}_{L_k^{(2)} + L_k^{(3)} + \cdots} \ . \end{aligned} \tag{4.10}$$

In the integral we have substituted a convergence factor $\exp(\eta\tau)$. The superscript i of $L_k^{(i)}$ indicates the power of V present in the expression. The function f can be obtained from the equation of motion of the density matrix which can be made to show relaxational effects by assuming a specific form for ρ. The Heisenberg equation of motion is $\partial_t \rho - \imath[\rho, H] = 0$. Assuming that ρ is a function of the macroscopic fields $\gamma(t)$ we can write

$$L_k(\gamma) \frac{\delta \rho}{\delta \gamma_k} - \imath[\rho(\gamma), H] = 0 \ , \tag{4.11}$$

where we have also made use of Eq. (4.9). This equation is now reorganized to give f:

$$L_k^{(0)}(\gamma)\frac{\delta\rho}{\delta\gamma_k} - \imath[\rho(\gamma), H_0] = \imath[\rho(\gamma), V] - \frac{\delta\rho}{\delta\gamma_k}(L_k(\gamma) - L_k^{(0)}(\gamma)) \equiv f(\gamma) \ . \tag{4.12}$$

Similarly to the functional L_k we can expand f in powers of V. To first order,

$$f^{(1)}(\gamma) = \imath[\rho^{(0)}, V] - \frac{\delta\rho^{(0)}}{\delta\gamma_k}L_k^{(1)}(\gamma) \ . \tag{4.13}$$

In order to obtain the second order result one needs to use the perturbation expansion of the density matrix ρ. The first order correction to ρ, which will be used in the computation of $f^{(2)}$ can be obtained by substituting $f^{(1)}$ into the expression of the full density matrix [164]

$$\rho(\gamma) = \rho^{(0)}(\gamma(t)) + \lim_{\eta\to 0}\int_{-\infty}^{0} d\tau \ e^{\eta\tau}e^{\imath H_0\tau}f(S_\tau^{(0)}\gamma)e^{-\imath H_0\tau} \tag{4.14}$$

Indeed, Eqs. (4.14), (4.12), (4.10) and (4.9) form a closed set, which can be iterated to give both the explicit form of the non-equilibrium density matrix and the equation of motion of the coarse-grained variables γ_k. The dissipation comes in through the late time boundary condition for the density matrix, which is required to relax to the equilibrium given by

$$e^{-\imath H_0\tau}\rho(\gamma)e^{\imath H_0\tau} \to \rho^{(0)}(S_\tau^{(0)}\gamma) \ . \tag{4.15}$$

Thus, no matter what the form of the full V-dependent density matrix is, the final state is assumed to be of Gibb's form with $H' = \sum_k X_k\hat{\gamma}_k$. This is consistent with our assumptions in the beginning of Chap. 4 where we said that the system Hamiltonian (H_0+V) can be different from the Hamiltonian H' appearing in the argument of the final Gibb's state. Moreover, the symmetries of the final state dictate the relevant variables of the problem. In fact, Peletminskii and Yatsenko assume that H_0 satisfies

$$[H_0, \hat{\gamma}_k] = a_{kl}\hat{\gamma}_l \ , \tag{4.16}$$

where a_{kl} are c-number coefficients. Relation (4.16) has been utilized in the derivation of the results above.

4.1.1 Analogs between NGF and PY formalisms

In this section we will show what the analogs are between the coarse-grained density matrix theory and the method used by Peletminskii and Yatsenko (PY) in Ref. [164]. The coarse-grained density matrix theory should produce results identical to those of the non-equilibrium generating functional method as what comes to the dynamics of macro variables. In other words, when computing the time evolution of some relevant observable, we can either average over the time-dependent coarse-grained density matrix or we can use the Legendre transformation of the generating functional and use the stationarity condition to yield the dynamics of the expectation value of any macro observable. Even though the coupling terms $(\sum_m' d_m\psi_m)$ in Eq. (4.4) are reminiscent of the conjugate field couplings present in the time evolution operators of the non-equilibrium generating functional (cf. Eq. (2.23)) they represent explicit or spontaneously broken symmetries only the latter of which can arise through the Legendre transformation of the action of the generating functional. (Of course, explicitly broken symmetries can be dealt with in the generating functional description but they are not dummy integration variables in the Legendre transformation). Thus, we should really be talking about the comparison of the PY method and the coarse-grained density matrix theory, but for the latter we use the acronym NGF, short for Non-equilibrium Generating Functional, since the time evolution of observables is the same for these two descriptions. The symbols of PY formalism are mapped to coarse-grained density matrix parameters NGF as

$$\begin{array}{rcl} \text{(PY)} & & \text{(NGF)} \\ \hat{\gamma}_k & \leftrightarrow & \hat{Q}_k, \hat{\psi}_k \end{array} \tag{4.17}$$

$$X_k \leftrightarrow s_n, d_m \tag{4.18}$$

$$\exp\Big(-\textstyle\sum_k X_k(\gamma(t))\hat{\gamma}_k \Big) \leftrightarrow \exp\Big(-\textstyle\sum_n s_n(t)\hat{Q}_n - \sum_m d_m(t)\hat{\psi}_m \Big) \tag{4.19}$$

$$[H_0, \hat{\gamma}_i] = a_{ij}\hat{\gamma}_j \leftrightarrow [\hat{Q}_i, \hat{\psi}_i] = a\hat{\psi}_i \ . \tag{4.20}$$

In the last equation we have chosen $a = const$ on the NGF side for a single component order parameter. In general, the PY symmetry condition is closer to the Lie group structure of the dynamic symmetry group if one assumes that $H_0 = \sum_n \hat{Q}_n$, where Q_n are the symmetry generators of the unperturbed system. To cast the density matrix of the NGF theory into the same format as the PY formalism, we first define the vector $\hat{\gamma}$, which contains all symmetry generators and their order operators (not just the ones, which correspond to the symmetries actually broken by the dynamics):

$$\hat{\gamma} = (\hat{\gamma}_1,\ \hat{\gamma}_2 \dots \hat{\gamma}_N, \hat{\gamma}_{N+1}, \hat{\gamma}_{N+2} \dots \hat{\gamma}_{2N}) \tag{4.21}$$

$$= (\hat{Q}_1, \hat{Q}_2 \dots \hat{Q}_N, \hat{\psi}_{N+1}, \hat{\psi}_{N+2} \dots \hat{\psi}_{2N}) \tag{4.22}$$

Furthermore, writing $H_0 = \sum_{n=1}^{2N} X_n \hat{\gamma}_n = s_1\hat{Q}_1 + s_2\hat{Q}_2 + \ldots + s_N\hat{Q}_N + d_1\hat{\psi}_1 + d_2\hat{\psi}_2 + \ldots + d_N\hat{\psi}_N$ and assuming $[\hat{Q}_n, \hat{\psi}_n] \propto \hat{\psi}_n$, we obtain the familiar relation $[H_0, \hat{\gamma}_i] = a_{ij}\hat{\gamma}_j$, where

$$a_{ij} = \theta(N-i)X_{i+N}\delta_{i+N,j} + \theta(i-(N+1))(-X_{i-N})\delta_{ij} \ . \tag{4.23}$$

The step function is denoted by θ above. It should be noted that the matrix a_{ij} does not have to be invertible in PY formalism. In fact, it can also consist of zero elements if we take H_0 to be just a function of the commuting symmetry generators. It should also be noted that those X_n's, which are conjugate to the order operators ψ_n of non-broken symmetries, should be set equal to 0 in the expression $H_0 = \sum_{n=1}^{2N} X_n \hat{\gamma}_n$, if the final state density matrix only contains those order operators, which correspond to genuinely broken symmetries.

4.1.2 Entropy production and Einstein's fluctuation formula

In this section we define the non-equilibrium entropy and derive from the PY formalism the rate of entropy production consistent with Einstein's fluctuation formula,

$$P(\Delta S) \propto e^{\Delta S_t / k_b} \ , \tag{4.24}$$

which states that the probability of a thermodynamic fluctuation ΔS to occur is exponentially dependent on the quadratic changes of the relevant variables from their equilibrium values [8]: $\Delta S_t = \sum_{ij} \gamma_i g_{ij} \gamma_j$, where γ_i are the relevant thermodynamic fields. This equation can also be written in terms of the free energy fluctuation at constant temperature according to the principle of minimum work [32]. The non-equilibrium entropy S is defined by using the final state density matrix:

$$S \equiv -\mathrm{Tr}\{\rho^{(0)} \ln \rho^{(0)}\} = X_i \gamma_i - \Omega \ , \tag{4.25}$$

where summation over repeated indices is implied and $\Omega \equiv -\ln \mathrm{Tr}\rho^{(0)} = -\ln \mathrm{Tr}\{\exp(-X_i \gamma_i)\}$. Differentiation with respect to time gives

$$\dot{S} = \frac{d}{dt} S(\gamma) = \dot{\gamma}_i \frac{dS}{d\gamma_i} = \dot{\gamma}_i X_i \ . \tag{4.26}$$

In terms of vocabulary of standard non-equilibrium thermodynamics we can call X_i generalized forces and $\dot{\gamma}$ are the fluxes or time rates of change of generalized coordinates (relevant macro-variables). Next, we need to find out what $\dot{\gamma}_i$ is.

If the relevant macro observables $\hat{\gamma}_k$ are symmetry generators of the unperturbed part of the Hamiltonian H_0 (equivalently, approximate symmetries of H, see Sect. 3.1.1), then $[H_0, \hat{\gamma}_k] = 0$. It then follows that $L_k^{(0)}(\gamma) = \imath a_{kl} \gamma_l = 0$, because $[H_0, \hat{\gamma}_k] = a_{kl} \hat{\gamma}_l = 0$. We also assume that the symmetry generators commute with each other: $[\hat{\gamma}_k, \hat{\gamma}_l] = 0$. Then,

$$L_k^{(1)}(\gamma) = \mathrm{Tr}\{\rho^{(0)}(\gamma)[V, \hat{\gamma}_k]\} = \mathrm{Tr}\{[\hat{\gamma}_k, \, \rho^{(0)}(\gamma)] \, V\} = 0 \ . \tag{4.27}$$

The final equality holds because $[\hat{\gamma}_k, \, \rho^{(0)}(\gamma)] = [\hat{\gamma}_k, \, \exp(\sum_n X_n \hat{\gamma}_n)] = 0$. Thus, to second order in perturbation potential V the equation of motion (4.9) reduces to

$$\partial_t \gamma_k = L_k^{(2)}(\gamma) \ . \tag{4.28}$$

Consequently, we can write the entropy production (4.26) as

$$\dot{S} = X_i \dot{\gamma}_i = X_i L_i^{(2)}(\gamma) \ . \tag{4.29}$$

The positivity of entropy production, $\dot{S} \geq 0$, can be shown by performing the trace operation in the expression $L_i^{(2)}$ using the mutual eigenstates $|n\rangle$ of $\hat{\gamma}_k$ and H_0. The equilibrium values of the generalized coordinates $X_i^{(0)}$ can be found from the condition of zero entropy production: $\dot{S} = X_i^{(0)} L_i^{(2)}(\gamma) = 0$. In Sect. 4.1.3 we will show that considering small fluctuatons $\Delta X_i \equiv X_i - X_i^{(0)}$ to linear order, we can write

$$\dot{\gamma}_i = g_{ij} \Delta X_j \ , \tag{4.30}$$

where g_{ij} is the Green-Kubo expression for transport coefficient. The entropy production under nonequilibrium conditions becomes

$$\dot{S} = \dot{\gamma}_i X_i = g_{ij} (\Delta X_j) X_i = g_{ij} \Delta X_j \Delta X_i \ . \tag{4.31}$$

In the final equality we have utilized the property of the equilibrium forces, $L_i^{(2)} X_i^{(0)} = 0 \Rightarrow g_{ij}(\Delta X_j) X_i^{(0)} = 0$, so it does not really matter if we use X_i or ΔX_i in the expression of the entropy production. Taking into account higher order corrections in $L_i^{(2)}$, one can now derive non-linear corrections to Einstein's fluctuation formula.

4.1.3 Green-Kubo expression for transport coefficients

Let us now derive the Gree-Kubo expression for the transport coefficients g_{ij}. The linear response argument assumes that

$$\Delta\dot{\gamma}_i = g_{ij}\Delta X_j \ , \tag{4.32}$$

where $\Delta\dot{\gamma}_i \equiv \dot{\gamma}_i - \dot{\gamma}_i^{(0)}$. For example, if the generalized current $\dot{\gamma}_j$ corresponds to the electric current J, then ΔX_j is the (small) force acting on the system, i.e the electric field, and the susceptibility matrix g_{ij} reduces to electric conductivity Σ:

$$J = \Sigma E \ . \tag{4.33}$$

(We could also rewrite this roughly as $\Delta J = \Delta\dot{\gamma} = M\partial_x \delta F/\delta\phi = M\partial_x\mu$, where $\partial_x\mu$ represents the force as gradient of (chemical) potential, corresponding to the thermodynamic force ΔX_j. Matrix M corresponds to g_{ij}. This representation should be compared with Eq. (3.4), where ΔJ should be replaced by $\mathbf{j}' - \mathbf{j}$.) To get an expression for g_{ij} one should expand the density matrix appearing in the expression $L_i^{(2)}$ to first order in the deviation ΔX_i. From Eq. (4.10) we have [164]

$$L_i^{(2)}(\gamma) = -\frac{1}{2}\int_{-\infty}^{\infty} d\tau \, \mathrm{Tr}\{\rho^{(0)}(\gamma)\,[V(\tau),\, [V, \hat{\gamma}_i]]\} \ , \tag{4.34}$$

where $V(\tau) \equiv \exp(\imath H_0\tau)V\exp(-\imath H_0\tau)$. The density matrix is approximated as $\exp(\Omega - \hat{\gamma}_i X_i) = \exp(\Omega - \hat{\gamma}_i(X_i^{(0)} + \Delta X_i)) \approx \rho_0(1 - \hat{\gamma}_i\Delta X_i)$ with

$$\rho_0 \equiv \exp(\Omega - \hat{\gamma}_i X_i^{(0)}) \ . \tag{4.35}$$

Denoting $[V, \hat{\gamma}_i] \equiv A_i$, we can immediately see that $\dot{\gamma}_i^{(0)} = 0$ leading to $\Delta\dot{\gamma}_i = \dot{\gamma}_i$:

$$\dot{\gamma}_i^{(0)} = -\frac{1}{2}\int_{-\infty}^{\infty} d\tau \ \underbrace{\mathrm{Tr}\{\rho_0\,[V(\tau),\, A_i]\}}_{\mathrm{Tr}\{[\rho_0, V(\tau)]A_i\}} = 0 \ , \tag{4.36}$$

because the equilibrium condition (zero entropy production) translates into $[\rho_0, \int_{-\infty}^{\infty} d\tau\, V(\tau)] = 0$. Thus, the time rate of change of the current is

$$\begin{aligned}
\Delta\dot{\gamma}_j &= \frac{1}{2}\int_{-\infty}^{\infty} d\tau \, \mathrm{Tr}\{\rho_0\hat{\gamma}_j\Delta X_j\,[V(\tau), A_i]\} && (4.37)\\
&= \frac{1}{2}\int_{-\infty}^{\infty} d\tau \, (\,\mathrm{Tr}\{\rho_0\hat{\gamma}_j V(\tau)A_i\}\Delta X_j - \mathrm{Tr}\{\rho_0\hat{\gamma}_j A_i V(\tau)\}\Delta X_j) && (4.38)\\
&= \frac{1}{2}\int_{-\infty}^{\infty} d\tau \, \mathrm{Tr}\{\rho_0(\hat{\gamma}_j V(\tau) - V(\tau)\hat{\gamma}_j)A_i\}\Delta X_j && (4.39)
\end{aligned}$$

In deriving Eq. (4.39) we have once again utilized the equilibrium condition $[\rho_0, \int_{-\infty}^{\infty} d\tau\, V(\tau)] = 0$ to commute the places of $V(\tau)$ and ρ_0. Finally, we arrive at Eq. (4.32) with transport coefficient matrix given by

$$\begin{aligned}
g_{ij} &= -\frac{1}{2}\int_{-\infty}^{\infty} d\tau \, \mathrm{Tr}\{\rho_0\,[V(\tau), \hat{\gamma}_j]\,[V, \hat{\gamma}_i]\} = -\frac{1}{2}\int_{-\infty}^{\infty} d\tau \, \mathrm{Tr}\{\rho_0\,[H(\tau), \hat{\gamma}_j]\,[H, \hat{\gamma}_i]\} && (4.40)\\
&= -\int_0^{\infty} d\tau \, \mathrm{Tr}\{\rho_0\,\dot{\hat{\gamma}}_j(\tau)\dot{\hat{\gamma}}_i(0)\} = -\int_0^{\infty} d\tau \, \langle J_j(\tau)J_i(0)\rangle \ , && (4.41)
\end{aligned}$$

where we have defined $J_i(\tau) \equiv \hat{\dot{\gamma}}_j(\tau)$ and $H(\tau) \equiv \exp(\imath H_0\tau)H\exp(-\imath H_0\tau)$. The second equality in Eq. (4.40) follows from the fact that $[H_0, \hat{\gamma}_i] = 0 \Rightarrow [V(\tau), \hat{\gamma}_i] = \exp(\imath H_0\tau)[H_0 + V, \hat{\gamma}_i]\exp(-\imath H_0\tau)$. Obviously, the transport coefficients are symmetric with respect to change of indices i and j. This is a consequence of the time reversal symmetry of the underlying microscopic equations. When discussing the similarity of the Peletminskii and Yatsenko approach to Zubarev's formulation of transport coefficients in Sect. 4.2 we will be needing the representation of g_{ij} derived above.

4.2 Zubarev's nonequilibrium statistical operator

Zubarev's nonequilibrium statistical operator method [186, 179] provides a powerful scheme for deriving equations of motion for relevant variables. It has been applied to a wide range of classical [191] and quantum kinetic problems [192, 193], and also in relativistic field theoretic setting [194]. Zubarev's formalism has some striking similaritities with Jayne's information theoretical approach [188] (Sect. 4.3) and the nonequilibrium generating functional (NGF) method, which we will clarify below.

The basic entity in Zubarev's theory is not the generating functional but the reduced density matrix of macro observables, which is called the nonequilibrium statistical operator. To define it one needs to postulate first a relevant statistical distribution ρ_{rel}, which acts as the initial density matrix:

$$\rho_{rel} \equiv \exp\Big(-\Phi(t) - \sum_n F_n(t)P_n\Big) , \tag{4.42}$$

where F_n are analogous to variables X_n of Peletminskii and Yatsenko (cf. Eq. (4.7)). Compared to the nonequilibrium generating functional method, they are analogous of the conjugate fields needed for the Legendre transformation. The Massieu-Planck functional,

$$\Phi(t) \equiv \ln \mathrm{Tr}\left\{ -\sum_n F_n(t)P_n\right\} , \tag{4.43}$$

is the time-dependent normalization weight whose equilibrium partner is denoted by Ω in Eq. (4.35). The index n in the summation can also take continuous values ($n = \mathbf{x}$).

In the NGF formalism the conjugate source fields are dummy variables in the sense that they get replaced by the expectation values of the relevant observables via the Legendre transformation. Yet, the values of the source fields are not irrelevant as they determine the values of their Legendre transformation partner fields. In a similar manner, the fields P_n are dummy variables in Zubarev's formalism, because they can be eliminated through a set of self-consistency conditions:

$$\langle P_n\rangle^t = \langle P_n\rangle^t_{rel} \equiv \mathrm{Tr}\{P_n\, \rho_{rel}(t)\} . \tag{4.44}$$

Notation $\langle\cdot\rangle^t$ means averaging over the full nonequilibrium statistical operator (density matrix) $\rho(t)$ defined as

$$(\partial_t + \imath L)\rho(t) = -\epsilon(\rho(t) - \rho_{rel}(t)) . \tag{4.45}$$

Expectation values of observables are calculated in such a manner that one first takes the thermodynamic limit ($V \to \infty$, $N/V = const$), after which one lets $\epsilon \to 0$. It is imperative that the limits are taken in this order in order to select out the retarded solution of the

Liouville equation, which is time-reversal symmetric without any source terms on the right hand side of Eq. (4.45). The use of the infinitesimal field ϵ is the time dependent analogue of Bogolubov's quasi-averaging method, which we have discussed in Sect. 2.1.2. It is a highly idealized way of taking into account the effect of the interaction of the system with its surroundings. It also automatically induces the arrow of time, which is a clear advantage compared to some other methods, where the emergence of the second law of thermodynamics results because of approximations and assumptions whose overall effect can be more difficult to assess. The negative thing about the way the irreversibility is put in is the fact that it is impossible to evaluate the precise effect of the system-bath coupling on the dynamics and steady-state conditions. However, if these things are not directly relevant, Zuabarev's approach gives more universal results with less effort than explicit heat bath models as the bath influence is hidden in a single parameter ϵ, which is taken to zero at the end of the calculation.

4.2.1 Relation to PY formalism

Let first compare the equations of motion at the operator level. Both in PY formalism and Zubarev's formalism the relevant observables obey Heisenberg equation of motion:

$$\begin{aligned} \partial_t \hat{\gamma}_k &= [\hat{\gamma}_k, H] \; . && \text{(PY)} && (4.46) \\ \partial_t P_k &= [P_k, H] \; . && \text{(Zubarev)} && (4.47) \end{aligned}$$

These are somewhat redundant, since we always consider averages over ensembles. The averaging induces the dissipative behaviour in the equations of motion:

$$\begin{aligned} \partial_t \langle \hat{\gamma}_k \rangle &= L_k(\gamma) \; . && \text{(PY)} && (4.48) \\ \partial_t \langle P_k \rangle &= \langle \dot{P}_k \rangle^t_{rel} + \sum_n \int_{-\infty}^t d\tau \, e^{-\epsilon(t-\tau)} \mathcal{L}_{kn}(t,\tau) F_n(\tau) \; , && \text{(Zubarev)} && (4.49) \end{aligned}$$

where the dotted variable is to be interpreted as $\langle \dot{P}_k \rangle^t_{rel} \equiv \mathrm{Tr}\{[P_k, H]\rho_{rel}(t)\}$. The first term on the right hand side of Eq. (4.49) corresponds to $L_k^{(1)}$ if we interpret ρ_{rel} as $\rho^{(0)}$ in Eq. (4.10). As pointed out in Sect. 4.1.2 This term vanishes if all P_k's (γ_k's) commute with the Hamiltonian. Then we are left with the dissipative higher order terms $L_k^{(2)} + L_k^{(3)} + \ldots$ which correspond to the second term on the right hand side of Eq. (4.49). Using linear response approximation to express F_n in terms of P_n's and replacing ρ_{rel} with Gibb's equilibrium density $\rho_{eq} \propto \exp(-\beta H)$ leads to the familiar (averaged) Langevin equation

$$\partial_t \delta \langle P_k \rangle^t = -\imath \sum_n \Omega_{kn} \delta \langle P_n \rangle^t - \sum_n \int_0^\infty d\tau \, e^{-\epsilon\tau} \sigma_{kn}(\tau) \delta \langle P_k \rangle^{t-\tau} \; , \qquad (4.50)$$

where $\delta \langle P_k \rangle^t \equiv \langle P_k \rangle^t - \langle P_k \rangle_{eq}$, Ω is the frequency matrix (stemming from the first term on the right hand side of Eq. (4.49)) and σ is the memory matrix. Both these have appeared previously in Sect. 3.2.4.

Indeed, let us now show under what kinds of approximations the Green-Kubo coefficient g_{mn} is consistent with the expression of the transport coefficient $\mathcal{L}_{mn}$ of Zubarev's theory. The general form for the latter is [186]

$$\mathcal{L}_{mn}(t,t') = \int_0^1 dx \, \mathrm{Tr} \left\{ I_m(t) U_{rel}(t,t') \rho_{rel}^x(t') I_n(t') \rho_{rel}^{1-x}(t') \right\} \; , \qquad (4.51)$$

where $U_{rel}(t,t') \equiv \hat{T}_+ \exp(-\imath \int_{t'}^{t} P_\perp^{KG}(\tau)L)$. The Kawasaki-Gunton projection operator is denoted by P^{KG}, and $P_\perp^{KG} = 1 - P^{KG}$. The generalized fluxes $I_n \equiv P_\perp^M \dot{P}_n$, where P^M is the Mori projection operator, and $P_\perp^M = 1 - P^M$. In the Markovian limit, we can simplify the exact expression (4.51) following again Ref. [186]

$$\mathcal{L}_{mn}(t) = \int_{-\infty}^{0} dt_1 e^{\epsilon t_1} (I_m(t), e^{\imath t_1 L} I_n(t))_{rel} \ , \tag{4.52}$$

where the nonequilibrium correlation function of two dynamical variables A and B is defined through

$$(A,B)_{rel} \equiv \int_0^1 dx \, \langle \Delta A \rho_{rel}^{x} \Delta B \rho_{rel}^{-x} \rangle_{rel}^{t} \ , \tag{4.53}$$

and $\Delta A \equiv A - \langle A \rangle_{rel}^{t}$ and similarily for ΔB. Replacing now ρ_{rel} by ρ_0 to make contact with PY approach, we get

$$\mathcal{L}_{mn}(t) \approx \int_{-\infty}^{0} dt_1 \, e^{\epsilon t_1} \langle \dot{P}_m(t) \dot{P}_m(t+t_1) \rangle_0 = \int_0^{\infty} d\tau \, e^{-\epsilon\tau} \mathrm{Tr}\{\dot{P}_m(t) \dot{P}_n(t-\tau) \rho_0\} \tag{4.54}$$

$$= \int_0^{\infty} d\tau \, e^{-\epsilon\tau} \mathrm{Tr}\{\dot{P}_n(0) \dot{P}_m(\tau) \rho_0\} \ . \tag{4.55}$$

The crucial approximation utilized in the first equality of (4.54) is to leave out the projectors $P_\perp^M$, which are missing from the PY treatment. Thus, we have replaced the currents $I_n = P_\perp^M \dot{P}_n$ by $\dot{P}_n$ directly. Eq. (4.55) assumes translational invariance of time in the equilibrium state. The result is the same as given in Eq. (4.41).

Finally, we note that the self-consistency relation of Zubarev's (Eq. (4.44)) is equally restrictive as what comes to the derivation of the equations of motion as the final state boundary condition used for density matrix by Peletminskii and Yatsenko. We show this by utilizing a special property of the final state density matrix of PY formalism given in Ref. [164]:

$$\mathrm{Tr}\{\hat{\gamma}_k \rho(\gamma)\} = \mathrm{Tr}\{\hat{\gamma}_k \rho^{(0)}(\gamma)\} \ . \tag{4.56}$$

This looks like the self-consistency condition of Zubarev's, but it should be noted that instead of $\rho^{(0)}$ Zubarev uses ρ_{rel}, which is rather the initial condition for the full density matrix $\rho(t)$. Using Eq. (4.56) and the symbols defined in the beginning of Sect. 4.1, gives

$$\mathrm{Tr}\{\hat{\gamma}_k \rho(\gamma)\} = \mathrm{Tr}\{\hat{\gamma}_k \rho^{(0)}(\gamma)\} \ \Rightarrow \ \int_{-\infty}^{0} d\tau e^{-\eta\tau} e^{-\imath a \tau} \mathrm{Tr}\{\hat{\gamma}_k f(S_\tau^{(0)} \gamma)\} = 0 \tag{4.57}$$

$$\Rightarrow \ \mathrm{Tr}\{\hat{\gamma}_k f(\gamma)\} = 0 \ \Rightarrow \ \imath \mathrm{Tr}\{\rho(\gamma)[V, \hat{\gamma}_k]\} - L_k(\gamma) + L_k^{(0)}(\gamma) = 0 \ . \tag{4.58}$$

Thus, we have arrived at the expression of $L_k(\gamma)$ consistent with Eq. (4.10). Since $\dot{\gamma}_k = L_k(\gamma)$ we have shown that the constraint property (4.56) fixes the form of the macrovariable evolution equation in a way, which is analogous to the derivation of Zubarev's equation of motion (4.49) by using the self-consistency condition (4.44).

4.2.2 Relation to NGF formalism

We commence the search for similarities between the nonequilibrium generating functional formalism and Zubarev's method by comparing the expressions of density matrices. First, let us take a look at the time reversible parts:

$$\begin{aligned} \rho^r_Z &= e^{\imath(t-t_0)H_s}\rho_{rel}(t_0)\, e^{-\imath(t-t_0)H_s} \ ; && (4.59)\\ \rho^r_s &= e^{\imath(t-t_0)H_s}\rho_0(t_0)\, e^{-\imath(t-t_0)H_s} \ ; && (4.60) \end{aligned}$$

We note that ρ^r_Z, where r refers to 'reversible', satisfies Zubarev's equation of motion (4.45) with $L = H_s$ and $\epsilon = 0$. Eq. (4.60) is just the time dependent system density matrix in the Heiseberg representation. We see that ρ_{rel} plays the role of ρ_0 in the usual many-body formalism. When dissipative effects are taken into account the expressions of the density matrices start to differ from each other more. This is because the irreversibility is can be induced in many ways: Zubarev uses time averaging, $\rho_Z(t) = \langle \rho^r_Z(t,t_0)\rangle_{t_0}$, wheras we resort to the bath averaging $\langle\cdot\rangle_B$: $\rho_s(t) = \langle \rho_s(t)\rangle_B$. We can also rewrite these expressions as

$$\begin{aligned} \rho_Z(t) &= e^{\imath t H_s}\langle e^{-\imath t_0 H_s}\rho_{rel}(t_0)\, e^{\imath t_0 H_s}\rangle_{t_0}\, e^{-\imath t H_s} \ ; && (4.61)\\ \rho_s(t) &= e^{\imath t H_s}\langle \hat{T}_+ e^{-\imath\int d\tau\, H_{SB}(\tau)}\rho_0^{SB}(t_0)\,\hat{T}_- e^{\imath\int d\tau\, H_{SB}(\tau)}\rangle_B\, e^{-\imath t H_s} \ . && (4.62) \end{aligned}$$

If one could show the equivalence of the ensemble average $\langle\cdot\rangle_B \equiv \mathrm{Tr}_B\{\cdot\}$ to the time average,

$$\rho_Z(t) = \lim_{\epsilon\to 0}\epsilon\int_{-\infty}^{t} dt'\, e^{-\epsilon(t-t')}\, e^{\imath(t-t')L}\,\rho_{rel}(t') = \lim_{t-t_0\to 0}\frac{1}{t-t_0}\int_{t_0}^{t} dt'\, e^{\imath(t-t')L}\rho_{rel}(t') \ , \qquad (4.63)$$

it would be possible to show that $\rho_Z(t) = \rho_s(t)$. This is, however, too strong a requirement, and not even necessarily true in all situations. We can settle for a weaker condition, which is the equivalence of the *expectation* values

$$\langle\psi(\mathbf{x})\rangle^t_s = \langle\psi(\mathbf{x})\rangle^t_Z \ . \qquad (4.64)$$

If this relation holds for all times and positions, also the ensuing equations of motion for the expectation values of observables will be the same. This is expected to be the case as the self-consistency relation of Zubarev's actually fits the Lagrange multipliers $F_n(t)$ in such a way that the (experimentally or otherwise) observed values of relevant variables are reproduced. This is because $\langle P_n\rangle^t_{rel}$ is chosen to respect any *known* information about the system. On the other hand $\rho_s(t)$ contains the full physics of the problem with no simplifying assumptions made at this point. Therefore, it should also give rise the same time (and spatial) dependence of the expectation values in agreement with the experiments.

There are some striking similarities between the Legendre transformation of the nonequilibrium generating functional and the Zubarev's nonequilibrium entropy, which coincides with the information entropy of the relevant ensemble, defined as as

$$S(t) \equiv -\mathrm{Tr}\{\rho_{rel}(t)\ln\rho_{rel}(t)\} = \Phi(t) + \sum_n F_n(t)\langle P_n\rangle^t \ . \qquad (4.65)$$

This is similar to the entropy of PY formalism given in Eq. (4.25): $S \equiv -\mathrm{Tr}\{\rho^{(0)}\ln\rho^{(0)}\} = \sum_i X_i\gamma_i - \Omega$. There is also a close connection to the entropy used in the early versions of variational formulation of statistical mechnics by De Dominics [42, 40] and others. Even more curiously, we can use S to define a 'Legendre transformation pair' [179]

$$\langle P_n\rangle^t = -\frac{\delta\Phi(t)}{\delta F_n(t)} \ ; \ F_n(t) = \frac{\delta S(t)}{\delta\langle P_n\rangle^t} \ . \qquad (4.66)$$

Even though these equations resemble the ones which are obtained from the nonequilibrium generating functioal theory (Sect. 2.3.3), we cannot identify the Zubarev's entropy directly with the action of the generating functional. This is because of the different way the Lagrange multipliers (conjugate source fields) are fed in: In Zubarev's formalism they are placed directly in the expresion of ρ_{rel}, which is then time evolved under the action of $\exp(\imath tL)$, whereas in the nonequilibrium generating functional the time dependent source fields are placed in the time evolution operator U itself (Eq. (2.23)).

4.3 Jaynes'es information theoretical approach

For starters, we wish to compare the Heisenberg equation of motion for a general opetor A with the Liouville-von Neumann equation for the density matrix. The latter is given by [195]

$$\frac{d}{dt}\rho(t) = -\imath[H(t), \rho(t)] \ , \tag{4.67}$$

where the Hamiltonian can be time-dependent. As pointed out in Ref. [196], frequently Eq. (4.67) is written (see e.g. [16, 197]) in the form $\partial_t \rho = -\imath[H, \rho]$ with partial time derivative on the left. Technically speaking it really does not matter for density matrix whether one uses the total derivative or the partial time derivative, because time is the only variable in the quantum case (as opposed to classical Liouville equation). Eq. (4.67) resembles the Heisenberg eqation of motion,

$$\frac{d}{dt}A_H(t) = \imath[H_H(t), A_H(t)] + \frac{\partial}{\partial t}A_H(t) \ , \tag{4.68}$$

where for explicitly time-dependent operator $A_S(t)$ in the Schrödinger picture the partial time derivative is defined as [195, 181]

$$\frac{\partial}{\partial t}A_H(t) \equiv U_S^\dagger(t, t_0)(\partial_t A_S(t))U_S(t, t_0) \ , \tag{4.69}$$

where it is important to notice that the time evolution operators U are also given in the Schrödinger picture as indicated by the subscripts. The noteworthy feature is that by setting $\rho = A$ in the Heisenberg equation of motion the sign of the commutator is reversed as compered to the Liouville-von Neumann equation for the density matrix. Therefore, the time dependendent density matrix cannot be said to be in the Heisenberg representation based on the form of the equation of motion. Builiding up the density matrix from time-dependent Schrödinger states,

$$\rho(t) \equiv \sum_n p_n(t)|\psi_n(t)\rangle\langle\psi_n(t)| \tag{4.70}$$

where the time-dependence of the occupation probabilities $p_n(t)$ results from the influence of the system with its surroundings (heat bath), it is straightforward to show that the equation of motion becomes [196, 198]

$$\frac{d}{dt}\rho(t) = \imath[\rho, H] + \frac{\partial}{\partial t}\rho \ . \tag{4.71}$$

The partial time derivative is defined as

$$\frac{\partial}{\partial t}\rho \equiv \sum_n \frac{dp_n(t)}{dt}|\psi_n(t)\rangle\langle\psi_n(t)| \ . \tag{4.72}$$

When the occupation probabilities do not change with time, Eq. 4.71 reduces to the Liouvielle-von Neumann equation.

The non-unitary time evolution of the density matrix in the Jaynes'es and Zubarev's formalism occurs because of bath interaction. In Zubarev's formalism an infinitesimal external field is introduced, which is taken to zero at the end of the calculation. Here, the origin of irreversibility is related directly to the time-change of the occupation probabilities. The non-equilibrium density matrix is constructed using information theoretical arguments (Shannon [199, 200]) based on the concept of information entropy. Time-dependent probabilities concerning the state of macroscopic observables are taken to depend on the experimentally available information of the system, which has accumulated over the time intervall $[t_0, t]$. In a manner analogous to derivation of Gibb's distribution based on constraints on maximum Gibb's entropy and normalizability, one can derive a maximum information entropy prediction for the time dependent probabilities [196]:

$$\rho \equiv p_i(t_0, t) = Z^{-1}[\lambda] \exp\Big(- \int_{t_0}^{t} ds\, \lambda(s) f_i(s) \Big) \ , \tag{4.73}$$

where λ is a Lagrange's multiplier (analogous to Zubarev's P_m-field). For spatially extended systems we can write the previous equation as

$$\rho = Z^{-1}[\lambda] \exp\Big(- \int_{t_0}^{t} ds \int d\mathbf{x}\, \lambda(\mathbf{x}, s) f(\mathbf{x}, s) \Big) \ . \tag{4.74}$$

If λ contains many components, we should write $\sum_k \lambda_k f_k(\mathbf{x}, s)$ instead of just $\lambda f(\mathbf{x}, s)$ as above. The 'partition functional' is given by

$$Z[\lambda] \equiv \mathrm{Tr} \Big\{ \exp\Big(- \int_{t_0}^{t} ds\, \lambda(s) f_i(s) \Big) \Big\} = \sum_i \Big\{ \exp\Big(- \int_{t_0}^{t} ds\, \lambda(s) f_i(s) \Big) \Big\} \ , \tag{4.75}$$

Eq. (4.75) looks a lot like Zubarev's generating functional. While both the Jaynes formalism and Zubarev's formalism are based on information theory (the concept of relevant ensemble ρ_{rel}), the functionals $Z[\lambda]$ is different from $Z[P]$: In Zubarev's theory the relevant variables appearing in the argument of the relevant distribution are functions of position only, where as in Eq. (4.75) the quantum observables f follow Heisenberg's equation of motion (4.68). In this sense, Jaynes formulation is closer to our non-equilibrium generating functional presentation of the time evolution operators (which make up the generating functional when initial distribution is left out), which contain Heisenberg fields coupled with the sources J as shown in Eq. (2.35) (cf. with Eq. (2.23)). However, if one only consideres the unaveraged equations of motion of the relevant variables (with no reference to the generating functionals), Heisenberg equations of motion are obeyed by construction in Jaynes formalism as well as in Zubarev and Peletminskii & Yatsenko cases as shown in Eq. (4.46) and Eq. (4.47).

Just like Zubarev's ρ_{rel}, $\rho(t)$ introduced in Eq. (4.73) divides the probablity mass as evenly as possbile in the phase space in the information theoretical sense maximizing the information entropy

$$S_{non-eq}[\lambda_k] \equiv k_B \ln Z[\lambda_k] + k_B \sum_k \int_{t_0}^{t} ds \int d\mathbf{x}\, \lambda_k(\mathbf{x}, t) \langle f_k(\mathbf{x}, t) \rangle \ , \tag{4.76}$$

It is possible to use a different domain R_k for each of the Lagrange's multipliers (corresponding to different spatial and temporal intervals, from which information has been gathered). In

Eq. (4.76) we have set all domains the same $\int_{R_k} dt\, d\mathbf{x} = \int_{t_0}^{t} ds \int_{-\infty}^{\infty} d\mathbf{x}$. The values of the Lagrange's multipliers can be fixed using the experimentally measured expectation values in the way familiar from the Peletminskii & Yatsenko (Sect. 4.1) theory and Zubarev theory (Sect. 4.2):

$$\langle f_k(\mathbf{x},t)\rangle \equiv \mathrm{Tr}\{\rho f_k(\mathbf{x},t)\} = -\frac{\delta}{\delta\lambda(\mathbf{x},t)} \ln Z \ . \tag{4.77}$$

The differential forms of equations of motion of the expectation values $\langle g(\mathbf{x},t)\rangle^t$ of relevant observables can be produced by differentiating the 'solution',

$$\langle g(\mathbf{x},t)\rangle^t = \sum_i g_i(t) p_i(t) \ , \tag{4.78}$$

where the short-hand notation $g_i(t) = g(\mathbf{x}_i, t)$. Differentiation of Eq. (4.78) with respect to time yields

$$\partial_t \langle g(\mathbf{x},t)\rangle^t = \sum_i (\partial_t p_i g_i(t) + p_i \partial_t g_i(t)) = \sum_i \partial_t p_i g_i(t) + \langle \dot{g}(\mathbf{x},t)\rangle^t \ . \tag{4.79}$$

Using Eq. (4.73) we obtain

$$\partial_t p_i = -\frac{1}{Z^2} \partial_t Z \, \exp\Big(- \int_{t_0}^{t} ds\, \lambda(s) f_i(s) \Big) - \lambda(t) f_i(t) p_i(t) \ . \tag{4.80}$$

On the other hand, differentiation of the partition functional (4.75) gives

$$\partial_t Z = -\sum_i \lambda f_i(t) \, \exp\Big(- \int_{t_0}^{t} ds\, \lambda(s) f_i(s) \Big) = -\lambda \langle f(\mathbf{x},t)\rangle^t Z \ . \tag{4.81}$$

Combining this result with Eq. (4.80) allows us to write $\partial_t p_i = -\lambda \Delta f_i(t) p_i(t)$, where $\Delta f_i(t) \equiv f_i(t) - \langle f(\mathbf{x},t)\rangle^t$. Plugging these into Eq. (4.78) finally yields the equation of motion for the relevant field:

$$\partial_t \langle g(\mathbf{x},t)\rangle^t = \langle \dot{g}(\mathbf{x},t)\rangle^t - \lambda(t) K_{fg}(\mathbf{x},t) \ . \tag{4.82}$$

The covariance function $K_{fg}(\mathbf{x},t) \equiv \sum_i \Delta f_i(t) g_i(t) p_i = \langle g(\mathbf{x},t) f(\mathbf{x},t)\rangle^t - \langle f(\mathbf{x},t)\rangle^t \langle g(\mathbf{x},t)\rangle^t$. Thus, the similarity between the equations of motion derived through other formalisms are obvious. Just like in Zubarev's case, the first term on the right hand side of Eq. (4.82) is the streaming term whereas the covariance term (correlation function) counts for dissipative effects and entropy increase consistent with the second law of thermodynamics [188]. Choosing $f = g$ allows us to cast Eq. (4.82) into

$$\partial_t \langle g\rangle^t = \langle \dot{g}\rangle^t - \lambda(t) K_{gg}(t) \ . \tag{4.83}$$

This should be compared with Zubarev's equation of motion for relevant variables P_m under the action of *external* fields h_n [179]:

$$\partial_t \delta \langle P_m\rangle^t = \langle \dot{P}_m\rangle^t - \beta \sum_n (\dot{P}_m, P_n) h_n(t) \ , \tag{4.84}$$

If the relevant ensemble is the equilibrium one, it follows that $\partial_t \delta\langle P_m\rangle^t = \partial_t \langle P_m\rangle^t$ and the Eq. (4.84) starts resembling Eq. (4.83) given that one considers only a single component in the former and associates $\beta h_n(t)$ with $\lambda(t)$. However, the correlation functions are not precisely the same: Zubarev's correlator contains a time derivative of the relevant variable, which is not present in Eq. (4.83).

Part II

Applications

Chapter 5

Hydrodynamics of macroscopic quantum systems

5.1 Derivation of Time Dependent Ginzburg Landau model of superconductivity

We will now apply the coarse-graining formalism explained in Chap. 2 to derivation of time-dependent Ginzburg-Landau theory of superconductivity. The subject has a long history [201, 202, 203] and the theory itself has found numerous applications in the fields of condensed matter and particle physics. A systematic scheme derivation scheme is necessary to enlargen the range of validity of the nonequilibrium theory of superconductivity: In its most elementary form, the time-dependent Ginzburg-Landau equation is only valid very close to the critical point and deviations from equilibrium must be small such that the quasiparticle exctitations remain essentially in equilibrium with the heat bath (phonons) [204]. The derivation presented below will be based on the generating functional formalism making use of some crucial approximations tested in context of other approaches. What we are trying to clarify and systematize is the choice of the order parameter. After it has been fixed, the equations of motion follow mechanically from the generating functional, in principle. The program in the nutshell will look as follows

(1) Fix the starting point of the coarse-graining process: Many-body theory with electrons and nucleons. Identify bath degrees of freedom (phonons) and establish Fröchlich Hamiltonian:

$$Z[J] = \int \mathcal{D}(\psi^*, \psi) \int \mathcal{D}(b^*, b)\ e^{\imath \int [\bar{\psi}(\imath\partial_t - \epsilon(\nabla))\psi + b\psi^*\psi + b^*(\imath\partial_t - w(\nabla))b + J\Delta]} \tag{5.1}$$

The electronic coordinates are denoted by ψ, phonons by b and Δ is the order operator. Operators $\epsilon(\delta)$ and $w(\delta)$ fix the electron and phonon energies.

(2) Integrate out phonons by tracing over the bath, which can be done exactly if phonon-phonon scattering is suppressed:

$$Z[J] = \int \mathcal{D}(\psi^*, \psi)\ e^{\imath \int [\bar{\psi}(\imath\partial_t + \nabla^2)\psi + \psi^*\psi^* V \psi\psi + J\Delta]} \tag{5.2}$$

Neglect retardation effects and assume constant attractive contact potential. Use *symmetry analysis of the action* to fix the order operator: $\Delta = \psi\psi$ = pair field. (Classically, $\Delta = \int g\psi\psi$, where g is the effective interaction.)

(3) Perform first stage of coarse-graining by going to the pair field representation:

$$Z[J] = \int \mathcal{D}(\Delta^*, \Delta)\ e^{\imath \int [\bar{\Delta}(\partial_t + \nabla^2)\Delta + g|\Delta|^4 + J\Delta]} \tag{5.3}$$

Systematic corrections can be computed, which extend the validity range from the vicinity of the critical point.

(4) Formation of tree level effective action for the expectation value of the order operator via Legendre transformed effective action $\mathcal{A}[\langle\delta\langle]$:

$$\frac{\delta \mathcal{A}[\langle\Delta\rangle]}{\delta[\langle\Delta(\mathbf{x}, t)\rangle]} = (\partial_t + \nu\nabla^2)\langle\Delta\rangle + m'\langle\Delta\rangle + g'|\langle\Delta\rangle|^2\langle\Delta\rangle^2 = 0\ . \tag{5.4}$$

The averaging over the nonequilbrium density matrix completes the second coarse-graining stage. Eq. (5.4) is the time-dependent Ginzburg-Landau equation for the order parameter (gauge fields left out).

The end result is the familiar Ginzburg-Landau theory, where time dependence is not put in by hand as in the phenomenological way of deriving critical dynamics (not based on projection operator formalism). The Kadanoff-Baym time-path Green's function technique [203] is equivalent to our CPT-formalism leading to the same result. However, the whole coarse-graining aspect is more hidden in the plain Green's function approach, which is why we prefer to use the generating functional. Its action offers a suitable starting point for the symmetry analysis, which will lead to reckognition of the relevant macro variables, and their (coupled) equations of motion can be conviniently derived using the stationarity of the effective action. In the usual Green's function technique, which is equivalent to the generating funcitonal method, one usually does not perform the change to collective coordinates (Δ is a composite operator). Here, other usufull information can be read off from the action in the new coordinates, too. The second coarse-graining stage, which is the nonequilibrium ensemble averaging of the order operator (the average being the physically observable order parameter) is performed automatically (in principle) without any BBGKY hierarchy problems as opposed to direct averaging of composite operators. Of course, in practice the construction of the effective action is not that easy, because of the nonlinearities. Symmetry principles are powerfull and can be used in direct (Ward-Takahashi) construction of the equations of motion as shown in Sect. 3.1.2. This is another advantage of the generating functional representation of the Green's function formalism.

5.2 From nuclear degrees of freedom to phonons

In Sect. 2.3.2 we discussed how the decoupling of the nuclear and electronic degrees of freedom result in an effective equation of motion for the slow nuclear degrees of freedom, where the effect of the electronic 'bath' is manifested in the appearance of effective potential and coupling to a vector potential. Conversely, the nuclear motion is reflectd in the effective equations of motion of the electrons to be derived in this section. While it might be wrong to call the nucleons themselves as bath variables (them being slow), we can describe their effect through the action of small vibrational motion around their equilibrium positions in terms of collective phonon coordinates. Integrating out the phonons from the equation of motion of the electrons results in a new type of interaction term between the electrons, which is responsible for superconductivity. The microscopic starting point is thus the many-body Schrödinger equation for electrons and nucleons. The full Hamiltonian,

$$H = H_e + H_N + V_{e-N} \ , \tag{5.5}$$

is a sum of the electronic (H_e) Hamiltonian, nuclear (H_N) Hamiltonian and the electron-nucleon interaction potential (V_{e-N}). Specifically,

$$\begin{aligned} H_e &= \sum_{i=1}^{N_e} \frac{1}{2m_e} p_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \ \equiv \ T_e + V_e \ ; & (5.6) \\ H_N &= \sum_{ji=1}^{N_N} \frac{1}{2m_N} P_i^2 + \frac{1}{2} \sum_{i \neq j} V_N(\mathbf{R}_i - \mathbf{R}_j) \ \equiv \ T_N + V_N \ ; & (5.7) \\ V_{e-N} &= \sum_{i=1}^{N_e} \sum_{j=1}^{N_N} v_{e-N}(\mathbf{r}_i - \mathbf{R}_j) \ . & (5.8) \end{aligned}$$

Thus, nuclei have been described by structureless ions, which obey Shrodinger equation with some effective pair potential V_N. Here is where the first coarse-graining trick comes into play. Due to the large mass difference between the electrons and the nuclei one assumes that their equations of motion can be approximately decoupled by separation of variables in the total wave function Ψ:

$$\langle \mathbf{r}, \mathbf{R} | \Psi_n \rangle \equiv \Psi_n(\mathbf{r}, \mathbf{R}) = \sum_{m=1}^{\infty} \chi_{nm}(\mathbf{R}) \psi_m(\mathbf{r}, \mathbf{R}) \ , \tag{5.9}$$

where χ is the nuclear wave function and ψ is the electronic one. Substituting the ansatz (5.9) into the Schrödinger equation, $H\Psi_n = E_n \Psi_n$ and projecting both sides by $\langle \Psi_k|$, we obtain [181]

$$[\hat{T}_e(\mathbf{r}) + \hat{V}_e(\mathbf{r}) + \hat{V}_{e-N}(\mathbf{r}, \mathbf{R})] \psi_n(\mathbf{r}; \mathbf{R}) = \epsilon_n(\mathbf{R}) \psi_n(\mathbf{r}; \mathbf{R}) \tag{5.10}$$

$$[\hat{T}_N(\mathbf{R}) + \hat{V}_N(\mathbf{R}) + \epsilon_k(\mathbf{R}) + \langle \psi_k | \hat{T}_N(\mathbf{R}) | \psi_k \rangle] \chi_{nk}(\mathbf{R}) = E_n \chi_{nk}(\mathbf{R}) \ . \tag{5.11}$$

The off-diagonal matrix elements $\langle \psi_n | \hat{T}_N(\mathbf{R}) | \psi_k \rangle$ $(n \neq k)$ have been dropped in the Born-Oppenheimer approximation. Utilizing the fact that the ions perform small vibriational motion around their equilbrium positions $\mathbf{R}^0$ we can expand $\mathbf{R}_i = \mathbf{R}_i^{0)} + \mathbf{u}_i$, where $\mathbf{u}_i$ is the ionic displacement. For small $\mathbf{u}_i$ Eq. (5.11) becomes

$$\left[T_N + \frac{1}{2} \sum_{n,m=1}^{N_N} \sum_{\mu,\nu=1}^{3} u_m^\mu u_n^\nu A_{mn}^{\mu\nu} + \ldots \right] \chi_{nk} = E_n \chi_{nk} \ , \tag{5.12}$$

where we have grouped all the potential terms in Eq. (5.11) into one term called W. Then W has been Taylor expanded and the coefficient of the quadratic term is called $A^{\mu\nu}_{mn} \equiv [\partial^2 W/(\partial R^{\mu}_m \partial R^{\nu}_n)]|_{\mathbf{R}^{(0)}}$. The first order term vanishes because the total force on the ion at its equilibrium position must vanish.

Expanding now similarily the electron-nucleon interaction term V_{e-N} in small displacements gives the following efective Hamiltonian for the electronic degrees of freedom (Eq. (5.10))

$$\underbrace{T_e + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N_e}\sum_{j=1}^{N_N} v_{e-N}(\mathbf{r}_i - \mathbf{R}^0_j)}_{H^0_e} + \underbrace{\sum_{i=1}^{N_e}\sum_{j=1}^{N_N} \mathbf{u}_i \cdot \nabla_{\mathbf{r}_i} v_{e-N}(\mathbf{r}_i - \mathbf{R}^{(0)}_j)}_{H_{e-ph}} + \ldots \; . \tag{5.13}$$

The problem can now be treated perturbatively in the basis of the eigenvectors of the effective zeroeth order Hamiltonian H^0_e, which determines a single electron problem in a periodic lattice of ions. The basis states so determined are called Bloch states [181] and their corresponding second quantized creation and annihilation operators are denoted as $c^\dagger_\sigma(\mathbf{k})$ and $c^\dagger_\sigma(\mathbf{k})$, where σ is the spin index and $\mathbf{k}$ is a wave vector in the first Brillouin zone. Replacing also the displacement position coordinate $\mathbf{u}$ in Eq. (5.13) by the sum of the creation ($b^\dagger(\mathbf{k})$) operators of phonon excitations, we obtain [205]

$$H_{e-ph} = \sum_{\mathbf{k},\mathbf{q},\sigma} V(k)\Big(b(\mathbf{q}) + b^\dagger(-\mathbf{q})\Big)c^\dagger_\sigma(\mathbf{k}+q)c_\sigma(\mathbf{k}) \; , \tag{5.14}$$

where the summation is over the first Brillouin zone and $V(k) \propto V_{e-N}(k)$ (Umklapp processes left out). We also restrict the analysis to a single phonon polarization state.

To make contact with our general coarse-graining scheme a few words on finding out the phonon variables from first principles are in order. Phonons are Goldstone modes, which can be read off from the Madelung representation of the order-parameter field(s), which in this case is the *Fourier transform* of the (number) density of the nuclei [162, 206], $\rho_G = |\rho_G|e^{\imath\theta}$, where $\theta = \mathbf{G}\cdot\mathbf{u}$ ($\mathbf{G}$ is the reciprocal lattice vector of the ions). More appropriately, one should call ρ_G the order operator and its cell average over a sufficiently large coarse-graining cell the order parameter. For sufficiently large cell size one can then define a single valued and continuous displacement field $\tilde{\mathbf{u}}$: $\langle\rho_G\rangle_{cell} \propto e^{\imath\mathbf{G}\cdot\tilde{\mathbf{u}}}$, which can be made in coarse-grained descriptions of hydrodynamics of solids [207]. Since we have stressed the importance of symmetries in indentification of the order parameters, and the algebraic approach for their extraction, we should now try to see, how ρ_G fits in the story. Trying to derive the conventionally used order parameters from first principles is not always so straightforward as we know. In this case we are merely trying to see, if we can give an operator formulation of ρ_G, which (if possible) conforms to the intuitive algegraic picture we have been using in many occasions in this book: Order operators $\psi^\dagger$ and ψ act as generalized ladder operators, and $\psi^\dagger\psi = Q$ is a generator of symmetry transformation of the Hamiltonian. In the traditional setting it is the Landau free energy $F[\langle\rho_G\rangle_{cell}]$ that is invariant under the symmetry transformations related to the (cell averaged) order parameter $\langle\rho_G\rangle_{cell}$. Here, if we want to see the symmetry transformation in the operator level, we can imagine that our Hamiltonian H_{eff} can be written as a function of generalized field operators $a^\dagger_{G_i}$ and a_{G_i}, which either create or annihilate a nucleus at site $\mathbf{G}$ of the reciprocal lattice. In fact, we can say that the order parameter vector $\rho_G = (\rho_{G_1}, \rho_{G_2}\ldots)^{\mathrm{T}}$ ('T' for transpose), where ρ_{G_i} are the values of the Fourier components of order parameter field at all lattice points, can be created by action of an order operator $\psi^\dagger \equiv (a^\dagger_{G_1}, a^\dagger_{G_2}\ldots)^{\mathrm{T}}$ on the vacuum state. When multiplied with its conjugate transpose,

$\psi \equiv (a_{G_1}, a_{G_2} \ldots)$ on obtains the total number density operator, which commutes with H_{eff}. We need a more stringend condition, however, since the Hamiltonian should be invariant in all local rotations which leave the nuclear lattice intact. Similar to our example in Sect. 2.4.2 we impose the following commutation relation for the component operators: $[a_{G_i}, a^\dagger_{G_i}]_+ = 1$ and all other pairs commute analogous to the spin operators. Then, we see that

$$e^{\imath \sum_n \alpha_n a^\dagger_{G_n} a_{G_n}}\, H_{eff}\Big(\{a^\dagger_{G_i}\}\Big)\, e^{-\imath \sum_n \alpha_n a^\dagger_{G_n} a_{G_n}} = H_{eff}\ , \tag{5.15}$$

whenever the rotation angle α_n is such that the operator prodcuts contained in H_{eff},

$$a^\dagger_{G_i} a^\dagger_{G_j} a^\dagger_{G_k} \ldots \mapsto \exp(\imath(\alpha_i + \alpha_j + \alpha_k + \ldots))\, a^\dagger_{G_i} a^\dagger_{G_j} a^\dagger_{G_k}\ , \tag{5.16}$$

stay invariant: $\alpha_i + \alpha_j + \alpha_k + \ldots = 2n\pi$. Thus, in this case it seems to be possible to express the crystal symmetry generator in the form $\psi^\dagger\psi$. In more complicated cases one has to resort to other types of order operator decompositions.

We also note that it is possible to device a similar kind of density functional theory for the nuclear degrees of freedom as for the electronic ones. This can be done by introducing a generating functional of the form

$$Z[J_N, J_e] = \int \mathcal{D}(c^*, c, \psi^*_N, \psi_N)\; e^{\imath S[c^*, c, \psi^*_N, \psi_N] + J_N \psi^*_N \psi_N + J_e c^* c}\ , \tag{5.17}$$

where (c^*, c) are the electron fields and (ψ^*_N, ψ_N) the fields of nuclei. In the more traditional representation the two-component density functional theory would take a form similar to Sect. 6.2. In the density functional approach the whole symmetry analysis together with the order operator identification could be dealt with in a more systematic manner from the beginning. This was not the case in the discussion above, where we were partly mixing classical and quantum mechanical ideas.

5.3 Fröhlich Hamiltonian and the effective interaction

Given the approximations of Sect. 5.2 leading to the nuclear (phonon) Hamiltonian (5.12) and to the electronic Hamiltonian (5.13) quadratic in canonical coordinates, we can cast the full Hamiltonian into the form

$$H \approx \underbrace{\sum_{\mathbf{k}} \epsilon(k) c^\dagger(\mathbf{k}) c(\mathbf{k})}_{H_{el}} + \underbrace{\sum_{k} w(k) b^\dagger(\mathbf{k}) b(\mathbf{k})}_{H_N = H_{ph}} + \underbrace{\sum_{k,q} V(k) c^\dagger_\sigma(\mathbf{k}+\mathbf{q}) c_\sigma(\mathbf{k}) \Big(b^\dagger(\mathbf{q}) + b^\dagger(-\mathbf{q})\Big)}_{V_{e-N}}\ . \tag{5.18}$$

This is the Fröchlich Hamiltonian of electrons in a quadratic phonon bath. Basically, V_{e-N} (combined with the short-range part of V_e) gives rise to the effective attraction of the electrons. Therefore, we have left out the electronic Coulomb potential V_e, which can always be added in the end of the calculation. We will futher simplify the problem by assuming that $V(k) = d$ is a constant. Replacing k-dependent Fröhlich interaction between electrons and phonons in the static theory by a constant is equivalent to introducing a constant attractive contact interaction in the Bardeen-Cooper-Schrieffer Hamiltonian [205] between the electrons. In the time dependent calculation, it turns out that even if we replace $V(k)$ by a constant, there will be a non-trivial frequency kernel present in the effective interaction between electrons. This will become clear in a moment. The third approximation is to use free electron annihilation (ψ) and creaction ($\psi^\dagger$) operator symbols for the states in the vicinity of the Fermi level instead of the Bloch state operators in Eq. (5.18). They will remind us of the fact that the band energy $\epsilon(k) \approx k^2/(2m)$, where m is the effective band mass. These approximations said and done, we can write the generating functional as

$$\int \mathcal{D}(\psi^*, \psi) \int \mathcal{D}(b^*, b)\ e^{\imath (S_e[\psi^*,\psi] + S_{ph}[b^*,b] + S_{e-ph}[\psi^*,\psi,b^*,b] + J_e \Delta)}\ , \tag{5.19}$$

where Δ is the order parameter. That is some functional of the electronic fields to be fixed soon. The explicit forms of the actions are given by

$$\begin{aligned}
S_{ph} &\equiv \int_P dt \int d\mathbf{x}\ b^*(\mathbf{x},t)\Big(\imath\partial_t - w(\nabla)\Big) b(\mathbf{x},t) = \int_P dt \sum_k b^*_{\mathbf{k}}(t)\Big(\imath\partial_t - w_k\Big) b_{\mathbf{k}}(t)\ ; & (5.20)\\
S_e &\equiv \int_P dt \int d\mathbf{x}\ \psi^*_\sigma(\mathbf{x},t)\Big(\imath\partial_t - \epsilon(\nabla)\Big)\psi_\sigma(\mathbf{x},t) = \int_P dt \sum_k \psi^*_{\mathbf{k},\sigma}(t)\Big(\imath\partial_t - \epsilon_k\Big)\psi_{\mathbf{k},\sigma}(t)\ ; & (5.21)\\
S_{e-ph} &\equiv \int_P dt \sum_k\ d_0 \rho_{\mathbf{k}}(b_{\mathbf{k}} + b^*_{-\mathbf{k}}) = \int_P dt \sum_k \Big(d_0\rho_{\mathbf{k}} b_{\mathbf{k}} + d_0 \rho^*_{\mathbf{k}} b^*_{\mathbf{k}}\Big)\ . & (5.22)
\end{aligned}$$

In the last equation we have made use of the fact that for constant interaction between electrons and phonons we can perform the summation over q in Eq. (5.18) (summation over repeated spin indices is assumed), and set $\sum_{q,\sigma} c^*_\sigma(\mathbf{k}+\mathbf{q}) c_\sigma(\mathbf{q}) = \sum_q \psi^*_\sigma(\mathbf{k}+\mathbf{q})\psi_\sigma(\mathbf{q}) = \rho(\mathbf{k}) = \rho^*(-\mathbf{k})$. We can perform the trace over the bath using

$$\begin{aligned}
&\int \mathcal{D}(b^*, b)\ e^{\imath \int_P dt \int d\mathbf{k} \int_P dt' \int d\mathbf{k}'\ [b^*(\mathbf{k},t) A(\mathbf{k},t;\mathbf{k}',t') b(\mathbf{k},t) + j^*(\mathbf{k},t) b(\mathbf{k},t)\delta(\mathbf{k}-\mathbf{k}')\delta(t-t') + h.c.]} \qquad (5.23)\\
&\qquad = e^{\imath \mathrm{Tr} \ln A - \imath \int_P dt \int d\mathbf{k} \int_P dt' \int d\mathbf{k}'\ j^*(\mathbf{k},t) A^{-1}(\mathbf{k},t;\mathbf{k}',t') j(\mathbf{k}',t')}\ .
\end{aligned}$$

In our case, the **k**-integration is understood to be taken over the first Brillouin zone and the determinant term can be dropped it being independent on electron fields. In fact, the **k**-integration has a more stringend restriction, when only the effective attractive electron-electron interaction is kept. From the perturbation theory it can be concluded that the energies of the electrons in momentum states $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$ should be less than the average phonon energy $\hbar\omega$ if one wants to approximate the potential $V(k)$ by a constant d [202]. The best values for d and ω can be found from variational principle. Identification of $A = (\imath\partial_t - w_k)$ and $j = d_0\rho^*$ leads to the following representation of the density matrix ρ_S (not to be confused with electronic density) of the system, which is expressed entirely in the electron coordinates

$$\rho_S(\psi_f, \psi'_f, t) = \int \mathcal{D}\psi_i \int \mathcal{D}\psi'_i\ \rho_{S0}(\psi_i, \psi'_i) \int_{\psi_i}^{\psi_f} \mathcal{D}\psi_+ \int_{\psi'_i}^{\psi'_f} \mathcal{D}\psi_-\ e^{\imath S[\psi_+,\psi_-]} I[\psi_+, \psi_-]\ , \tag{5.24}$$

where cluttering of notation has been avoided by not showing the integration measures over the conjugate Grassmann fields. I is the influence functional defined in Sect. 2.2.4. For generality, we have also included the initial density matrix here to remind us of the possibility of modeling a situation with nontrivial initial correlations. In the generating functional we will take the initial time to $-\infty$ when comparing with results from the literature. For finite times we have

$$S[\psi_+, \psi_-] = \int_{-\infty}^t ds \int d\mathbf{x}\ \psi^*_+\Big(\imath\partial_s - \epsilon(\nabla)\Big)\psi_+ - \int_{-\infty}^t ds \int d\mathbf{x}\ \psi^*_-\Big(\imath\partial_s - \epsilon(\nabla)\Big)\psi_-\ . \tag{5.25}$$

The energy $\epsilon(\nabla) = \nabla^2/(2m)$ and the influence functional is given in terms of the countour Green's functions defined in Eqs. (2.73) – (2.76):

$$I = \exp\left(\frac{\imath}{2}\int_{-\infty}^{t} ds \int d\mathbf{x} \int_{-\infty}^{t} ds' \int d\mathbf{x}' \; [d_0\rho_a(\mathbf{k}, s)] D_{ab}(\mathbf{k}, s; \mathbf{k}', s')[d_0\rho_b^*(\mathbf{k}', s')]\right) \tag{5.26}$$

It is pointed out the the electron density field ρ is a product of two anticommuting variables so it transforms like a bosonic object [208, 209]. Also, the signature of the initial thermal distribution will remain in the propagators even if we decouple the thermal countour and extend the time integrations over the entire real axis. The generating functional now reads

$$Z[J_+, J_-] = \int \mathcal{D}(\psi_f, \psi_f')\, \delta(\psi_f - \psi_f')\rho_S(\psi_f, \psi_f', t)e^{\imath \int_{-\infty}^{\infty} dt \int d\mathbf{x}\, (J_+(\mathbf{x},t)\Delta_+(\mathbf{x},t) - J_-(\mathbf{x},t)\Delta_-(\mathbf{x},t))} \tag{5.27}$$

which reduces to Eq. (5.19) when the initial correlations (ρ_{S0}) are left out. The remaining task is to find out an explicit representation for the order operator Δ. This can be done more easily if we introduce some approximations for the expression of the effective interaction of the electrons present in the influence functional. This is the subject of the next section.

5.4 Approximating retarded interaction by a static one

The standard methods of deriving the phonon mediated effective interaction for the electrons give different results from what we have shown in the previous section. One should not draw any far reaching conclusions from the time dependence of the effective interaction as we have assumed that the parameters such as w_k are the bare phonon frecuencies which have not been renormalized by electronic effets and vice versa [210]. We also assumed that the band energy $\epsilon_k = k^2/2m$, where is free electron like with the mass of the electron replaced by effective mass m. This is not such a bad approximation for the states close to Fermi surface in an unstrained crystal [211]. What about the effective interaction then? In the single time path formalism the propagators are simpler because there are no thermal factors. We can write [212]

$$D(k, z) = \frac{w_k}{z^2 - w_k^2}\ , \tag{5.28}$$

($\mathrm{Im}(z) > 0$). In the static limit we can just set $z = 0$ and the whole effective interaction term goes basically like $(-d_0^2/w_k)\rho_k\rho_k^*$, where we have also assumed that $V(k)$ is constant d_0. Thus, the interaction is attractive. This is consistent with the second order static perturbation calculations for energy eigenvalues presented in Refs. [211, 181]. The justification for setting the frequency $z = 0$ in the dynamic formulation is equivalent to the static perturbation calculation where z^2 in the denominator of $D(k, z)$ is replaced by the energy difference $(\epsilon_q - \epsilon_{k+q})^2$. Indeed, close to the Fermi surface it holds that $|\epsilon_q - \epsilon_{k+q}| \ll \hbar w_k$ (see Ref. [205]) justifying the use of static interaction.

Based on these arguments we are now going replace D_{ab} in the generating functional by an attractive static contact interaction $-g$, which does not depend on wavevectors or time ($g = d_0^2/w_k \approx const$). Hence,

$$Z[J_+, J_-] = \int \mathcal{D}(\psi^*, \psi)\ \exp\left\{\imath \int_P dx \left(\psi_\alpha^*\Big(\imath\partial_t - \epsilon(\nabla)\Big)\psi_\alpha - g\psi_\alpha^*\psi_{\alpha'}^*\psi_{\alpha'}\psi_\alpha + J\Delta + h.c.\right)\right\}\ , \tag{5.29}$$

where initial correlations have been left out and spin indices are denoted by σ. All fields are evaluated at the same space-time position $x \equiv (\mathbf{x}, t)$. For simplicity, we have also decoupled the different time paths from each other by the choice of the contact interaction given in Eq. (5.29).

5.5 Pair field as the order operator

We can now give a recipe for determination of the order operator Δ in Eq. (5.29). After all the nontrivial approximations employed in reducing the interaction to the contact form, the action of the generating functional is now simple enough that a mechanical isolation of symmertry generator(s) and order parameter(s) is possible. Following the general approach given in Chap. 3 we first search for a generator of continuous symmetry. At this stage one can resort either to algebraice techniques, intuition or experimental information. Because electric charge is conserved, a natural candidate for continuous symmetry generator in real space represention is

$$Q = \int d\mathbf{x} \left(\psi_\uparrow(\mathbf{x})\psi_\uparrow(\mathbf{x}) + \psi_\downarrow(\mathbf{x})\psi_\downarrow(\mathbf{x}) \right) \ , \tag{5.30}$$

where arrow symbol are used to indicate the spin labels. Obviously Q commutes with the free field part of the action. Using the commutator identities

$$[AB, C]_- = +A[B, C]_+ - [A, C]_+ B \ \ ; \ \ [A, BC]_- = -B[A, C]_+ + [A, B]_+ C \ ; \tag{5.31}$$

$$[AB, C]_+ = +A[B, C]_+ - [A, C]_- B \ \ ; \ \ [A, BC]_+ = -B[A, C]_- + [A, B]_+ C \ . \tag{5.32}$$

For fermionic operators it is straightforward to show that the *commutator* of Q and the effective electron-electron interaction term vanishes. In the following we will use the symbol Q for the conserved variable and its local density ($Q = \int d\mathbf{x}\, q(\mathbf{x})$). This meaning should be clear from the context. We get

$$[Q \ , \ g\psi_\uparrow^\dagger \psi_\downarrow^\dagger \psi_\downarrow \psi_\uparrow]_- = 0 \ . \tag{5.33}$$

where all field operators are evaluated at the same spatial location. By Pauli principle the electrons should have opposite spins (of course, one must be carefull when talking about the entities created by the operators $c^\dagger \approx \psi^\dagger$ as individual 'electrons'). More rigorously the spin attachement can be justified by considering the energy of the lowest lying excitations: Opposite spins cost less energy as shown in Ref. [211]. Of course, there are also other conserved observables, which can be expressed as a function of Q. The same rule applies to the construction of the symmetry operator and conserved charge as to finding the complete set of commuting variables: only the basis generators are considered.

The order operator Δ is now easily constructed in terms of Q, which was just shown to be a generator of a continuous symmtery of the action. The simplest candidates should satisfy the generalized ladder operator requirement: $[\Delta, Q]_- \propto \Delta$ based on the simple arguments on spontaneous symmetery breaking in Sect. 2.1.3. Substituting $\Delta = \psi^\uparrow \psi^\downarrow$ gives

$$[Q, \Delta]_- = -2\Delta \ . \tag{5.34}$$

Thus, we draw the conclusion that $\Delta(\mathbf{x}) = \psi^\uparrow(\mathbf{x})\psi^\downarrow(\mathbf{x})$ is a valid order operator and its expectation value, the anomalous Green's function $\langle \hat{T}_P(\psi_\uparrow \psi_\downarrow) \rangle$ is the order parameter. The same is true for $\Delta = \psi_\uparrow^\dagger \psi_\downarrow^\dagger$.

It is now time to perform the next coarse-graining step by going to a pair field representation from the single fermionic fields ψ. Based on the operator analysis presented above, we can now define a local pair field (a collective coordinate or collective quantum field) through

$$\Delta_{\alpha\beta}(\mathbf{x},t) = g\psi_\alpha(\mathbf{x},t)\psi_\beta(\mathbf{x},t)\ . \tag{5.35}$$

To be more precise, Eq. (5.35) turns out to be the same as the classical constraint equation (no quantum corrections), which follows from extremizing the pair field representation of the action of the generating functional (Eq. (5.29) without the source fields) with respect to Δ^*. This can be seen by representing the interaction part of the generating functional in terms of $\Delta_{\alpha\beta}$

$$\exp\left(\frac{\imath}{2}g\sum_{\alpha,\beta}\int dx\,\psi^\dagger_\alpha(x)\psi^\dagger_\beta(x)\psi_\beta(x)\psi_\alpha(x)\right) = \tag{5.36}$$
$$const\int\mathcal{D}(\Delta^*,\Delta)\ \exp\left\{-\frac{\imath}{2}\sum_{\alpha,\beta}\int dx\left(|\Delta_{\alpha\beta}(x)|^2/g - \Delta^*_{\alpha\beta}\psi_\alpha\psi_\beta - \Delta_{\alpha\beta}\psi^*_\alpha\psi^*_\beta\right)\right\}\ .$$

Taking variation $\delta/\delta\Delta^*_{\alpha\beta}$ leads immediately to the classical condition of Eq. (5.35). A bilocal interaction can also be decomposed in the same way as shown in Ref. [213]. The use of the bilocal field is an important generalization, which makes the extraction of the order operator more involved at the operator level. However, since we can easily generalize Eq. (5.36) for interaction potential $V(x,x')$ the extraction of the order parameter at classical level is readily obtained by requiring the stationarity of the action with respect to Δ^*. Without quantum corrections, the order parameter then turns out to be $\Delta_{\alpha\beta}(x,x') = V(x,x')\psi_\alpha(x)\psi_\beta(x')$, which would indicate that in the first order approximation the order operator would include the potential V: $\hat{\Delta}_{\alpha\beta}(x,x') = V(x,x')\hat{\psi}^\dagger_\alpha(x)\hat{\psi}_\beta(x')$, where we have indicated the operator character of the symbols by carets to separate them from their ensemble averaged expectation values, which appear in the classical constraint equation. (Saddle point equaton corresponds to the tree level effective action.) This can be readily generalized for more complicated cases (where direct operator analysis might be hard) such as fermionic superfluid ^{3}He, whose order parameter can be related to the expectation value of the pair field in a similar fashion as above. Several equivalent representaion exist as demonstrated in Refs. [214, 215, 216]

To obtain the effective action, we can now make use of Eq. (5.23) by generalizing it for field doublets $\tilde{b} \equiv (\psi_\uparrow, \psi^*_\downarrow)$, where $\tilde{b}$ is now a Grassmann vector and the free field part of the action (5.29) is given by a quadratic form whose kernel A becomes a two-by-two matrix:

$$A(x,x') = \left(\begin{array}{cc} (\imath\partial_t - \epsilon(\nabla))\,\delta_{\alpha\beta}\delta(x-x') & -\Delta_{\alpha\beta}(x)\,\delta(x-x') \\ -\Delta^*_{\alpha\beta}(x)\,\delta(x-x') & -(\imath\partial_t + \epsilon(\nabla))\,\delta_{\alpha\beta}\delta(x-x') \end{array}\right)\ . \tag{5.37}$$

When integrating out the single fermion fields the effective action can be read off from Eq. (5.23). Expanding the logarithmic term resulting form exponentiating the determinant we obtain

$$Z[J_+,J_-] = \int\mathcal{D}(\Delta^*,\Delta)\exp(\imath S[\Delta^*,\Delta,J^*,J])\ . \tag{5.38}$$

It should be remembered that the time integrals run over the path P in the previous expression. The action in Eq. (5.38) is not yet the effective action, which generates the equation of motion, but an exact representation of the generating functional in the new collective (integration) variables Δ. Explicitly we have

$$S[\Delta^*,\Delta,J^*,J]=-\frac{1}{2}\mathrm{Tr}_{spin}\int dx\ \frac{1}{g}\ |\Delta(x)|^2 \tag{5.39}$$
$$-\imath\sum_{n=1}^{\infty}\frac{(-1)^n}{2n}\mathrm{Tr}\mathrm{Tr}_{spin}\left\{\left[(\imath\partial_t-\epsilon(\nabla))^{-1}\delta\right]\Big((\Delta+J)\delta\Big)\ \left[(\imath\partial_t+\epsilon(\nabla))^{-1}\delta\right]\Big((\Delta^*+J^*)\delta\Big)\right\}^n\ ,$$

where $\delta\equiv\delta(x-x')$, Tr is the trace over space-time degrees of freedom, and Tr_{spin} is the trace over the spin degrees of freedom.

5.6 Order parameter dynamics

The dynamics of the expectation value of the order operator is generated in standard manner by forming the effective action (second stage of coarse-graining) and using its stationarity property. We have kept the source field J in the description from the beginning and due to the change of variables from single fermion fields to pair fields, the form of the generating functional is awkward since the powers of the source are mixed with the powers of the field Δ making it difficult to form even the tree level action. To circumvent this problem we can imagine doing the following. Let us not include the source fields before in the final stage where $S[\Delta^*,\Delta]$ has been formed. Only then we add linearily coupled fields in the generating functional. Thus,

$$Z[J_+,J_-]\equiv e^{\imath W[J_+,J_-]}=\int\mathcal{D}(\Delta^*,\Delta)\ e^{\imath(S[\Delta^*,\Delta]+J\Delta+h.c.)} \tag{5.40}$$

where the action can be obtained from Eq.(5.39) by setting $J^*=J=0$. Analytically continuing the imaginary time path result of Ref. [213] the pair field Lagrangian density can be written as

$$L=a_1\Delta^*(x)(-\partial_t)\Delta(x)+a_2|\nabla\Delta(x)|^2+a_3|\Delta(x)|^2+a_4|\Delta(x)|^4+\ldots \tag{5.41}$$

This series describes the physics close to the critical point and picking up more terms from Eq. (5.39) one can extend its validity range. The remarkable fact is that the coefficient

$$a_3=N(0)\left(1-\frac{T}{T_c}\right) \tag{5.42}$$

changes its sign at critical temperature signalling the emergence of the phase transition. The parameters are [213] $N(0)=(mp_F)/(2\pi^2)$, where p_F is the Fermi momentum. The critical temperature goes like $T_c=\omega_D\exp(-1/(N(0)g))$. One ends up with similar result using a direct 'internal bath' coarse-graining method by integrating out the rapidly oscillating modes of the basic fermion and only then utilizing the pair field representation for the slow modes [217]. Of course, the same approximations must be present in the direct coarse-graining process, but the fact that it can be done increases the confidence on the idea that predictions on coarse-grained behaviour of systems, which are not experimentally and theoretically as well understood as low-T_c supercondutors, can be made.

The Lagrangian density is clearly invariant under a global transformation $\Delta\to e^{-\imath\alpha}\Delta$ just like the original Lagrangian density expressed in terms of the basic field ψ. Naturally, this has to be so, because the introduction of the pair field is an exact transformation into collective coordinates system, which cannot alter the symmetries of the theory. The orginal Lagrangian can be made invariant also under a *local* space-time dependent gauge transformation

$$\psi(\mathbf{x},t) \to e^{-\imath\alpha(\mathbf{x},t)}\psi(\mathbf{x},t) \tag{5.43}$$

by introduction a gauge field coupling to electric and magnetic vector potentials $(V_E, \mathbf{A})$. The simplest way of doing this is to use the minimal substitution, which leads to the following pair field Lagrangian density

$$\begin{aligned} L \;=\; & a_1\Delta^*(x)\Big(-\partial_t + \imath 2eV_E\Big)\Delta(x) + a_2\Big|\Big(\nabla - \imath 2(e/c)\mathbf{A}\Big)\Delta(x)\Big|^2 \\ & + a_3|\Delta(x)|^2 + a_4|\Delta(x)|^4 + a_5\Big(-V_E\nabla^2 V_E + \dot{A}^2/c^2 + \mathbf{A}\cdot\nabla^2\mathbf{A}\Big) \end{aligned} \tag{5.44}$$

in the Coulomb gauge $\nabla\cdot\mathbf{A} = 0$. The factors of two arise naturally in the pair representaion. Using Eq. (5.44) the equation of motion for the order parameter follows immediately. First, the effective action for the expectation value of the order operator at tree level is given by $\mathcal{A}_{tree}[\langle\Delta\rangle_+, \langle\Delta\rangle_-] = S[\langle\Delta\rangle_+, \langle\Delta\rangle_-]$, where $S = \int dx\, L$. Using the methods of Sect. 2.3.3 we get

$$\begin{aligned} & \frac{\delta\mathcal{A}[\langle\Delta\rangle_+, \langle\Delta\rangle_-]}{\delta\langle\Delta\rangle_+(\mathbf{x},t)}\bigg|_{\langle\Delta\rangle_+ = \langle\Delta\rangle_-} = \\ & a_1\Big(-\partial_t + \imath 2eV_E\Big)\Delta(x) - a_2\Big(\nabla - \imath 2(e/c)\mathbf{A}\Big)^2\Delta(x) + a_3\Delta(x) + a_4|\Delta(x)|^2\Delta(x) = 0\ , \end{aligned} \tag{5.45}$$

which is nothing but the familiar time-dependent Ginzburg-Landau equation. Variation with respect to the gauge degrees of freedom would give rise to the current equation. One should keep in mind, though, that we did not introduce the gauge fields from the beginning as coarse-grained dynamic variables.

It should be remembered that a whole bunch of approximations has been made use of in the derivation. We did not carry out the analysis as far as to include the dissipative effects which be come relevant for higher temperatures. Retarded effects of the non-renormalized phonon interaction were left out in Sect. 5.4. We also utilized the single time path Lagrangian in Eq. (5.44) and substituted it directly into the CPT-formalism. Thus, the effect of initial correlations and any higher order path interactions are not taken into account in the present derviation. Combining these effects with the phenomena taking place further away from the critical point (such as phonon-phonon) scattering and dissipation will be an interesting exercise. Hopefully it will turn out to be possible to extend the validity range of the time-dependent description in this way to facilitate comparison with more advanced theories [204] of nonequilibrium superconductivity.

5.7 Weakly interacting Bose fluids

Compared to the superconductors, the task of finding out the order parameter and its dynamics in the case of weakly interacting Bose superfluids (He^4) is considerably simpler due to the simplicity of the order parameter: Double field representation is not needed nor do we need to integrate out (external lattice) phonons to obtain the lowest order approximation for the dynamics.

5.7.1 Derivation of dynamics of the condensate

Let us first present some standard ways of deriving the Gross-Pitaevskii equation, which describes the dynamics of the Bose condensate. The starting point is already a coarse-grained effective theory as soon as we call the basic field operators $\psi^\dagger$ and ψ the creation and annihilation operators of Helium atoms, which are composite objects. Expasion in the basis states α allows us to decompose the field operator $\psi(\mathbf{x}) = \sum_\alpha f_\alpha(\mathbf{x}) a_\alpha$, where a_α annihilates field excitations in the general state labeled by quantum number α. Choosing plane wave basis, the single particle wavefunctions $f_\alpha(\mathbf{x}) = \exp(\imath\mathbf{k}{\cdot}\mathbf{x})$. Bose-Einstein condensation means that a macroscopic number of particles occupy the zero momentum state $\mathbf{k} = 0$, and consequently we can write the field annihilation operator as

$$\psi(\mathbf{x}) = \sum_{\mathbf{k}} e^{\imath\mathbf{k}\cdot\mathbf{x}} a_{\mathbf{k}} = a_0 + \sum_{\mathbf{k}\neq 0} e^{\imath\mathbf{k}\cdot\mathbf{x}} a_{\mathbf{k}} \equiv \Phi + \psi'(\mathbf{x}) \ , \tag{5.46}$$

where the condensate wavefunction Φ is just a space independent constant, $\Phi = \sqrt{n_0}$, where n_0 is the homogeneous condensate density (number of condensate particles per unit volume) for a suitable definition of the phase. If the condensate is in motion or there the external constraints (coupling fields, boundary conditions) depend on time, the condensate can form but it is not anymore homogenous in time and space. Therefore, Eq. (5.46) must be generalized to the form

$$\psi(\mathbf{x}, t) = \Phi(\mathbf{x}, t) + \psi'(\mathbf{x}, t) \ , \tag{5.47}$$

where $\Phi \equiv \langle\psi\rangle$ is the expectation value of the field operator ψ. Because of its spatial dependence, the condensate wavefunction must now contain also other than zero momentum states [201].

The idea is now to write down the Heisenberg equation of motion for the field operator $\psi(\mathbf{x}, t)$ and separate out the condensate part. Using an effective pair potential U_{eff} to describe the interaction between two helium atoms, we obtain immediately

$$\imath\hbar\frac{\partial}{\partial t}\psi(\mathbf{x}, t) = [\psi(\mathbf{x}, t), H] = \left(\frac{\hbar^2}{2m} + \int d\mathbf{x}'\, \psi^\dagger(\mathbf{x}, t) U_{eff}(\mathbf{x} - \mathbf{x}')\psi(\mathbf{x}, t)\right)\psi(\mathbf{x}, t) \ , \tag{5.48}$$

where we used the Hamiltonian $H = \int \psi^\dagger(-\hbar^2/(2m))\psi + \int\int \psi^\dagger\psi^\dagger U_{eff}\psi\psi$. Using now the decomposition (5.47) and the approximation $U_{eff} \approx g\delta(\mathbf{x} - \mathbf{x}')$ yields the Gross-Pitaevskii [218, 219, 220] equation for the condensate (ψ' terms are dropped as 'small'):

$$\imath\hbar\frac{\partial}{\partial t}\Phi(\mathbf{x}, t) = \frac{\hbar^2}{2m}\Phi(\mathbf{x}, t) + g|\Phi(\mathbf{x}, t)|^2\Phi(\mathbf{x}, t) \ . \tag{5.49}$$

In this equation Φ is a not an operator but complex valued function, which can be parametrized as

$$\Phi(\mathbf{x}, t) = \sqrt{n_0(\mathbf{x}, t)}\, e^{\imath\theta(\mathbf{x}, t)} \ , \tag{5.50}$$

where θ is the phase of the condensate wave function Φ. The phase will play an important part in the determination of the order operator as we will now see from the generating functional approach.

The nonequilibrium generating functional is easily constructed based on the approximative form of the Hamiltonian. Exactly as in the case of superconductors we used a constant attractive interaction potential, we use here a constant repulsive potential. This is not a bad approximation because binary s-wave scattering at low energies [221] is independent of the details of the two-body potential. Thus,

$$Z[J_+, J_-] = \int \mathcal{D}(\psi^*, \psi)\; e^{\imath \int_P dx\; (\psi^*(\imath\partial_t - \epsilon(\nabla))\psi + g\psi^*\psi^*\psi\psi + J\psi)} \tag{5.51}$$

We have written the order operator as ψ directly, because taking the saddle point approximation, which is equivalent to forming the tree level effective action,

$$\mathcal{A} = \int_P dx\, \langle\psi^*\rangle(\imath - \epsilon(\nabla))\langle\psi\rangle + g|\langle\psi\rangle|^4 \;, \tag{5.52}$$

one obtains immediately the Gross-Pitaevskii equation (5.49) for the expectation value of the order operator. Thus, the generating functional formalism leads to the same result on tree level as the direct averaging of Heisenberg's equation of motion. The identification of the order operator is easy to justify more rigorously by using our algebraic approach (Sect. 2.1.3, Chap. 3) as shown below.

5.7.2 Isolating the order operator based on symmetry

The conserved charge in the case of superfluids is the number of particles $[N, H] = 0$, where $N = \int \psi^\dagger\psi$. The low energy approximation for H is

$$H(\mathbf{x}) \approx -\psi^\dagger(\mathbf{x})\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{x}) + g\psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\psi(\mathbf{x}) \;. \tag{5.53}$$

Thus, N generates the continuous symmetry transformation $e^{-\imath\alpha N}\psi e^{\imath\alpha N} = e^{\imath\alpha}\psi$ under which the action of the generating functional (Hamiltonian) is invariant. As easily seen, the equilibrium density matrix

$$\rho^J_{eq} \equiv e^{-\beta H + J\psi} \tag{5.54}$$

does not commute with the number operator N because of the presence of the field J. Thus, in the broken symmetry phase, which is described by the J-ensemble weight (5.54) (η-ensemble, Sect. 2.1.2), the order operator will gain a non-zero expectation value:

$$\langle\psi\rangle = \mathrm{Tr}\{\psi\, \rho^J_{eq}\} = \mathrm{Tr}\{[\psi, Q]\, \rho^J_{eq}\} = \mathrm{Tr}\{[Q, \rho^J_{eq}]\, \psi\} \neq 0 \;, \tag{5.55}$$

because $[Q, \rho^J_{eq}] \neq 0$. In the symmetric phase, which is described by ρ^0_{eq}, the expectaion value is zero. In exactly the same manner we can see the symmetry breaking related to super conductivity. We just have to replace the symmetry generator N with the conserved charge $Q = \psi^\dagger_\uparrow\psi_\uparrow + \psi^\dagger_\downarrow\psi_\downarrow$ and the order operator ψ with the pair field $\Delta = \psi_\uparrow\psi_\downarrow$ and the same argumentation falls through. The spontaneously broken $U(1)$ symmetry manifests itself in the form of the expectation value of the order-operator in the symmetry broken phase: It will not stay intact in the symmetry transformation because the state does not remain intact. This is the reason why we use two different density matrices ρ^0_{eq} and ρ^J_{eq} to describe the symmetric and symmetry-broken states. In the symmetry broken state (ensemble) the Hamiltonian part of the action of Z remains invariant in the substitution $\psi \to e^{\imath\alpha}\psi$ but the order parameter transforms as $\langle\psi\rangle \to e^{\imath\alpha}\langle\psi\rangle$. For superconductors, the pair field Hamiltonian part is invariant under replacement $\Delta \to e^{\imath 2\alpha}\Delta$ but when symmetry is spontaneously broken $\langle\Delta\rangle \to e^{\imath 2\alpha}\langle\Delta\rangle$. The appearance of a single constant phase is analogous to appearance of the spontaneous homogenous orientation (relative to some reference direction) of spins in the

Heisenberg model of a ferromagnet. When a certain direction of magnetic moments has been established, the rotational invariance has been (spontaneously) broken.

Of course, the symmetry can be also broken explictly, but this is not what we are doing here, even though it may appear so from the form of the density matrix ρ_{eq}^{J} we use to describe the broken symmetry phase! After, all Bogoliubov's quasi-averaging method only revels the spontaneous symmetry breaking, when the field J (which explicitly breaks the symmetry in ρ_{eq}^{J}) is taken to zero. Similarily, it should be remembered that the Legendre transformation, which is why we introduce the sources of the generating functional, does not generate symmetry breaking, because the order operator acts as a dummy variable which vanishes when we express the effective action in terms of its expectation value. Its effect is to make the emergence of the anomalous solutions visible, when other control parameters of the theory are in suitable range. This is why we use the field dependent density matrix in Eq. (5.55), where the symmetry is explictly broken in terms of the field J even though the symmetry-breaking is spontaneous, not explicit, in reality.

In conclusion we find that the dynamics of the superconductors and superfluids is very similar as what comes to the tree level equations of motion. In both cases the scattering of the constituent objects can be described in terms of s-wave process and contact interaction, which is repulsive for Bose-fluid and attractive for superconductor. In both cases we we also able to give an interpretation for the order parameter based on the symmetry analysis of the action. For super conductors it is the pair field of the Bloch states participating in the scattering characterized by the contact potential. For superfluids the order parameter is the (annihilation/creation) field expectation value for helium atoms whose scattering is well-approximated by the s-wave contact interaction in the weak coupling approximation. The present derivation suggests that as far as we can call $\Phi = \langle\psi\rangle$ the macroscopic wave function of the condensate, these two are one and the same thing. Calling Φ a wavefunction is misleading in the sense that it is a complex classical field, which does not have the same probability interpretation as the quantum wavefunctions [222] (Φ is the expectation value of the field operator). In a finite size sample, where the gauge symmetry breaking or off-diagonal order arguments cannot be strictly speaking applied, people have defined the condensate wavefunction through diagonalization of the one-body density matrix ρ_1:

$$\int d\mathbf{x}\, \rho_1(\mathbf{x}, \mathbf{x}')\Psi_i(\mathbf{x}) = N_i \Psi_i(\mathbf{x}) \tag{5.56}$$

Condensate wavefunction Ψ is the one corresponding to the largest eigenvalue N_i. The connection between the condensate wavefunction determined through Eq.(5.56) and the concept of the order parameter commonly used in the theory of superfluidity is a nontrivial problem according to Ref. [221].

The difference between Bose-fluids and superconductors is that because there was no need to go to pair field representation for the former, no temperature dependence is generated in the coefficients of the equation of motion at tree level when neglegting the initial correlations (it should be remembered that the propagators of the CPT formalism do carry the thermal signature even if the initial time $t_i = -\infty$, but the tree level derivation does not involve any propagators). Therefore, there is no 'double well' potential in variable $\langle\psi\rangle$ in the free energy (effective action) of the superfluids unlike in Eq. (5.44) for superconductors, even though there is spontaneous symmetry breaking. Another important difference [204] is that in front of the time derivative there is an imaginary unit in the Gross-Pitaevskii equation (nondissipative dynamics) whereas the Δ-field of superconductors evolves in real time (dissipative dynamics). This will be discussed in the next section.

5.8 Hydrodynamic balance equations for superfluids

To derive equations of motion for the mass and momentum densities of superconductors and weakly interacting Bose fluids we can try to gain some insight by considering the *microscopic* Lagrangian [222]

$$L = -\imath\hbar\psi^*\partial_t\psi + \frac{1}{2m}\Big[(\hbar\nabla - i(e/c)\mathbf{A})\psi\Big]^*\Big[(\hbar\nabla - i(q/c)\mathbf{A})\psi\Big] + qV\psi^*\psi \ , \tag{5.57}$$

where V is the external potential and q is the charge. Taking variation with respect to ψ^* produces Schrödinger's equation of motion. We can parametrize the wave function as $\psi = \sqrt{\rho}\, e^{\imath\theta}$, and rewrite the Lagrangian as

$$L = -\imath\hbar\partial_t\rho + \hbar\rho\partial_t\theta + \frac{1}{2m}\rho\Big(\hbar\nabla\theta - (q/c)\mathbf{A}\Big)^2 + \frac{\hbar^2}{2m}(\nabla\sqrt{\rho})\cdot(\nabla\sqrt{\rho}) + qV\rho \ . \tag{5.58}$$

Forming the Lagrange's equations of motion ($\delta L/\delta\rho = 0$ and $\delta L/\delta\theta = 0$) for the variables ρ and θ leads to the following pair of equatons

$$\begin{aligned} \partial_t\rho + \nabla\cdot(\rho\mathbf{v}) &= 0 \ ; & (5.59)\\ \hbar\partial_t\theta + mv^2/2 + p + qV &= 0 \ , & (5.60) \end{aligned}$$

where the velocity field $\mathbf{v} \equiv (\hbar\nabla\theta - (q/c)\mathbf{A})/m$ and $p \equiv \frac{\hbar^2}{2m}\frac{1}{\sqrt{\rho}}\nabla^2\sqrt{\rho}$ is interpreted as the pressure. Hitting on both equattions with ∇, they can be recast into

$$\begin{aligned} \partial_t\rho + \nabla\cdot(\rho\mathbf{v}) &= 0 & (5.61)\\ m(\partial_t\mathbf{v} + (\mathbf{v}\cdot\nabla)\mathbf{v}) &= q\mathbf{E} - (q/c)\mathbf{v}\wedge\mathbf{B} - \nabla p \ . & (5.62) \end{aligned}$$

To obtain the second equation have used the definition of $\mathbf{v}$, which allows us to write $\nabla v^2 = 2(\mathbf{v}\cdot\nabla)\mathbf{v} + 2\mathbf{v}\wedge(\nabla\wedge\mathbf{v}) = 2(\mathbf{v}\cdot\nabla)\mathbf{v} - 2q/(mc)\mathbf{v}\wedge\mathbf{B}$. The magnetic induction is $\mathbf{B} = \nabla\wedge\mathbf{A}$ and electric field $\mathbf{E} = -\nabla V - \partial_t\mathbf{A}/c$. Eq. (5.61) and Eq. (5.62) seem to form hydrodynamical balance equations of the 'electron fluid': The first equation looks like the conservation of mass equation and the second looks like the conservation of momentum equation, when the variables are identified as we have done.

The crucial point here is that the the mass and momentum conservation equations presented above are still microscopic, i.e. not coarse-grained. In the case of Bose fluids, the coarse-graining is readily done at tree level, so we can replace the basic fields in Eq. (5.58) by their expectation values ($\mathcal{A}[\langle\psi^*\rangle, \langle\psi\rangle] = \int dx\, L[\langle\psi^*\rangle, \langle\psi\rangle]$). However, the interpretation of the Madelung transformation becomes more difficult: For hydrodynamics it makes a difference if we write $\langle\psi\rangle = \langle\sqrt{\rho}\exp(\imath\theta)\rangle = \sqrt{\langle\rho\rangle}\exp(\imath\langle\theta\rangle)$. Even if ρ and θ degrees of freedom are independent, averaging the nonlinear functions in the mean-field manner does not necessarily lead to a consistent description. This fact is discussed for classical hydrodynamics in Chap. 9 (cf. also App. D.2.2). In fact, treating ρ and θ as expectation values of some operators $\hat{\rho}$ and $\hat{\theta}$ is approaching Landau's attempt of construction of quantum hydrodynamics [201], which was later on criticized by Feynman [222] for not taking into account the quantum indistinguishability of the particles. On the other hand, if we just decide to call $\langle\psi\rangle = \sqrt{\rho}\exp(\imath\theta)$, without any operator association for density and phase variables. Then, we can proceed as above and obtain the hydrodynamic equations (5.61) and (5.62) at the cost of loosing the possibility of being able to tell, what kind of microscopic field operators ρ and θ are made of.

To obtain the correct quantum hydrodynamic description we have a few options available. First, it is possible to construct the quantum mechanical operator equivalents of the conserved variables directly and then average their equations of motion. This approach is discussed in more detail in App. D.3. The disadvantage of this approach is not so easy to express the expectation values of nonlinear operator products in terms of the expectation values of mass, momentum and energy densities. The second option, where this is done automatically, is to use the nonequilibrium generating functional formalism and proceed via the Legendre transformation. Now the difficulty is transferred to the formation of the effective action functional. This is equivalent to the construction of the balance equations from time-dependent density functionals [120] as we have shown in Sect. 2.3.2. The fourth option is to use coupled cluster methods, whose cluster amplitudes are somewhat similar to our averaged macro observables. Arponen et al. have provided a detailed description of the non-dissipative superfluid hydrodynamics at zero temperature in Ref. [104].

In fact, there is no need to try to extract the hydrodynamic balance equations of conserved variables from the equations of motion of the order parameters as done in the beginning of Sect. 5.8. Both the order parameters and the conserved variables obey their own equations of motion, which is why we have kept them separate in our general expression for the generating functional (Eq. (2.22) and Eq. (2.23)). For Bose fluids we should have also added the conserved momentum and mass density terms in the evolution operator by introducing additional source terms. Now Eq. (5.51) for the generating functional only contains the order parameter of the theory. Of course, there is nothing wrong with developing the equation of motion for the order parameter alone: The fact that the interactions and fluctuations will be correctly taken into account in the averaging process of the Legendre transformation even for 'incomplete set of macrovariables' is of course one of the beautiful features of the generating functional formalism. However, the physical interpretation might be easier, albeit technically more involved, if one uses both conserved and symmetry broken variables in the formulation of the macro dynamics.

The problems in trying to extract hydrodynamic equations for number and momentum densities become clearer if we try to use the Lagrangian (effective action) of the superconductor (5.44) instead of the the superfluid Lagrangian. The difference is that the time derivative term in Eq. (5.44) does not contain imaginary time unit. Consequently, proceeding just like in the superfluid case, the momentum balance equation will have the same form as in Eq. (5.60), corresponding to nondissipative momentum flow (only the normal current experiences dissipation) but in the number density equation there is an extra imaginary factor in front of the time derivative, which is unphysical. As far as the identification of the probability current (momentum current) $\mathbf{j}$ determined from the microscopic Schrödinger equation,

$$\mathbf{j} \equiv \frac{1}{2m}\left\{\psi^*(-\imath\hbar\nabla - (q/c)\mathbf{A})\psi + \left[(-\imath\hbar\nabla - (q/c)\mathbf{A})\psi\right]^*\psi\right\} \ , \tag{5.63}$$

can be associated with the macroscopic electric current $\mathbf{j}_{GL}$ determined from the Ginzburg-Landau effective action, the two seem to match when setting $e\mathbf{j} = \mathbf{j}_{GL}$, $q = 2e$ and replacing ψ by Δ. However, there is another inconsistency present already in the forms of the effective actions (Lagrangians) of Eq. (5.57) and Eq. (5.44). Leaving out the gauge terms, we see that the superconductor action contains a term $|\Delta|^4$, which is required for the stability of the equilibrium condensate density. When using Eq. (5.57) to form the equations of motion, the stabilizing term must be put in by hand [222].

To summarize, Eq. (5.44) and Eq. (5.52) are valid descriptions for generation of order parameter dynamics. When trying to extract information from the conserved quantities (or other relevant variables) by using nonlinear transformations like

$$\Delta = \sqrt{\rho}\exp(\imath\theta) \ , \tag{5.64}$$

one should be carefull. Eq. (5.64) should be seen as transformation into Goldstone coordinate representation. It should not be seen as mapping between the order parameter and other relevant variables $(\rho, \mathbf{v})$ except in some special cases: θ turns out to be the analogy of the (compactified) velocity potential for superfluids and superconductors. Then we are making no other implications than saying that the order parameter has a well-defined magnitude χ and phase θ. When extracting the low energy effective action for variable θ it is possible to show the complete equivalence [215, 223] of the two descriptions despite the fact that Eq. (5.52) contains the imaginary factor in front of the time derivative and Eq. (5.44) does not.

Chapter 6

Density Functional Theory

The purpose of this chapter is to give some background information on techniques, which enable the construction of the density functional which is another name for the free energy functional of an inhomogeneous system. The relevance of the free energy functional can be seen to arise from the dynamics: The time evolution of an equilibriating system should be designed in such a way that we get relaxation to Gibb's equilibrium state governed by the probability weight

$$\frac{1}{Z}\exp(-\beta F[\phi]) \ , \tag{6.1}$$

where the normalization constant Z is the equilibrium partition function. The precise way in which F appears in the equations of motion is discussed more throughly in Chap. 7 and Chap. 9 which address dynamics related questions. In this chapter we concentrate only on the static properities and construct the free energy functional F using different approaches.

In Sect. 6.3 we coarse-grain the free energy from the partition function and compare the result with another derivation based on the Legendre technique presented in Sect. 2.3.3. The third method for obtaining free energy functionals, which is very powerful, is the classical density functional theory. It is the main focus of this chapter. Classical DFT has a long history and therefore many results and approximations can be directly borrowed from the literature. We also point out the similarities in the traditional formulations of the classicical and quantum density functional theories (Sect. 6.2), which might have been blurred to some extent due to the fact that they have been developed as separate theories. In particular, the quantum DFT makes little reference to its 'thermodynamic roots' (Mermin [108]) in its traditional exposition [224] being a zero temperature theory. The time dependent density functional theory TDFT will not be discussed in this section as we have already covered the topic in Sect. 2.3. For numerical techniques on computation of the free energy one can consult e.g Refs. [225, 226]. Experimental construction of the free energy functional [5] is based on the knowlegde of the 2-point function (structure factor). That is briefly discussed in the context of the phase-field modeling in Chap. 7.

6.1 Quantum and classical density functional theories

We review some basic relations and results of density functional theory below to complement the material presented in Sect. 2.3.1. We will not discuss the practical implementation of the computational program but rather concentrate on those ideas from the litrature, which display the similarity aspects of quantum and classical theories [227].

6.1.1 Quantum density functional theory

The basic idea of density functional theory is get rid of the many-body nature of the underlying Hamiltonian description and replace the large number of entries $\{\mathbf{x}_i\}$ $(i = 1, \dots N)$, which are the single electron coordinates of the Schröedinger wave function, with a density function $n(\mathbf{x})$. The procedure is thus similar to the (quantum or classical) derivation of Boltzmann's transport equation [16] from Liouville's many-body description in the sense that instead of many position coordinates $\mathbf{x}_i$ one uses the reduced density matrix with single entry $\mathbf{x}$ to describe some aspects of dynamics. In contrast, the density functional theory originally concentrated only on the static ground state properties of many-electron systems. Density functional theory is a coarse-grained theory in the sense that the spatial information encoded in the many-body ground state wave function cannot be recovered from the electron density alone.

Let us now describe some of the basic concepts of the theory. First, we define the Hamiltonian H to be a sum of three contributions,

$$H = T + U + V \ . \tag{6.2}$$

The second quantized representation of the kinetic energy T, one-body potential V and two-body potential U are:

$$\begin{aligned} T &\equiv \int d\mathbf{x}\, \psi^\dagger(\mathbf{x}) \Big(-\frac{\hbar^2}{2m_e}\nabla^2 \Big) \psi(\mathbf{x}) \ ; && (6.3) \\ U &\equiv \frac{1}{2}\int d\mathbf{x} \int d\mathbf{x}'\, \psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')\, \frac{e^2}{|\mathbf{x}-\mathbf{x}'|}\, \psi(\mathbf{x}')\psi(\mathbf{x}) \ ; && (6.4) \\ V &\equiv \int d\mathbf{x}\, \psi^\dagger(\mathbf{x})\, V_{ext}(\mathbf{x})\, \psi(\mathbf{x}) \ , && (6.5) \end{aligned}$$

where m_e is the mass of the electron and e is its charge. The density of electrons in the ground state $|\Psi\rangle$ is

$$n_0(\mathbf{x}) \equiv \langle\Psi|\psi^\dagger(\mathbf{x})\psi(\mathbf{x})|\Psi\rangle \ . \tag{6.6}$$

Clearly, n_0 is a functional of the external one-body potential V_{ext}. Conversely, we can regard V_{ext} as a unique functional of the density n_0. Fixing V_{ext} fixes the form of the Hamiltonian H and thereby its ground state $|\Psi\rangle$. Thus, the ground state energy can be seen to be a functional of n_0 as shown by Hohenberg and Kohn [224]:

$$E_V[n_0] = \langle\Psi|H|\Psi\rangle = \int d\mathbf{x}\, V_{ext}(\mathbf{x})\, n_0(\mathbf{x}) + F[n_0] \ , \tag{6.7}$$

where $F[n_0] \equiv \langle\Psi|T + U|\Psi\rangle$ is a universal functional, which does not depend on the chosen V_{ext}. As a matter of fact, Eq. (6.7) can be seen as a Legendre transformation for the pair of variables (V_{ext}, n_0), which is the reason for writing $E_V[n_0]$ instead of $E[n_0]$. It has become customary to separate out the long range Coulomb energy and rewrite

$$F[n_0] = \frac{e^2}{2}\int \frac{n_0(\mathbf{x})n_0(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} + G[n_0] \ , \tag{6.8}$$

which specifies another universal functional $G[n_0]$. Its explicit representation in terms of one-particle density matrix, $\rho_1(\mathbf{x},\mathbf{x}') \equiv \langle\Psi|\psi^\dagger(\mathbf{x})\psi(\mathbf{x}')|\Psi\rangle$, and pair correlation function $g^{(2)}$ reads

$$G[n_0] = \frac{\hbar^2}{2m_e}\int d\mathbf{x}\,\nabla_x\nabla_{x'}\rho_1(\mathbf{x},\mathbf{x}',[n_0])|_{\mathbf{x}=\mathbf{x}'} + \frac{e^2}{2}\int d\mathbf{x}d\mathbf{x}'\,\frac{n_0(\mathbf{x})n_0(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}\,g^{(2)}(\mathbf{x},\mathbf{x}',[n_0])\ . \quad (6.9)$$

The form of the pair correlation function will be derived in Sect. 6.2. The full energy functional becomes

$$E_V[n_0] = \int d\mathbf{x}\,V_{ext}(\mathbf{x})\,n_0(\mathbf{x}) + \frac{e^2}{2}\int\frac{n_0(\mathbf{x})n_0(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} + G[n_0] \quad (6.10)$$

Since the correlation function depends on expectation values of products of density matrices, we are facing a similar hierarchy problem as in the case of the so-called Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy [220], which expresses lower order reduced distribution functions in terms of higher order ones. Eq. (6.10) can be generalized for any density n

$$E_V[n] = \int d\mathbf{x}\,V_{ext}(\mathbf{x})\,n(\mathbf{x}) + \frac{e^2}{2}\int\frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} + G[n] \quad (6.11)$$

When $n = n_0$, the functional $E_V[n]$ reaches its minimum value which correponds to the ground state energy [224]. The search of the ground state can thus be converted into a minimization problem of the density functional $E_V[n]$.

The generalization of the ground state formalism to finite temperatures is rather straightforward [108]. One basically needs to replace the ground state expection values with thermal averages and consider free energy (which includes entropic effects) instead of plain energy. The equilibrium density n_0 is now defined as the thermal average over distribution ρ_0:

$$n_0(\mathbf{x}) \equiv \langle\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\rangle_0 \equiv \mathrm{Tr}\{\rho_0\,\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\}\ . \quad (6.12)$$

The grand canonical density matrix ρ_0 is defined as

$$\rho_0 \equiv \frac{1}{Z}\,e^{-\beta(H-\mu N)}\ , \quad (6.13)$$

and $Z \equiv \mathrm{Tr}\{\exp(-\beta(H-\mu N))\}$. In order to obtain a functional minimization problem similar to the ground state formalism, we define the functional $\Omega[\rho]$ for arbitrary density matrix ρ:

$$\Omega[\rho] \equiv \mathrm{Tr}\{\rho\,(H-\mu N+\beta^{-1}\ln\rho)\}\ , \quad (6.14)$$

where $H = T+U+V$. Arbitrary ρ here means that it has the same grand canonical form as ρ_0 but the external potential V_{ext} will differ from that of ρ_0. When $\rho = \rho_0$, Eq. (6.14) gives the equilibrium grand potential $\Omega = -k_BT\ln Z$. Because to each

$$n(\mathbf{x}) \equiv \mathrm{Tr}\{\rho\,\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\}\ , \quad (6.15)$$

there is a unique $V_{ext}(\mathbf{x})$, which determines the density matrix $\rho[V_{ext}]$, we can say that the entire N-body density matrix ρ is a functional of $n(\mathbf{x})$. Then, for the particular case $\rho = \rho_0$, Eq. (6.14) gives

$$\Omega[\rho_0] \equiv \Omega_V[n_0] = \int d\mathbf{x}\,V_{ext}(\mathbf{x})\,n_0(\mathbf{x}) + F[n_0] - \mu\int d\mathbf{x}\,n_0(\mathbf{x})\ , \quad (6.16)$$

which is the thermal analogue of Eq. (6.7). The universal functional $F[n_0]$ is defined as

$$F[n_0] = \mathrm{Tr}\{\rho_0\,(T + U + \beta^{-1}\ln\rho_0)\}\ . \tag{6.17}$$

In the finite temperature case Eq. (6.8) has exactly the same form also. The only difference is that thermal averages should be taken when calculating ρ_1 and $g^{(2)}$. For general density n, which does not correspond to the external potential V_{ext} associated with n_0, Eq. (6.16) becomes

$$\Omega_V[n] = \int d\mathbf{x}\, V_{ext}(\mathbf{x})\, n(\mathbf{x}) + F[n] - \mu\int d\mathbf{x}\, n(\mathbf{x})\ , \tag{6.18}$$

This can be seen in the following way: Separating out the term $\int d\mathbf{x}\,\psi^\dagger(\mathbf{x})V_{ext}(\mathbf{x})\psi(\mathbf{x})$ from the Hamiltonian H in Eq. (6.14) and tracing over the non-equilibrium density matrix ρ (Eq. 6.15) gives immediately rise to the first term on the right hand side of Eq. (6.18). Similar arguments can be applied to the chemical potential term. Furthermore, owing to the universality of the functional F its form stays the same no matter what density matrix we use. Therefore we can directly replace $F[n_0]$ by $F[n]$. As we will see in the next section, Eq. (6.16 – 6.18) will can be used directly in the classical regime as well.

6.1.2 Classical density functional theory

In the classical regime we replace the quantum mechanical trace by summation over classical degrees of freedom. Thus, the defining equation Eq. (6.14) stays the same but

$$\mathrm{Tr}_{cl} \equiv \sum_{N=0}^{\infty} \frac{1}{h^{3N}N!}\int d\mathbf{x}_1\ldots d\mathbf{x}_N\int d\mathbf{p}_1\ldots d\mathbf{p}_N \tag{6.19}$$

The other definitions are the same as in the quantum mechanical case. The N-body Hamiltonian is a sum of three pieces: $H = T + U + V$, where

$$T \equiv \sum_{i=1}^{N}\frac{p_i^2}{2m}\quad ;\quad U \equiv U(\mathbf{x}_1,\ldots,\mathbf{x}_N)\quad ;\quad V \equiv \sum_{i=1}^{N} V_{ext}(\mathbf{x}_i)\ , \tag{6.20}$$

The interaction potential U can contain m-body ($m > 2$) interaction terms, too. There is nothing that would have stopped us from using higher order than two-body interaction terms in the quantum mechanical case either. Their presence leads to appearance of higher order correlation functions in the functional G in Eq. (6.9). The functional Ω_V is defined [228] as in Eq. (6.14)

$$\Omega[\rho] \equiv \mathrm{Tr}_{cl}\{\rho\,(H - \mu N + \beta^{-1}\ln\rho)\}\ , \tag{6.21}$$

The average density for distribution ρ is $n(\mathbf{x}) \equiv \mathrm{Tr}_{cl}\{\rho\sum_{i=1}^{N}\delta(\mathbf{x}-\mathbf{x}_i)\}$. In terms of n, we can cast Eq. (6.21) into the follwing form:

$$\Omega[\rho] \equiv \Omega_V[n] = \int d\mathbf{x}\, V_{ext}(\mathbf{x})\, n(\mathbf{x}) + F[n] - \mu\int d\mathbf{x}\, n(\mathbf{x})\ , \tag{6.22}$$

which is just the same as the quantum equation (6.18). The minimization property of the density functional is now conviniently expressed as

$$\left.\frac{\delta\Omega_V[n]}{\delta n(\mathbf{x})}\right|_{n_0} = 0\ . \tag{6.23}$$

As in the quantum case, the equilibrium density n_0 satisfies $\Omega_V[n_0] = \Omega$, where Ω is the equilibrium grand potential. As will be discussed in Sect. 6.1.3 and Sect. 7.4, the functional F appearing in Eq. (6.22) can be called the intrinsic (Helmholtz) free energy. When the inhomogenous field is added, we get the total (Helmholtz) free energy F_V, which can be seen as the functional Legendre transformation of the intrinsic one:

$$F_V[n] \equiv F[n] + \int d\mathbf{x}\, V_{ext}(\mathbf{x})\, n(\mathbf{x}) \ . \tag{6.24}$$

Using Eq. (6.23) together with (6.22), we can define analogously the concept of intrinsic chemical potential $\mu_{in} \equiv \delta F[n]]/\delta n(\mathbf{x})$. It satisfies

$$V_{ext}(\mathbf{x}) + \mu_{in}[n_0] = \mu \ . \tag{6.25}$$

Hence, the $\mathbf{x}$-dependence of $\mu_{in}(\mathbf{x})$ must exactly cancel that of $V_{ext}(\mathbf{x})$ in order for the global chemical potential μ to be a constant.

Let us now derive some explicit representaions of $F[n]$ which will be utilized in the subsequent sections. The simplest many-body system is the ideal gas with no interactions: $U = 0$. The intrinsic free energy becomes $\beta F_{id}[n] = \int d\mathbf{x}\, n(\mathbf{x})[\ln(\lambda_T^3 n(\mathbf{x})) - 1]$, where λ_T it the thermal wavelength. Depending on the system under study, one usually separates the free energy (and other functionals) into two parts,

$$F = F_{ref} + \Delta F_{ref} \ . \tag{6.26}$$

The first contribution to F on the right hand side is the reference free energy of a system, whose properties are well-known. For example, approximating a weakly interacting system by the ideal one, we would set $F_{ref} = F_{id}$ Then the effect of the particle interactions would be in ΔF. In terms of the decomposition (6.26) the intrinsic chemical potential becomes

$$\beta\mu_{in}[n] \equiv \beta\frac{\delta F[n]}{\delta n(\mathbf{x})} = \frac{\delta F_{id}[n]}{\delta n(\mathbf{x})} + \frac{\delta \Delta F_{id}[n]}{\delta n(\mathbf{x})} = \ln(\lambda_T n(\mathbf{x})) - c(\mathbf{x}, [n]) \ , \tag{6.27}$$

where $c(\mathbf{x}, [n]) \equiv -\delta\Delta F_{id}[n]/\delta n(\mathbf{x})$ is the so-called direct correlation function, which contains the effect of interactions. It will be made use of later on in Sect. 7.4.

With attractive interactions present, one obtains in many cases [229] a more accurate pertubative result for $F[n]$ if one separates out the hard-core repulsive part of the potential and sets $F_{ref} = F_{HS}$, where F_{HS} is the hard sphere reference free energy [230]. Assuming for simplicity that the interaction potential $U = \sum_{i<j} u(x_{ij})$ consists of pair potentials only, the grand potential Ω_V can be seen as a functional of $u(x_{ij})$. By varying the pair potentials, while keeping the one-body potential $V = \sum_i V_{ext}(\mathbf{x}_1)$ fixed, we obtain

$$\begin{aligned} \delta F = -k_B T\, \delta \ln Z &= \frac{1}{Z}\sum_{N=0}^{\infty} \frac{\lambda^N}{\lambda_T^{3N} N!} \int d\mathbf{x}_1 \ldots d\mathbf{x}_N\ e^{-\beta(U+V)} \sum_{i<j} \delta u(x_{ij}) & (6.28) \\ &= \frac{1}{2}\int d\mathbf{x}_1 \int d\mathbf{x}_2\, \rho^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \delta u(x_{12}) \ , & (6.29) \end{aligned}$$

where $\lambda \equiv e^{\beta\mu}$ is the fugacity. Using the symmetries of the summand we expressed the variation in terms of the pair distribution function $\rho^{(2)}$ on the second line. Thus,

$$\frac{\delta F}{\delta u(x_{12})} = \frac{1}{2}\rho^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \ . \tag{6.30}$$

The variational equation (6.30) can be solved by a process called functional integration (not to be confused with the usual meaning of path integral). Depending on the way one chooses to parametrize the variation, the end results seem a bit different superficially [229, 231, 230]. Here we define the following test system potential:

$$u_\alpha(x_{12}) \equiv u_0(x_{12}) + \alpha u_1(x_{12}) \ , \tag{6.31}$$

where $0 \leq \alpha \leq 1$. For $\alpha = 0$ the potential of the test system is just the reference potential u_0. When α reaches value one, the test system potential has become the full interaction potential of the system under study $u_{\alpha=1} = u = u_0 + u_1$. Solution of Eq. (6.30) reads

$$F[n] = F_0[n] + \frac{1}{2}\int_0^1 d\alpha \int d\mathbf{x}_1 \int d\mathbf{x}_2 \ \rho^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \alpha)\, u_1(x_{12}) \ . \tag{6.32}$$

By restricting the variation $\delta u = \delta u_1$ it is easy to see through functional differentiation that Eq. (6.30) is reproduced. Eq. (6.32) is exact but useless unless we can compute $\rho^{(2)}([u_\alpha])$. In the so-called Random Phase Approximation (RPA) one ignores all the correlations between the particles and replaces $\rho^{(2)} \approx n(\mathbf{x}_1)n(\mathbf{x}_2)$, which leads to

$$F[n] \approx \int d\mathbf{x}_1\, f_{HS}(n(\mathbf{x}_1)) + \frac{1}{2}\int d\mathbf{x}_1 \int d\mathbf{x}_2 \ n(\mathbf{x}_1)n(\mathbf{x}_2)\, u_1(x_{12}) \ . \tag{6.33}$$

We have also used the Local Density Approximation (LDA) in setting the replacing the homogeneous argument of the hard sphere fluid reference free energy with spatially dependent density $n(\mathbf{x})$. This is the simplest approximation one can think of but it seems to work reasonably well for the situations which we will be considering later on.

6.1.3 Formal similarity and Wigner's representation

The question we are posing now, is whether the quantum and classical density functional approaches can both be represented in a unified form, which allows for the use of the Legendre trasformation technique? The positive answer is to be found in Sect. 2.4 The concept, which in the current literature is known by the name v-representablility [51], has probably become more well-known to the general audience in the context of quantum density functional theory. It allows to expresse the density and the external potential v as unique functionals of each other. This property facilitates the emergence of the expectation values of the density to appear in the functional F as we have seen above. Thus the intrinsic free energy F and the total free energy F_V can be seen as generalized thermodynamic potentials. Indeed,

$$F_V[n[V_{ext}]] = F[n[V_{ext}]] + \int d\mathbf{x}\, V_{ext}(\mathbf{x})\, n(\mathbf{x}, [V_{ext}]) \ , \tag{6.34}$$

Going from variable n to conjugate variable V_{ext} is easy. They are related through

$$n(\mathbf{x}, [V_{ext}]) = \frac{\delta F_V}{\delta V_{ext}(\mathbf{x})} \tag{6.35}$$

In the previous sections we have presented a few possibilities to construct these functionals. To add to the selection we now present an alternative way of constructing the free energy functionals, which makes direct contact with the usual equilibrium formulation of statistical mechanics, and can be even extended to cover the non-equilibrium phenomena as discussed in

Chap. 2. Moreover, the extension to other types of theories, which make use of more complicated variables than single particle densities, is very transparent in the new formulation. As we pointed out in Sect. 2.3, both the ground state and finite temperature density functional theories can be derived from the following generating functional $W(J)$:

$$e^{-\beta W[J]} \equiv Z[J] \equiv \mathrm{Tr}\left\{ e^{-\beta\hat{H}+J\hat{Q}} \right\} \ , \tag{6.36}$$

where $\hat{H} = \hat{T} + \hat{U}$ is the many-body Hamilton's operator consisting of kinetic term and interactions. Note that V_{ext} whose only function is to transmit the v-representability condition is not needed, its role is played by the source field J. The quantum density functional theory is generated by choosing the operator

$$\hat{Q} = \hat{n}(\mathbf{x}) = \psi^\dagger(\mathbf{x})\psi(\mathbf{x}) \ . \tag{6.37}$$

Once $Z[J]$ is known, it is straightforward to obtain the density functional via the Legendre transformation:

$$F[n] = W[J] - \int d\mathbf{x} J(\mathbf{x}) n(\mathbf{x}) \ . \tag{6.38}$$

It is important to notice that $F[n]$ is truly a function of the expectation value of $\hat{n}$. Eq. (6.38) should be compared with Eq. (6.24) with F_V replaced by $W[J]$ and V_{ext} by J. In the classical case we cannot unfortunately just add a source term of the same form as in the quantum case to the Hamiltonian:

$$J\hat{Q} = \int d\mathbf{x}\, J(\mathbf{x})\hat{n}(\mathbf{x}) \ . \tag{6.39}$$

Trying the same in the classical case will not work because integral expressions of the form $\int d\mathbf{x}J(\mathbf{x})n(\mathbf{x})$ cannot appear in the classical Hamiltonian of point particles. Thus, one is naturally led to formulate the Legendre transformation using a local potential $V_{ext}(\mathbf{x}_i)$ which just takes us back to the classical starting point. To overcome this problem we propose to use the mapping presented in Sect. 2.4. The second quantization representation of Doi [3] enables us to write the following generating functional for a classical system

$$Z_{cl}[J] = \langle 0| e^{-\beta\hat{H}'_{cl}+J\hat{Q}} |0\rangle = \mathrm{Tr}\left\{ e^{-\beta\hat{H}'_{cl}+J\hat{Q}}\, |0\rangle\langle 0| \right\} \tag{6.40}$$

where the 'shifted' second quantized classical Hamiltonian $\hat{H}'_{cl}(\psi^\dagger, \psi) \equiv \hat{H}_{cl}(\psi^\dagger + 1, \psi)$, and

$$\begin{aligned} \hat{H}_{cl} = & \int d\mathbf{x}_1 \int d\mathbf{p}_1\ \psi^\dagger(\mathbf{x}_1, \mathbf{p}_1)\, \frac{p_1^2}{2m}\, \psi(\mathbf{x}_1, \mathbf{p}_1) \\ & + \frac{1}{2}\int d\mathbf{x}_1 \int d\mathbf{p}_1 \int d\mathbf{x}_2 \int d\mathbf{p}_2\ \psi^\dagger(\mathbf{x}_1, \mathbf{p}_1)\psi^\dagger(\mathbf{x}_2, \mathbf{p}_2)\, u(\mathbf{x}_1 - \mathbf{x}_2)\, \psi(\mathbf{x}_1, \mathbf{p}_1)\psi(\mathbf{x}_2, \mathbf{p}_2) \end{aligned} \tag{6.41}$$

The remarkable thing is that this method allows the construction of the density functional (or more generally, free energy functional in any variables, not just particle density) for *any* classical point particle system where the interaction forces are known. Higher order than pair potentials can naturally be included.

Owing to the similarity, of the expressions $Z[J]$ and $Z_{cl}[J]$ one is tempted to ask whether there it is possible to coarse-grain the quantum mechanical generating functional and obtain the classical one. The differences between Eq. (6.36) and Eq. (6.40) are the following: First, Z_{cl} is the vacuum-to-vacuum expectation value whereas Z has trace over all states. In the path integral representation this only sets an extra constraint for the boundary values of the fields when computing Z_{cl}. Second, the field operators of $\hat{H}_{cl}$ have both $\mathbf{x}$ and $\mathbf{p}$ as their arguments. Moreover, in the classical case they are commuting numbers, not operators. But this is exactly what one would expect from a coarse-grained model: When the coarse-graining cell size grows big enough, the cell averaged operators $\langle\hat{\mathbf{x}}\rangle_{cell}$ and $\langle\hat{\mathbf{p}}\rangle_{cell}$ start approaching their classical counterparts (numbers $\mathbf{x}$ and $\mathbf{p}$), which commute. At the level of density matrices ($\hat{\rho} \propto \exp(\hat{H} + J\hat{Q})$) one expects that when averaging over cells $\Delta\mathbf{x}\,\Delta\mathbf{p}$ much larger than $(2\pi\hbar)^3$ the classical density matrix should emerge [186]. Using Wigner representation of the single particle density matrix ρ_W as an example, it is possible to show [232] that

$$\int\limits_{\Delta\mathbf{x}\Delta\mathbf{p}} d\mathbf{x}d\mathbf{p}\,\rho_W(\mathbf{x},\mathbf{p}) = \int\limits_{\Delta\mathbf{x}\Delta\mathbf{p}} d\mathbf{x}d\mathbf{p}\,\rho_{cl}(\mathbf{x},\mathbf{p}) + \mathcal{O}\left(\frac{(2\pi\hbar)^2}{\Delta\mathbf{x}\Delta\mathbf{p}}\right) \tag{6.42}$$

It remains to be seen if the second quantized generating functional description makes it any easier in practice to cross the quantum-classical boundary for some simple systems at least. It sort of reverses the task: Instead of trying to represent the quantum system in classical kind of form using the Wigner representation, one can cast the classical system in a quantum form using Doi's second quantized notation.

6.2 Multi-component density functional theory

This section generalizes the concept of density functional for several interacting particle species, which is important for some later developements of our formalism. Just as in the case of single component density functional theory, it is advantageous to decompose the pairwise additive intermolecular potential as

$$V_{ij} = V_{ij}^R + \lambda V_{ij}^A\ . \tag{6.43}$$

The first term on the right is the interaction of the reference system (typically hard sphere fluid) and the second contains the attractive part of the potential. The perturbation parameter λ describes the deviation of the system from the noninteracting case $\lambda = 0$. For $\lambda = 1$, the interaction potential V_{ij} has become that of the system of interest (p. 462, Ref. [230]). Correspondingly, the free energy of the system is

$$F = F^R + F^A\ , \tag{6.44}$$

where the free energy of the reference system can be further decomposed into the free energy of the ideal noninteracting system (ideal gas) F^I and the excess free energy F^E arising from the interactions of the molecules of the reference system: $F^R = F^I + F^E$. The ideal gas part,

$$F^I = k_B T \sum_i \int d\mathbf{x}\,\phi_i(\mathbf{x})\ln(\phi_i(\mathbf{x}))\ . \tag{6.45}$$

There are many ways of obtaining an expression for F^E [229, 233] Analogously to the local density approximation of the exchange energy of quantum case (Sect. 6.1.1), one can define (weighted) local density apporximation [234]:

$$F^E = k_B T \int d\mathbf{x}\,\phi(\mathbf{x}) f_{ex,u}(\bar{\phi}_i(\mathbf{x}))\ , \tag{6.46}$$

where $\phi(\mathbf{x}) \equiv \sum_i \phi_i(\mathbf{x})$ is the total density and $f_{ex,u}$ is the excess free energy per particle in a uniform fluid taken at some weighted density $\bar{\phi}_i(\mathbf{x})$. The excess free energy $f_{ex,u}$ is assumed to be a known for any value of density. If we set $\bar{\phi}_i(\mathbf{x}) = \phi_i(\mathbf{x})$, we obtain the normal LDA approximation. Details on how to choose $\bar{\phi}_i$ and modifications of WDA can be founs in Ref. [229]. Finally,

$$F^A = \frac{1}{2}\sum_{ij} \int_0^1 d\lambda \int d\mathbf{x} \int d\mathbf{x}'\, \phi_i(\mathbf{x})\phi_j(\mathbf{x}')g_{ij}^{(2)}(\mathbf{x},\mathbf{x}',\lambda)V_{ij}(|\mathbf{x}-\mathbf{x}'|) \ . \tag{6.47}$$

This is an exact representation of the free energy contibution due to the attractive part of the interaction potential. Still, the non-trivial task of finding out the form of the pair correlation function g_{ij} for arbitraty λ remains. Finally, the grand potential is given by the Legrande transformation:

$$\Omega[\{\phi_i\}] = F[\{\phi_i\}] - \sum \int d\mathbf{x}\, \mu_i \phi_i(\mathbf{x}) \ , \tag{6.48}$$

where the chemical potentials of the ith particle species is denoted by μ_i.

To point out the analogy to the quantum mechanical case, let us quote the corresponding results of the two-component density functional theory of two fermion species (electrons and positrons) with densities n_+ and n_-. The total energy (not free energy) of the system is given by [235]:

$$E[n_-,n_+] = E_s[n_-] + E_s[n_+] + \int d\mathbf{x}\, V_{ext}(\mathbf{x})[n_-(\mathbf{x}) - n_+(\mathbf{x})] - V_{-+}^C + E_c^{e-p}[n_-,n_+] \ , \tag{6.49}$$

where V_{ext} is an external potential and E_c^{e-p} is the electron-positron correlation energy. Coulombic interaction energy functional is given by

$$V_{ij}^C \equiv \int d\mathbf{x} \int d\mathbf{x}'\, \frac{n_i(\mathbf{x})n_j(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \ , \tag{6.50}$$

where $i,j = +/-$. The single component energy functional E_s in Eq. (6.49) consists of the following pieces:

$$E_s[n_i] \equiv T[n_i] + \tfrac{1}{2}V_{ii}^C + E_{xc}[n_i] \ . \tag{6.51}$$

The kinetic energy of the non-interacting electrons or positrons is denoted by $T[n_\pm]$ and the exhange-correlation energy of single particle species is E_{xc}. The exchange-correlation contains both the effect of caused by the mixing of basis orbitals of the ground state wave function ansatz (exchange) and the so-called correlation energy. The latter contains all the effects which go beyond the Hartree-Fock approximation such that when summed up with the kinetic, Coulobic and exchange contributions the exact ground state energy E_s is obtained. There is no electron-positron exchange term present in Eq. (6.49) because the different species are distinguishable from each other and the Slater determinant ground state wave function ansatz does not mix basis states of the two species. But the correlation energy E_c^{e-p} is still needed in order to get the correct ground state energy of a system with interacting electrons and positrons. As stated above, the correlation energies E_c^{e-e} and E_c^{p-p} are hidden in the terms $E_{xc}[n_-]$ and $E_{xc}[n_+]$, respectively.

Let us see how far the analogous structure of the quantum and classical theories goes. Leaving out the kinetic energy, which is only present in the classical formulation through de Broglie wavelength, we can see that the external potential $V_{ext}(\mathbf{x})$ of the quantum theory plays the role of an inhomogeneous chemical potential in the classical case. The exchange-correlation energy can be represented as [51] (pp. 184-185)

$$E_{xc}[n_i] = \frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\, n_i(\mathbf{x})V(\mathbf{x},\mathbf{x}')n_i(\mathbf{x}')\int_0^1 d\lambda\left(g_{ii}^{(2)}(\mathbf{x},\mathbf{x}',\lambda,[n]) - 1\right) , \tag{6.52}$$

where g_{ii} is the pair correlation function of the system (p. 158, Ref. [51]). Although this result seems very nontrivial at first sight, it is a straightforward consequence of the second quantization and parametric perturbation similar to the classical case as shown below. We assume that the reference system consists just of non-interacting particles in an external potential v_λ. The parameter λ determines the strength of the two-body forces:

$$\hat{H}_\lambda = \hat{T} + \sum_\alpha \int d\mathbf{x}\, v_\lambda(\mathbf{x})\hat{\psi}_\alpha^\dagger(\mathbf{x})\hat{\psi}_\alpha(\mathbf{x}) + \frac{\lambda}{2}\sum_{\alpha\beta}\int d\mathbf{x}\int d\mathbf{x}'\, V(\mathbf{x},\mathbf{x}')\,\hat{\psi}_\alpha^\dagger(\mathbf{x})\hat{\psi}_\beta^\dagger(\mathbf{x}')\hat{\psi}_\beta(\mathbf{x}')\hat{\psi}_\alpha(\mathbf{x}) . \tag{6.53}$$

The spin index $\alpha = \pm$. The values of the parameter λ are restricted to range $0 \le \lambda \le 1$. The external potential $v_\lambda(\mathbf{x})$ is chosen in such a way [51] that the ground state density $n(\mathbf{x})$ is independent of λ:

$$n(\mathbf{x}) = n_\lambda(\mathbf{x}) \equiv \langle\Psi_\lambda|\hat{n}(\mathbf{x})|\Psi_\lambda\rangle , \tag{6.54}$$

where $\sum_\alpha \hat{\psi}_\alpha^\dagger(\mathbf{x})\hat{\psi}_\alpha(\mathbf{x}) \equiv \hat{n}(\mathbf{x})$ is the density operator. The ground state wave function of the test system is denoted by $|\Psi_\lambda\rangle$. When $\lambda = 1$, the Hamiltonian $\hat{H}_\lambda$ of the test system becomes that of the true system $\hat{H}$: $\hat{H}_{\lambda=1} = \hat{H}$. Thus, $v_{\lambda=1}(\mathbf{x}) = v(\mathbf{x})$ is the prescribed external potential and $v_{\lambda=0}(\mathbf{x}) = v(\mathbf{x}) + v_H(\mathbf{x}) + v_{xc}(\mathbf{x})$ is by definition the effective Kohn-Sham potential. Differentiation of the ground state energy of the test system with respect to λ can be computed using the Hellman-Feynman theorem:

$$\frac{dE(\lambda)}{d\lambda} = \langle\Psi_\lambda|\,\frac{\partial\hat{H}_\lambda}{\partial\lambda}\,|\Psi_\lambda\rangle \tag{6.55}$$

$$= \frac{\partial}{\partial\lambda}\int d\mathbf{x}\, v_\lambda(\mathbf{x})n(\mathbf{x}) + \frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\, V(\mathbf{x},\mathbf{x}')n(\mathbf{x})n(\mathbf{x}')g^{(2)}(\mathbf{x},\mathbf{x}',\lambda,[n]) , \tag{6.56}$$

where we have made use of the definition (6.54) and the fact that the pair correlation function can be related to the expectation values of the field operators in the following manner:

$$\sum_{\alpha\beta}\langle\Psi_\lambda|\hat{\psi}_\alpha^\dagger(\mathbf{x})\hat{\psi}_\beta^\dagger(\mathbf{x}')\hat{\psi}_\beta(\mathbf{x}')\hat{\psi}_\alpha(\mathbf{x})|\Psi_\lambda\rangle = \langle\Psi_\lambda|\hat{n}(\mathbf{x})\hat{n}(\mathbf{x}') - \delta(\mathbf{x}-\mathbf{x}')\hat{n}(\mathbf{x})|\Psi_\lambda\rangle \tag{6.57}$$

$$= n(\mathbf{x})n(\mathbf{x}')g^{(2)}(\mathbf{x},\mathbf{x}',\lambda,[n]) . \tag{6.58}$$

Eq. (6.58) follows from the definition of the pair distribution function $g^{(2)}$, which is defined to be the conditional probability of finding a particle at $\mathbf{x}$ given that there is another particle at $\mathbf{x}'$:

$$g^{(2)}(\mathbf{x},\mathbf{x}') \equiv \frac{\langle\sum_{i\neq j}^N \delta(\mathbf{x}-\hat{\mathbf{x}}_i)\delta(\mathbf{x}'-\hat{\mathbf{x}}_j)\rangle}{n(\mathbf{x})n(\mathbf{x}')} = \frac{\langle\hat{n}(\mathbf{x})\hat{n}(\mathbf{x}')\rangle}{n(\mathbf{x})n(\mathbf{x}')} - \frac{\delta(\mathbf{x}-\mathbf{x}')}{n(\mathbf{x})} . \tag{6.59}$$

where $\hat{n}(\mathbf{x}) = \sum_{i=1}^N \delta(\mathbf{x}-\hat{\mathbf{x}}_i) = \sum_\alpha \psi_\alpha^\dagger(\mathbf{x})\psi_\alpha(\mathbf{x})$ is another representation of the density operator with summation over all N particles. The state vectors in the expectation value above $\langle\cdot\rangle$ have been left unspecified.

The crucial assumption leading to Eq. (6.56) is that the potential $V(\mathbf{x},\mathbf{x}')$ is independent of the spin labels. With this assumption we have now shown how the the pair correlation function arises upon taking the expectation value of the interaction part of the Hamiltonian. Integrating Eq. (6.56) we obtain the ground state energy

$$E[n] = E(\lambda = 1) = E(0) + \int_0^1 d\lambda \, dE(\lambda)/d\lambda \tag{6.60}$$

$$= T_0[n] + \int d\mathbf{x}\, v(\mathbf{x})n(\mathbf{x}) + \frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\, V(\mathbf{x},\mathbf{x}')n(\mathbf{x})n(\mathbf{x}') + E_{xc}[n] \tag{6.61}$$

$$= T_0[n] + \int d\mathbf{x}\, v(\mathbf{x})n(\mathbf{x}) + \frac{1}{2}\int_0^1 d\lambda \int d\mathbf{x}\int d\mathbf{x}'\, V(\mathbf{x},\mathbf{x}')n(\mathbf{x})n(\mathbf{x}')g^{(2)}(\mathbf{x},\mathbf{x}',\lambda,[n]) \; .$$

where the exchange-correlation functional can be written as in Eq. (6.52). The kinetic energy of the non-interacting system T_0 plays the role of free energy of the reference system in the classical density functional theory. The external potential acts like an inhomgeneous chemical potential and finally, the structure of the interaction term containing the pair correlation function is exactly the same both in classical and quantum density functional theories. However, in quantum theory we did not separate out the attractive part of the interaction. The second important difference is the missing of the mixed pair correlation functions the exchange correlation functional (6.52). In the corresponding classical expression (6.47) the distinguishability of the species gave rise to g_{ij}, $i \neq j$.

6.3 Derivation of classical free energy

Two different types of methods are used to construct an approximate expression for the free energy. The first one is the classical cell technique [236, 237, 197] (for a field theoretic Green's function based analog, see Ref. [58]). An alternative techique is presented in Sect. 6.3.2, where the poor man's version of the use of functional Legendre transformation is given. It will hopefully make the somewhat abstract presentation given in Chap. 2 more transparent.

6.3.1 Restricted trace and the cell technique

Density functional techniques can be applied to any interacting many-particle system whether it is solid, liquid or gas. We will now focus on a classical fluid system (liquid-gas system), where there is no long-range crystal order. Using a so-called cellular coarse-graining method we derive the free energy F. We start with the definition of classical N-particle partition function

$$Z(T,V,N) = \mathrm{Tr}_{cl}\left\{e^{-\beta H_N}\right\} = \frac{1}{\lambda_T^{3N} N!}\int d\mathbf{x}^N \, e^{-\beta \sum_{i<j} u(x_{ij})} \; , \tag{6.62}$$

where V is the volume the system occupies. We have integrated out the momenta leaving only the configurational part unintegrated: $d\mathbf{x}^N \equiv d\mathbf{x}_1 \ldots d\mathbf{x}_N$. Let us now use the same trick, which gives rise to the ϕ^4-field theory in the case of Ising model. We divide the system into large number of cells, whose volume $\Delta \ll V$, but which are large enough to contain many particles. The form of the pair potential U is assumed to be such that it gives rise to a hard core radius a and has a long range attractive tail.

$$U(\mathbf{x}_i - \mathbf{x}_j) = U(x_{ij}) = \begin{cases} +\infty \; , & x_{ij} < a \; ; \\ -w(x_{ij}) \; , & x_{ij} > a \; . \end{cases} \tag{6.63}$$

To allow the presence of many particles in one cell we require $a \ll \Delta^{1/3} \ll V^{1/3}$. Furthermore, we assume that the attractive tail is sufficiently weakly decaying to be able to approximate the attractive interactions between particles in the same cell by a constant potential. Performing the trace operation in Eq. (6.62) in two stages we can write

$$Z = \frac{1}{\lambda_T^{3N} N!} \sum_{\{N_\alpha\}}{}^{\prime} \int d\mathbf{x}^N \prod_\alpha \delta\Big(N_\alpha - \int_{\Delta_\alpha} d\mathbf{x}'\, \phi(\mathbf{x}')\Big)\, e^{-\beta \sum_{i<j} u(x_{ij})} \ . \tag{6.64}$$

Restricted summation $\sum'$ takes into account only such configurations, which fulfil $\sum_\alpha N_\alpha = N$. There are N_α particles in cell α, which occupies the volume Δ around point $\mathbf{x}_\alpha$. The density of particles at point $\mathbf{x}$ is denoted by $\phi(\mathbf{x}) \equiv \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i)$. The configurational phase space volume Y available in a cell with N_α particles is

$$Y(N_\alpha) \equiv (\Delta - N_\alpha \delta)^{N_\alpha} \ , \tag{6.65}$$

where $\delta \equiv (4/3)\pi a^2$ is the hard core volume of one particle. In terms of Y the partition function becomes

$$Z = \frac{1}{\lambda_T^{3N} N!} \sum_{\{N_\alpha\}}{}^{\prime} \frac{N!}{\Pi_\alpha N_\alpha!} Y(N_\alpha)\ e^{(\beta/2)\sum_{\alpha\alpha'} w_{\alpha\alpha'} N_\alpha N_{\alpha'}} \tag{6.66}$$

The combinatorial term $N!/\Pi_\alpha N_\alpha!$ tells in how many ways one can divide N particles into N_α cells. The phase space volume in each cell is given by Y. Finally, $w_{\alpha\alpha'}$ characterizes the attractive part of the interaction between cells α and α'. Exponentiating all factors yields

$$Z = \lambda_T^{-3N} \sum{}^{\prime} \exp\Big(-\beta F_c[N_\alpha]\Big) \ ; \tag{6.67}$$

$$F_c[N_\alpha] \equiv \sum_\alpha \left[N_\alpha \ln\left(\frac{\Delta - N_\alpha \delta}{N_\alpha}\right) + N_\alpha + \frac{1}{2}\beta \sum_{\alpha\alpha'} w_{\alpha\alpha'} N_\alpha N_{\alpha'} \right] . \tag{6.68}$$

Going over to density $n \equiv N_\alpha/\Delta$ measured in units of δ we arrive at the continuum approximation of the free energy functional [236, 197]:

$$F[n] = \int d\mathbf{x} \left[n(\mathbf{x}) \ln\left(\frac{1 - n(\mathbf{x})}{n(\mathbf{x})}\right) + n(\mathbf{x}) \right] + \frac{1}{2}\beta \int d\mathbf{x} \int d\mathbf{x}'\ w(\mathbf{x} - \mathbf{x}') n(\mathbf{x}) n(\mathbf{x}') \ . \tag{6.69}$$

This should now be compared with density functional results of Eq. (6.32) and Eq. (6.33). The cell technique corresponds leads to the same expression as the use of LDA and RPA approximations in the case of density functionals. It should be noted, though, that the reference free energy f_{HS} in Eq. (6.33) has a different functional dependence on the density than the expression in the square brackets in Eq. (6.69). However, when one plots F as a function of constant density, it is easy to see that the well structure is the same in both cases: There is a single well above critical temperature T_c (which can be worked out in terms of model parameters). Below T_c the (mean field) free energy density becomes non-convex giving rise to coexistence of liquid and gas phases. The non-convexity is a result of the mean field like cell approximation combined with the use of homogeneous density field to approximate the pointwise free energy density. As will be discussed more thoroughly in Sect. A, the the pointwise free energy density does not have to be convex in contrast to the homogeneous free energy density (F/V), which is convex in the thermodynamic limit.

6.3.2 Legendre transformation technique

Let us now repeat the derivation of the free energy of a dilute fluid (liquid-gas) system using the Legendre transformation technique, which has already been introduced in Chap. 2. Moreover, in Sect. 6.1.3 we discussed the interpretation of the v-representability as a Legendre transformation between variables V_{ext} and the density n. Here we will carry out the same procedure but with constant fields, which means that we do not have to introduce a spatially dependent fields $V_{ext}(\mathbf{x})$ and $n(x)$ but we can do with constant fields μ and n and put in the spatial dependence in the final result by hand. (Remember that V_{ext} can be seen as the spatially dependent part of the chemical potential μ.)

Following Ref. [238] we expand the grand potential $\beta\Omega = -\ln Z$ to order $\mathcal{O}(\lambda^2)$ in the fugacity, which should be reasonable for dilute system:

$$\begin{aligned}
\beta\Omega &= -\ln \sum_{N=0}^{\infty} \frac{\lambda^N}{N!} \int d\mathbf{x}^N \, e^{-\beta H_N} && (6.70) \\
&\approx -\ln\Big(1 + \tilde{\lambda} V + (\tilde{\lambda}^2/2) \int d\mathbf{x}_1 \int d\mathbf{x}_2 \; e^{-\beta u(x_{12})} + \dots\Big) && (6.71) \\
&\approx -V\Big(\tilde{\lambda} - (\tilde{\lambda}^2/2)\, a + \dots\Big) \;, && (6.72)
\end{aligned}$$

where $a \equiv \int d\mathbf{x}\, (1 - e^{-\beta u(\mathbf{x})})$ is the virial coefficient and $\tilde{\lambda} \equiv \lambda/\lambda_T^3$. Eq. (6.72) follows from expanding the logarithm. Next, we need to find a relation between the variables μ and n. Thermodynamic identity (which holds in equilibrium only),

$$nV = N = -\frac{\partial \Omega}{\partial \mu} \;, \tag{6.73}$$

leads to the following equation of state: $n \approx \tilde{\lambda} - a\tilde{\lambda}^2$. Solving for $\tilde{\lambda}$ in terms of the density gives

$$\tilde{\lambda} \approx n + an^2 + \mathcal{O}(n^3) \;. \tag{6.74}$$

Now that we know what $\tilde{\lambda}(n)$ is (or more properly, what $\mu(n)$ is) we can use the Legendre transformation to compute the Helmholtz free energy, which has density as its natural variable:

$$\frac{1}{V} F(n) = \frac{1}{V} \Omega[\mu(n)] - \mu(n) n \;. \tag{6.75}$$

This equation should be compared with Eq. (6.34). It is clear that the role of F_V is played by Ω and V_{ext} corresponds to μ. By making $V_{ext} = \mathit{const}$ and dividing both sides of Eq. (6.34) by the volume V generates exactly Eq. (6.75). Substitution of $\mu[n] = -\beta^{-1} \ln \tilde{\lambda}(n)$ yields the explicit representation

$$F(n) = \beta^{-1} V \Big(n \ln(\lambda_T^3 n) - 1\Big) + (a/2) n^2 \;. \tag{6.76}$$

Using local density approximation and replacing the constant fields with $n(\mathbf{x})$ the previous expression becomes the exactly same as the density functional result (6.33) when one uses the ideal gas result F_{id} as the reference free energy functional instead of F_{HS}, and approximates the virial coefficient $a \approx u(x)$, which holds in the limit $\beta u \ll 1$.

Thus, all methods (density functional, cell coarse-graining and Legendre technique) seem to give consistent results at least for low enough densities. There are a few subleties, though, which should be kept in mind. The Legendre transformation technique used above made use of homogeneous fields. Had we computed the full equation of state with no approximations, and inverted it to find out $\mu(n)$, the $F(n)/V$ obtained through Legendre transformation would have been convex in the limit $V \to \infty$ as required by conventional equilibrium thermodynamics. It is only due to the approximations that the double well potential emerges in this case. However, the pointwise free energy density (see Sect. A), which is used in the functional Legendre transformation for spatially dependent fields, does not have to be convex. When we try to find the pointwise free energy density by replacing the homogeneous values n by space dependent ones in $F(n)$, there is no guarantee in general that we should obtain exactly the same result as with density functional treatment or by using the cell method. In this example the results seem to agree, though.

6.4 Fluid-solid density functional and wall potential

Let us start by discussing the classical density functional theory, which forms the basis of the phase-field approximation to be introduced in Sect. 7.3. Wetting of a solid can be described in terms of the following density functional for spatially inhomogeneous number density ϕ (cf. dimensionless phase-field C.2) [228, 239]:

$$\Omega([\phi], T, \mu_0) = \frac{1}{2}\int_D d\mathbf{x} \int_D d\mathbf{x}'\, \tilde{w}(|\mathbf{x}-\mathbf{x}'|)\phi(\mathbf{x})\phi(\mathbf{x}') + \int_D d\mathbf{x}\, f_{HS}(\phi(\mathbf{x}), T) + \int_D d\mathbf{x}\,[V_S(\mathbf{x}) - \mu_0] \ . \tag{6.77}$$

As usual, T denotes temperature and μ_0 is the equilibrium chemical potential, which determines the average number density. The domain occupied by the fluid is D. As explained in Sect. 6.1, f_{HS} is the hard sphre reference chemical potential responsible for repulsive interactions, and the first term on the right hand side of Eq. (6.77) describes the effect of attractive fluid-fluid particle interactions within the mean-field theory. In the simplest approximation, the effective interaction $\tilde{w}$ is the attractive part of the pair potential. In a more refined theory, $\tilde{w}$ becomes the pair distribution function as explained in the begining of this chapter, which in turn can be connected with the total pair correlation function (p. 159 Ref. [229]). Even though the nonlocality of the short-range particle-particle correlations, which become important close to the substrate surface, are negelected in Eq. (6.77), it still provides a reasonable description of wetting phenomena when the thickness of the adsorbed liquid film is much larger than the diameter σ_f of the fluid particles [239].

The parameters of the density functional theory described above can be computed for a Lennard-Jones fluid with pair potential strength ϵ_f:

$$w(r) = 4\epsilon_f[(\sigma_f/r)^{12} - (\sigma_f/r)^6] \ . \tag{6.78}$$

The full potential is then split into the attractive part w_{att} and repulsive part w_{rep}. Within the Weeks-Chandler-Andersen (WCA) approximation, the latter gives rise to an effective temperature dependent hard sphere diameter:

$$d(T) = \int_0^{r_{co}} dr\,[1 - \exp(-\beta w_{rep}(r))] \ , \tag{6.79}$$

where the cut-off $r_{co} \equiv 2^{1/6}\sigma_f$. In terms of the hard sphere diameter we can express the dimensionless packing fraction $\zeta \equiv (\pi/6)d^3(T)$, which allows us to write the Carnaghan-

Starling approximation of the hard sphere reference free energy as

$$f_{HS}(\phi, T) = \beta^{-1}\phi\left(\ln(\phi\lambda_T^3) - 1 + \frac{4\zeta - 3\zeta^2}{(1-\zeta)^2}\right) , \tag{6.80}$$

where λ_T is the thermal de Broglie length. It turns out to be computationally advantageous to approximate the WCA result for attractive part of the pair potential by the simpler form [239]:

$$w_{att}(r) \approx \tilde{w}(r) = -\frac{4w_0\sigma_f^3}{\pi^2}(r^2 + \sigma_f^2)^{-3} , \tag{6.81}$$

where the prefactor $w_0 = -(32\sqrt{2}/9)\pi\epsilon_f\sigma_f^3$. The choice of w_0 guarantees that the integrals of $\tilde{w}$ and the attractive part of the pair potential, w_{att}, become the same.

6.4.1 Interaction of the solid wall with the fluid

The volume occupied by the fluid particles is D over which all integrals are performed. Thus, the solid phase is manifest only through the presence of the potential term V_S whose origin's we now look into more carefully. To be able to derive V_S we need to introduce a new density field ρ hich describes the solid phase. In order to homogenize the notation to be used later on (see Sect. 7.3) let us denote the fluid density field $\phi \equiv \phi_1$ and the solid $\rho \equiv \phi_2$. Quite generally, we can write the intrinsic part of the free energy as (p. 214, Ref. [229])

$$\begin{aligned} F[\phi_1, \phi_2] &= \frac{1}{2}\sum_{i,j=1}^{2}\int d\mathbf{x}\int d\mathbf{x}'\,\phi_i(\mathbf{x})v_{ij}^A(\mathbf{x},\mathbf{x}')\phi_j(\mathbf{x}') + \int d\mathbf{x}\,V(\phi(\mathbf{x})) && (6.82)\\ &\approx \int d\mathbf{x}\left\{\frac{1}{2}\sum_{i,j=1}^{2} m_{ij}\nabla\phi_i\cdot\nabla\phi_j + \tilde{V}(\phi_1,\phi_2)\right\} , && (6.83)\end{aligned}$$

where we have performed the gradient expansion of the attractive part v^A of the pair potential and combined the non-gradient terms with the potential V thus generating an effective potential $\tilde{V}$.

As we are interested neither in the variation of the solid density nor its dynamics, we leave out all terms having gradients in the solid density in the free energy (6.83). Thus, we obtain something like

$$F[\phi_1, \phi_2] = \int d\mathbf{x}\,\frac{1}{2}|\nabla\phi_1|^2 + \int d\mathbf{x}\int d\mathbf{x}'\,\phi_1(\mathbf{x})w_S(\mathbf{x},\mathbf{x}')\phi_2(\mathbf{x}') + \ldots\ . \tag{6.84}$$

The second term on the right describes the interaction of the fluid and solid particles. As there is no obvious reference state for both the solid and the fluid, no reference free energy will be constructed here in contrast to the liquid-gas case. The interaction of the fluid and solid particles is taken to of the Lennard-Jones type:

$$w_S(r) = 4\epsilon_S[(\sigma_S/r)^{12} - (\sigma_S/r)^6] . \tag{6.85}$$

Let us integrate out the solid density field,

$$\int d\mathbf{x}\int d\mathbf{x}'\,\phi_1(\mathbf{x})w_S(\mathbf{x},\mathbf{x}')\phi_2(\mathbf{x}') = \int d\mathbf{x}\,\phi_1(\mathbf{x})V_S(\mathbf{x}) , \tag{6.86}$$

where we have defined $V_S(\mathbf{x}) \equiv \int d\mathbf{x}'\, w_S(\mathbf{x},\mathbf{x}')\phi_2(\mathbf{x}')$. If the solid density field is approximated by a constant average density with infinite extent, $\phi_2(\mathbf{x}) \propto \theta(-u')$, where u' is the normal coordinate of the solid surface, the effective potential $V_S(\mathbf{x})$ will not depende on the coordinates in the plane of the surface. In this case we can approximate $V_S(\mathbf{x})$ with the laterally averaged potential $V_S(z)$. In Sect. 7.3 we intoduce a phase-field description of the model which utilizes a field A, called wall potential. This field is linearily coupled with ϕ and therefore it plays a role analogous to the substrate potential V_S. As will be described in more detail below, making $A = A(z)$, where z is the coordinate perpendicular to the wall, the spatially varying thickness of the wetting layer can also be controlled, in addition to the contact angle.

6.4.2 Equivalent macroscopic variables for fluid- fluid system

The choice of hydrodynamically important coarse-grained variables is discussed in Sect. 9.5.3. For static purposes the relevant set of macroscopical fields consists of the the densities of the fluid components, that is ϕ_1 and ϕ_2. The density field of the solid does not appear anymore explicitly: its presence is taken into account through the potential V_S derived in the previous section. For mixing components the concentration $C \equiv \phi_1/\phi$, and the total density $\phi \equiv \phi_1 + \phi_2$ form another pair of variables on which the density functional theory can be based. A third possibility is to choose the pair $\{C, \phi_1\}$. Let us see what the typical free energy of a multi-component system looks like when expressed in different variables. Start with pair $\{\phi_1, \phi_2\}$. By choosing different fundamental variables and substituting into Eq. (6.83) we obtain representations of free energy, which superficially may look quite different from each other. However, when we are approaching the sharp interface limit, the variables the concentration and total density become less and less independent. In the limit they are related through

$$\phi(\mathbf{x}) = \overline{\phi}_1\, C(\mathbf{x}) + \overline{\phi}_2\, (1 - C(\mathbf{x}))\ , \tag{6.87}$$

where $\overline{\phi}_1$ and $\overline{\phi}_2$ are the constant bulk values of the densities of the components. Thus, the free energy, whether expressed in variable $\phi(\mathbf{x})$ or $C(\mathbf{x})$ looks almost the same, only the positions of the minima of the potential wells have been shifted and the magnitude of the order parameter field has become scaled by factor $\Delta_{12} = \overline{\phi}_1 - \overline{\phi}_2$. In other words, $F[\phi] = F[2C-1] \equiv F'[C]$ for typical choice of phase-field parameters $\overline{\phi}_1 = +1$, and $\overline{\phi}_2 = -1$. Of course, in the sharp interface limit the concentration plays the role of the characteristic function of the fluid domains and its derivatives are not well defined right at the border line separating the fluids. When mixing takes place (and it does, even for so-called immiscible fluids), we can consider a perturbation theory in variable pair $\{C, \phi_1\}$, which was one of the choices mentioned in the beginning of this section. The total density $\phi(\mathbf{x}) = \overline{\phi}_1 C(\mathbf{x}) + \overline{\phi}_2(1 - C(\mathbf{x})) + r(\phi_1(\mathbf{x}), C(\mathbf{x}))$, where

$$r(\phi_1(\mathbf{x}), C(\mathbf{x})) \equiv \left[\phi_1(\mathbf{x}) - \overline{\phi}_1\, C(\mathbf{x})\right] + \left[\phi_1(\mathbf{x})\frac{1 - C(\mathbf{x})}{C(\mathbf{x})} - \overline{\phi}_2(1 - C(\mathbf{x}))\right]\ . \tag{6.88}$$

Clearly, the correction term is negligible everywhere else except in the vicinity of the boundary of the two fluids. The two-component density functional can be decomposed by writing $F[\phi_1, \phi_2] \equiv F'[\phi_1, C] = F'_1[C] + F'_2[\phi_1, C]$, where F'_2 is the contribution to the total free energy from regions where the correction terms r is nonvanishing. However, if one wishes to use the Poisson bracket formalism to be introduced in Sect. 7 to generate the dynamics of the relevant macrosocopic degrees of freedom including ϕ_1 and C, one should be carefull not to throw away the free energy F_2' even though it only collects contribution from the regions where $r \neq 0$. The Poisson bracket formalism involves functional derivatives of the free energy with respect to fields ϕ_1 and C which are pointwise quantities. For example, close to boundary it may hold for some spatial region in the system that $\delta F_2/\delta C(\mathbf{x}) > \delta F_1/\delta C(\mathbf{x})$, and therefore the contribution from F_2 cannot be left out.

6.5 Internal energy and emergence of temperature

So far we have been predominantly been talking about the mass (number) density when addressing density functional description of a many-body system. But there are other important densities, relevant for hydrodynamic characterization, which can and must also be taken into account especially when modeling dynamics. As will be discussed in more detail in Chap. 9 and App. D for simple fluids the relevant macrovariables consist of the expectation values over (trace over dynamic density matrix) of the following quantities:

$$\phi(\mathbf{x},t) \equiv \sum_\alpha m\,\delta(\mathbf{x}-\mathbf{x}^\alpha(t)) \ . \tag{6.89}$$

$$\mathbf{j}(\mathbf{x},t) \equiv \sum_\alpha \mathbf{p}^\alpha(t)\,\delta(\mathbf{x}-\mathbf{x}^\alpha(t)) \ . \tag{6.90}$$

$$\mathcal{E}(\mathbf{x},t) \equiv \Big(\textstyle\sum_\alpha (p^\alpha)^2/(2m) + (1/2)\sum_{\alpha\neq\beta} V(\mathbf{x}^{\alpha\beta})\Big)\,\delta(\mathbf{x}-\mathbf{x}^\alpha(t)) \ . \tag{6.91}$$

Instead of n, we use here the generic symbol ϕ for mass density, momentum density is denoted by $\mathbf{j}$ and internal energy density by $\mathcal{E}$. The microscopic coordinate are $\mathbf{x}^\alpha$ and the difference $\mathbf{x}^\alpha - \mathbf{x}^\beta \equiv \mathbf{x}^{\alpha\beta}$. Finally, $\mathbf{p}^\alpha$ is the microscopic momentum of particle α.

In the next chapter 7 we will be utilizing the generalized free energy $F(\langle\phi\rangle,\langle j\rangle,\langle\mathcal{E}\rangle)$ as a generator of the non-equilibrium time evolution for so-called phase-field models, which constitute a powerful way of describing the coarse-grained dynamics of rather complicated systems. The question we are posing is, how do we find a generalized free energy (or rather, action) functional as a function of $\langle\phi\rangle$, $\langle j\rangle$ and $\langle\mathcal{E}\rangle$? As to mass density ϕ, we have already given many ways of doing this in this chapter. The most true to the original idea of block-spin transformation [87] is the cellular coarse-graining method, which can be formalized by using a delta function constrained trace operation as shown in Sect. 6.3.1. Leaving out the summation over the cells $\sum'_{\{N_\alpha\}}$ from Eq. (6.64) we get

$$F[\langle\phi\rangle] = -k_B T \ln Z'[\langle\phi\rangle] \ ; \tag{6.92}$$

$$Z'[\langle\phi\rangle] = \mathrm{Tr}_{cl}\left\{\prod_{\mathbf{x}} \delta\Big(\langle\phi(\mathbf{x})\rangle - \Delta^{-1}\int_{\Delta_\mathbf{x}} d\mathbf{x}'\,\phi(\mathbf{x}')\Big)\,e^{-\beta H_N}\right\} . \tag{6.93}$$

The logic is thus that only those configurations of atomic positions whose density inside each of the cells Δ coincides with the *given* average density $\langle\phi(\mathbf{x})\rangle$ contribute to the coarse-grained free energy $F[\langle\phi\rangle]$ (some prefer the word coarse-grained Hamiltonian). It should be noted that the average $\langle\phi\rangle$ appearing in Eq. (6.93) must be interpreted as the spatial average because the given values $\langle\phi\rangle$ are compared against a spatial cell average in the constraining delta function.

Continuing this type of process for other relevant macrovariables leads to physically sensible free energies. For example, using

$$H_N = \sum_{\alpha} \frac{1}{2m}(p^{\alpha})^2 + \frac{1}{2}\sum_{\alpha\neq\beta} V(x^{\alpha\beta}) \tag{6.94}$$

we can find the generalized free energy, which takes into account the average momentum flux $\langle j\rangle$:

$$F[\langle\phi\rangle, \langle j\rangle] = -k_B T \ln Z'[\langle\phi\rangle, \langle j\rangle] \ ; \tag{6.95}$$

$$Z'[\langle\phi\rangle, \langle j\rangle] =$$
$$\mathrm{Tr}_{cl}\left\{\prod_{\mathbf{x}} \delta\Big(\langle\phi(\mathbf{x})\rangle - \Delta^{-1}\int_{\Delta_{\mathbf{x}}} d\mathbf{x}'\,\phi(\mathbf{x}')\Big)\ \delta\Big(\langle j(\mathbf{x})\rangle - \Delta^{-1}\int_{\Delta_{\mathbf{x}}} d\mathbf{x}'\,j(\mathbf{x}')\Big)\, e^{-\beta H_N}\right\}. \tag{6.96}$$

Using this approach Langer and Turski [240] we able to derive $F[\langle\phi\rangle, \langle j\rangle]$, which we will be utilizing later on in Chap. 9. However, as they point out, one should be careful with the size of the cell Δ. Naively one would think that the bigger Δ becomes the more the spatial average $\langle\rho\rangle$ approaches a smooth function, which can be used as the argument of the functional free energy, with its coarse-grained derivatives well-behaving on the cell scale $\mathbf{x}_c$. As argued in Ref. [240] the optimal cell size relevant for condensation problem is of the order of the correlation length. The cell size restriction becomes relevant also when one tries to apply the delta function restricted trace method to internal energy dependence of the free energy. In principle we can just add a third delta function into Eq. (6.96). Dropping the mass and momentum densities for simplicity, we obtain $F[\langle\mathcal{E}\rangle] = -k_B T \ln Z'[\langle\mathcal{E}\rangle]$, and

$$Z'[\langle\mathcal{E}\rangle] = \mathrm{Tr}_{cl}\left\{\prod_{\mathbf{x}} \delta\Big(\langle\mathcal{E}(\mathbf{x})\rangle - \Delta^{-1}\int_{\Delta_{\mathbf{x}}} d\mathbf{x}'\,\mathcal{E}(\mathbf{x}')\Big)\, e^{-\beta H_N}\right\} \tag{6.97}$$

Clearly, we do not obtain a sensible answer if we let the cell size approach the system size V. Because $\int_V d\mathbf{x}\,\mathcal{E}(\mathbf{x}) = H_n$ it follows for $\Delta = V$ that

$$Z'[\langle\mathcal{E}\rangle_V] \propto e^{-\beta\mathcal{E}} \ , \tag{6.98}$$

which would mean that the free energy is the same as the internal energy. Of course, there is another problem in keeping total volume V finite and letting $\Delta \to V$: The coarse-grained system consists of a single cell located around its central point $\mathbf{x}$, so one cannot talk about a real density of points $\mathbf{x}$. Therefore, it seems to be necessary to take the thermodynamic limit $V \to \infty$ first before starting to increase the cell size Δ.

In fact, we will not be needing $F[\langle\mathcal{E}\rangle]$ since energy transport will not be one of the phenomena we have chosen to concentrate on in this work. Let us, however consider methods that have been suggested in the literature to reveal the form $F[\langle\mathcal{E}\rangle]$. One possibility is to use quasi-thermodynamic arguments and represent the internal energy density in temrs of other thermodynamic variables such as temperature and density. For example, to linear order in small deviations from equilibrium we can relate the local temperature $\delta T(\mathbf{x})$, energy density $\delta\mathcal{E}(\mathbf{x})$ and the mass density $\delta\phi(\mathbf{x})$ through

$$\delta T(\mathbf{x}) = \left(\frac{\partial T}{\partial U}\right)_n \delta\mathcal{E}(\mathbf{x}) + \left(\frac{\partial T}{\partial n}\right)_U \delta\phi(\mathbf{x}) \ , \tag{6.99}$$

where normal chain rule has been used. Moreover, the average space independent values of the macrovariables at linearization point are denoted as n for density and U for internal energy. Based on fluctuation analysis, the coarse-grained free energy can near the expansion point be written as [241]

$$F[\langle\delta T(\mathbf{x})\rangle, \langle\delta\phi(\mathbf{x})\rangle] = \int d\mathbf{x}\, \left(\frac{C_V}{2T}\langle\delta T(\mathbf{x})\rangle^2 + \frac{1}{2n^2K_T}\langle\delta\phi(\mathbf{x})\rangle^2\right), \tag{6.100}$$

where we have assumed that the microscopic realization of the fluctuation can be replaced with its average value. Substitution of $\delta T(\mathbf{x})$ from Eq. (6.99) then produces the lowest order approximation to the free energy density expressed in terms of the local internal energy density. In order to be able to describe the whole phase transition region and not just the vicinity of one equilibrium state some authors have drawn the physically sensible conclusion that the well-structure of the free energy should be present in the internal energy representation also, not just in the normal mass density. For example, in nucleation studies of relativistic particles the free energy, when assumed to be just a function of $\langle\mathcal{E}\rangle$, becomes [242, 243]

$$F[\langle\mathcal{E}\rangle] = \int d\mathbf{x}\, \frac{K}{2}|\nabla\langle\mathcal{E}\rangle|^2 + V(\langle\mathcal{E}\rangle)\ , \tag{6.101}$$

where the potential V can taken to be of the usual double well form.

If we do not want to get confused by the complicated interactions between cells or we do not trust the quasi-thermodynamic arguements presented above, perhaps the most convinient way of obtaining the free energy as a functional of expectation values of any desired set of macroscopic observables is to use the functional Legendre transformation [49]. In this formalism temperature appears naturally as the space dependent 'source' field whose elimination in exchange for $\langle\mathcal{E}(\mathbf{x})\rangle$ appears naturally. To compute the effective action (free energy) for the mass, momentum and internal energy variables we first define the generating functional (in the quantum language)

$$e^{-W[J_\mathcal{E}, J_\phi, \mathbf{J}_j]} \equiv Z[J_\mathcal{E}, J_\phi, \mathbf{J}_j] = \mathrm{Tr}\left\{e^{-J_\mathcal{E}\hat{H}_N - J_\phi\hat{n} - \mathbf{J}_j\cdot\hat{\mathbf{j}}}\right\}\ , \tag{6.102}$$

whereintegrals are understood, e.g. $J_\phi\hat{n} = \int d\mathbf{x}\, J_\phi(\mathbf{x})\hat{n}(\mathbf{x})$. The operators are defined as $\hat{n} = \psi^\dagger(\mathbf{x})\psi(\mathbf{x})$, $\hat{\mathbf{j}} = (\hbar/(2m\imath))\,[\psi^\dagger(\mathbf{x})\nabla\psi(\mathbf{x}) - (\nabla\psi^\dagger(\mathbf{x}))\psi(\mathbf{x})]$ and $\hat{H}_N$ is given by Eq. (6.2). In case one is dealing with a classical problem, one can always transform it into the form Eq. (6.102) by using the methods explained in Sect. 6.1.3. The effective action then reads

$$\begin{aligned} &F[\langle\hat{H}_N\rangle, \langle\hat{n}\rangle, \langle\hat{\mathbf{j}}\rangle] = \\ &W[J_\mathcal{E}, J_\phi, \mathbf{J}_j] - \int d\mathbf{x}\, \Big(J_\mathcal{E}(\mathbf{x})\,\langle\hat{H}_N(\mathbf{x})\rangle + J_\phi(\mathbf{x})\ \langle\hat{n}(\mathbf{x})\rangle + \mathbf{J}_j(\mathbf{x})\cdot\langle\hat{\mathbf{j}}(\mathbf{x})\rangle\Big)\ , \end{aligned} \tag{6.103}$$

where the expectation values are averages over the relevant quantum ensemble e^{-W}. There are some interesting relationships that these formula have some related formulations of thermodynamics of non-equilibrium systems. First, we point out the similarity of our generating functional (6.102) to the density matrix of non-homogeneous systems proposed by Kadanoff and Martin [244] (for a related work, see Ref. [245]). Their idea was to perturb the grand canonical density matrix ρ_G by adding spatially varying components to intensive variables (Lagrange's multipliers). For a system moving with average velocity $\mathbf{v}$,

$$\rho_G = Z_G^{-1}\exp(-\beta H_v) \equiv Z_G^{-1}\exp\left(\Big[H_0 - \mu N + (1/2)mv^2N - \int d\mathbf{x}\,\mathbf{j}(\mathbf{x})\cdot\mathbf{v}\Big]\right) \tag{6.104}$$

where $Z_G = \mathrm{Tr}_{cl}\exp(-\beta H_v)$. Note that there is no $\mathbf{x}$-dependence in $\mathbf{v}$ to begin with, which means that ρ_G is a valid description of thermodynamics. Adding small perturabations $\delta\mu(\mathbf{x})$, $\delta T(\mathbf{x})$ and $\delta\mathbf{v}(\mathbf{x})$ to the chemical potential, velocity and temperature, we can to first order in fluctuations still write the perturbed density matrix in equilibrium form:

$$\rho' = (Z'_G)^{-1}\exp(-\beta H'_v) \ , \tag{6.105}$$

where $Z'_G = \mathrm{Tr}_{cl}\exp(-\beta H'_v)$ and $H'_V \equiv H_v + \delta H_v$. The first order perturbation correction reads

$$\delta H_v \equiv -\int d\mathbf{x}\,\left(\frac{\delta T(\mathbf{x})}{T}[\mathcal{E}(\mathbf{x}) - \mu n(\mathbf{x})] + \delta\mu(\mathbf{x})n(\mathbf{x}) + \delta\mathbf{v}(\mathbf{x})\cdot\mathbf{j}(\mathbf{x})\right) \ , \tag{6.106}$$

where we have used the densities $\int d\mathbf{x}\,\mathcal{E}(\mathbf{x}) + \mu n(\mathbf{x}) = H_0 + \mu N$, etc. Let us also note that we do not have to separate out the temperature dependence explicitly, but we could define a new set of intensive variables as β, $\beta\mu \equiv \nu$ and so on. Adding the small variations $\beta + \delta\beta(\mathbf{x})$, $\nu + \delta\nu(\mathbf{x})$ and forming the perturbed density matrix would lead to the same result (6.106), which is completely analogous to our usage of external fields in Eq. (6.102). Using ρ'_G one can easily construct the linear responses for small perturbations and study the emerging hydrodynamics (when the fields $\mathcal{E}$, n and $\mathbf{j}$ are made t-dependent as well as being $\mathbf{x}$-dependent in terms of correlation functions. In effect, this approach becomes very close to the information theoretical construction of the density matrix presented in Ref. [188]:

$$\hat\rho(t) \propto \exp\Big(-\beta\hat H + \int d\mathbf{x}\int_{-\infty}^{t} dt'\lambda(\mathbf{x}',t')\,\hat{\mathcal{E}}(\mathbf{x}',t')\Big) \ , \tag{6.107}$$

where $\lambda(\mathbf{x}',t')$ is the Lagrange's multiplier equivalent to our source field $J_{\mathcal{E}}$. Differences of these approches from our generating functional formalism are discussed in Chap. 2.

Finally, we want to point out the difference with the ensemble average constraint used in the Legendre transformation techinque and the spatial average constraint used in the restricted trace method (cellular coarse-graining) For concreteness, we momentarily consider the Ising model of interating spins instead of point particles. For Ising model, the coarse-grained free energy corresponding to Eq. (6.93) reads

$$e^{-\beta F_s(M,T)} \equiv \sum_{\{s_i\}} \delta\Big(M - N^{-1}\sum_{j=1}^{N} s_j\Big)\, e^{-\beta H_I} \ , \tag{6.108}$$

where the nearest neighbor interactions fix $H_I = \sum_{i\neq j} s_i s_j$ and N is the total number of spins. As discussed in Sect. A, there is another way to obtain the coarse-grained free energy, which can be formalized using the functional Legendre transformation and discussed more thoroughly in Sect. A. By introducing a coupling of the spins to external magnetic field h one obtains

$$e^{\beta G(h,T)} = \sum_{\{s_i\}} e^{-\beta H_I + \beta h\sum_{i=1}^{N} s_i} \tag{6.109}$$

If we can associate (as we usually do) F_s with the thermodynamic Helmholtz free energy F and M as the magnetization, we can switch between the representations via the Legendre transformation $G = F - hM$. To be able to use this type of identification, we have made the crucial assumption that the ensemble average

$$\frac{1}{\beta N}\frac{\partial g(h,T)}{\partial h} = \langle N^{-1}\sum_{i=1}^{N} s_i\rangle = -M(h,t) \tag{6.110}$$

is the same as the spatial average, which constrained the trace in Eq. (6.108). This assumption is valid in self-averaging systems, but in general we know that not all systems are like that. Therefore, one should be careful in relating the free energy functionals which have been obtained by spatial cell averaging and functional Legendre methods.

Chapter 7

Phase-field models and density functionals

In many cases the construction of the free energy functional using the currently existing coarse-graining methods can be so laborous that it makes more sense to postulate the form of F using experimentally known phase diagram and symmetries of the system. The free energy (or coarse-grained Hamiltonian) can then be used as the generator of the relaxational dynamics towards thermodynamic equilibrium state. Historically one calls the class this type of modeling attempts Time-Dependent-Ginzburg-Landau models, models of critical dynamics or phase-field modeling [246]. There exists a number of ways to determine the form of the time evolution of the coarse-grained variables. The models of critical dynamics [126] can be derived at least by projection operator [14] formalism, mode-coupling techniques [247] and correlation functions [244] approach but none of these methods makes the free energy such a central concept as the phase-field technique. One of the major goals of this chapter is to try to convince the reader that phase-field models can be derived from microscopics in pratice, too. For this, one needs too things. First, we need to get the form of the equation of motion. This is given to us by the nonequilibrium generating functional method as detailed in Sect. 7.1. Second, we need an explicit representation of the free energy functional in the relevant field variables. This can be obtained either phenomenologically (Sect. 7.2), or from density functional theory (Sect. 7.3).

7.1 Connections with the general formalism

We will first show how the form of the stochastic evolution equation of phase-field formalism rises from the general principles in Sect. 7.1.1. It turns out that postulating a simple set of rules, which govern the evolution and relaxation to thermal equilibrium at the classical level, result in the same equation as shown in Sect. 7.1.2. Even if the reader has doubts about the validity of going from quantum world to classical as presented above, it is always possible to resort solely to the postulates of Sect. 7.1.2 to generate the equation of motion with no recourse to quantum mechanics.

7.1.1 Form of the evolution equation

Let us remind ourselves on the general principles presented in Chap. 2. There we showed how the stationarity condition of the effective action $\mathcal{A}$ generates the equation of motion of relevant macrovariable fields $\langle\psi_\mu\rangle$:

$$\frac{\delta\mathcal{A}[\langle\psi\rangle]}{\delta\langle\psi_\mu\rangle(\mathbf{x},t)} = 0 \ , \tag{7.1}$$

where we have set external sources to zero. Separating out the time derivative terms of the action we can write the previous equation as

$$\partial_t\langle\psi_\mu\rangle + \hat{\Xi}_{\mu\nu}\frac{\delta\tilde{F}[\langle\psi\rangle]}{\delta\langle\psi_\nu\rangle(\mathbf{x},t)} = 0 \ . \tag{7.2}$$

This equation of motion is exact, in principle. Our first approximation assumes that in the classical limit, where $\hbar$ becomes small compared to the value of the action, classical Poisson brackets will replace any quantum commutators appearing in the streaming (non-dissipative) part of Eq. (7.2). Thus, as we have argued in Sect. 3.1.2, the classical approximation to the full evolution equation (7.2) should for conserved multicomponent field ψ look like

$$\partial_t\langle\psi_\mu\rangle = -\int d\mathbf{x}'\int dt' \ \{\langle\psi_\mu\rangle(\mathbf{x},t), \langle\psi_\nu\rangle(\mathbf{x}',t')\} \frac{\delta\tilde{F}[\langle\psi\rangle]}{\delta\langle\psi_\nu\rangle(\mathbf{x},t)} - \hat{\Gamma}_{\mu\nu}\frac{\delta\tilde{F}[\langle\psi\rangle]}{\delta\langle\psi_\nu\rangle(\mathbf{x},t)} \ , \tag{7.3}$$

Due to the extremely high degree of nonlinearity of $\tilde{F}$ we expect that the completely deterministic dynamic system described by Eq. (7.2) may relaxe to a steady state even if the underlying microscopic many-body system was isolated (Hamiltonian). Periodic motion is also possible but not the focus here. If the underlying microscopic model is an open system, dissipation will result and steady-state relaxation is again expected. In case the steady-state is Gibbsian, we can approximate the approach with a *stochastic* evolution equation

$$\partial_t\psi_\mu = -\int d\mathbf{x}'\int dt' \ \{\psi_\mu(\mathbf{x},t), \psi_\nu(\mathbf{x}',t')\} \frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x}',t')} - \hat{\Gamma}_{\mu\nu}\frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x},t)} + \eta_\mu \ . \tag{7.4}$$

The expectation values from the field $\langle\psi_\mu\rangle$ have been dropped since the introduction of the noise field η_μ means that some degrees of freedom have been left unaveraged. The properties of the noise η can be in principle obtained from Eq, (7.2). In practice this means that we have to perturbatively expand $\tilde{F}$ around the chosen steady-state. Sometimes this works, but in general obtaining the noise requires the use of some non-perturbative tools. However, when relaxation towards thermodynamic Gibbs equilibrium is concerned, we know that the properties of η can be fixed at Gaussian level from the known value of the dissipative coefficient (operator) $\hat{\Gamma}$ through the fluctuation-dissipation theorem, which must hold at equilibrium. Instead of trying to derive F from first principles by first computing $\tilde{F}$, we can utilize less heavier techniques, which lead to fully satisfactory results as will be shown in this chapter.

There are many ways of obtaining the coarse-grained equations of motion for the relevant set of macro-observables. Sect. 7.1.2 first presents the general framework called Poisson bracket formalism, which yields a set of stochastic evolution equations reproducing standard thermodynamics in the limit of observation time going to infinity. in Sect. 7.3 it will be shown how the key ingredient of the formalism, the free energy functional F, can be obtained from classical density functional theory of fluids, and how its appearance can be simplified for further analytic and numerical work. We also point out that similar equations of motion for the relevant variables are arrived at by employing Mori type of projection operator methods either to the time dependent observables directly [27] or to the distribution functions [248].

7.1.2 Cookery book recipe for Poisson bracket formalism

There are several ingredients needed for coarse-graining the macroscopic phase-field model out of microscopic many-particle description. Below we will freely quote the most important features of the state-of-the-art method [5, 126] for construction of phase-field models.

- Need to assume a Gibbsian equilibrium distribution that the microscopic many-body system, which we wish to coarse-grain, will relax to in the limit $t \to \infty$.

  $$\lim_{t\to\infty} P(t) \to P_{eq} \propto e^{-\beta\mathcal{H}_N} \ , \tag{7.5}$$

  where $\mathcal{H}_N$ is the *microscopic* Hamiltonian of the N-particle system.

- There exists a coarse-grained probability distribution for macroscopically relevant degrees of freedom, which is obtained by tracing out (Tr') fast degrees of freedom of the microscopic distribution:

  $$\mathrm{Tr}'\, e^{-\beta\mathcal{H}_N} \sim e^{-\beta F[\psi]} \ . \tag{7.6}$$

  Hamiltonian $\mathcal{H}_N$ has been replaced by free energy F and the microscopic degrees of freedom by a macroscopic (phase) field $\psi = \{\psi_\mu\}$.

- One assumes that there is a *macroscopic* Poisson bracket relation giving the time evolution of any macrovariable analogous to the *microscopic* Poisson bracket relation

  $$\partial_t A_\mu = \{\mathcal{H}_N, A_\mu\} \longrightarrow \partial_t \psi_\mu = \{F, \psi_\mu\} + R_\mu \tag{7.7}$$

  Above, operators A_μ are just some functions of the microscopic coordinate and momenta. The form of the terms in R_μ are fixed by the final requirement below.

- The probability distribution of the macro system in equilibrium should be $e^{-\beta F[\psi]}$. This gives rise to stochastic and dissipative terms in the equation of motion for the components ψ_μ of phase field (order parameter field). Typically,

  $$R_\mu = -\hat{\Gamma}_{\mu\nu}\frac{\delta F}{\delta \psi_\nu} + \eta_\mu \tag{7.8}$$

  Comparing Eq. (7.7) and Eq. (7.8) with Eq. (7.4) shows that plausible but ad-hoc assumptions about the phase-field dynamics generate an equation of motion, which approximates the complicated true dynamics of Eq. (7.3) with the aid of a stochastic process.

Above the underlying microscopic Hamiltonian mechanics was manifest in two ways. First, the macrovariable equilibrium distribution is of the form $e^{-\beta F}$, which is convinient for calculations. Second, the way the macroscopic Poisson brackets are obtained from the microscopic ones assumes the existence of the microscopic Hamiltonian equations of motion. However, if our starting point is not a microscopic Hamiltonian system but an intermediate mesoscopic scale description having stochastic elements due to the effect of coarse-graining, the effective description on an even higher level of coarse-graining given in terms of the Langevin equation (7.7) still makes sense. The methods, have to be changed, though, since the Poisson bracket formalism, which we employ here, assumes the existence of microscopic Poisson brackets. For example, one can try to come up with macroscopic Poisson bracket relations based on intuition, or one can derive the terms of the Langeving equation by various projection operator methods [31]. The Langevin of Eq. (7.7), especially the structure of the Poisson bracket terms $\{F, \psi_\mu\}$ will be a subject of further study in Chap. 9. In particular, in App. D.4 we show how the form of the macroscopic Langevin equation becomes fixed through the requirement of relaxation into Gibb's equilibrium.

7.2 Construction of free energy from phase diagram

The simplest and in many cases the most efficient way of obtaining the free energy $F[\psi]$ introduced in Eq. (7.6) is to utilize the phase diagram and any other experimental information one may have on statics or dynamics of the system. For concreteness sake, let us build up the free energy for our three phase system, which we will use later on to study the wetting of different solid surfaces structures. For simplicity, we will concentrate on a single conserved, macroscopic density field $\psi_\mu = \phi$, which we call a phase-field. Different phases are distinguished by the different value the phase field takes in each of the bulk phases as will become clear soon.

So, how to derive the free energy functional, which supports the coexistence of three different phases (solid, liquid, gas)? Since thermodynamics tells us that systems seek for minimum of free energy, we expect F to have (at least) three wells corresponding to each of the stable equilibrium bulk phases. Hence, in the first approximation we write a Landau [32] type of attempt free energy

$$F = \int d\mathbf{x} \; \tfrac{1}{2}|\nabla\phi|^2 + V(\phi) \; , \tag{7.9}$$

where the function of the first term is to punish for rapid spatial variations of the phase-field ϕ. The emergence of the gradient term can be seen quite naturally from the experimental scattering data. Intensity of the reflected radiation I is proportional to the structure factor, which in the non-critical region is typically seen to have the following k-dependence [249]:

$$I \propto S(k) \sim \frac{1}{m^2 + k^2} \; , \tag{7.10}$$

where m^2 is a parameter that can be related to the compressibility of the system. On the other hand, $S(k) = \langle \phi(k)\phi(-k) \rangle$. The probability weight $\exp(-\beta F)$ over which the thermal average is calculated must have a free energy of the form

$$F[\phi] = \int d\mathbf{k} \; \phi(-\mathbf{k})(m^2 + k^2)\phi(\mathbf{k}) = \int d\mathbf{x} \; |\nabla\phi(\mathbf{x})|^2 + m^2\phi^2(\mathbf{x}) \tag{7.11}$$

to the lowest order in powers of ϕ. The mass term $m^2\phi^2$ can be adsorbed into the potential $V(\phi)$ and the remaining contribution is just the gradient term shown in Eq. (7.9). As we will see in the next section, the density functional theory, which gives a more precise form for the free energy, generates a term like $|\nabla\phi|^2$ only in the lowest order approximation. The improved form of the free quadratic interaction term of the free energy contains a non-local operator (Sect. 7.4), whose local approximation leads to the square gradient term.

In addition to the square gradient term, the information of the phase diagram has been encoded in the well structure of the potential $V(\phi)$, too. In case we would like to model a system (like water) in its triple point, we could write

$$V(\phi) = a\phi^2 - b\phi^4 + c\phi^6 \; , \tag{7.12}$$

where the constants a, b and c are all positive. Denoting the minima of $V(\phi)$ with ϕ_i $(i = a, b, c)$, three phase coexistence is guaranteed if $V(\phi_a) = V(\phi_b) = V(\phi_c)$. It turns out, however, that a free energy with potential V can only support a complete wetting regime, where the contact angle $\theta = 0$ by definition. In other words, the stable equilibrium situation towards which the system develops consists of a layer of water in between ice and vapor. We would like to be able to study partial wetting conditions where the contact angle can be freely adjusted. Moreover, we would like to be able to model a system, where the solid phase is not made up of the same type of molecules as the liquid and the gas. These two requirements lead to the introduction of a new thermodynamic degree of freedom, which we call ρ_S. Increasing the number of thermodynamic variables is the simplest construction which guarantees the ability to model partial wetting situation [231, 250].

The function of ρ_S is to act as an indicator field or characteristic function of the solid phase: when $\rho_S(\mathbf{x})$ takes a certain value, say $+1$ in scaled units, then the point $\mathbf{x}$ belongs to the fluid phase. When $\rho_S(\mathbf{x})$ takes another value, say -1, the point $\mathbf{x}$ is situated within the solid phase. As we will see in the next section, by shifting and scaling ρ_S suitably, we can make its physical interpretation as the density of the solid more apparent. Because the fluid phase hosts both the liquid and the gas phase, the potential needs to have a double well structure there. On the other hand, inside the solid phase the phase-field must have a single well structure as there is just one phase there. The simplest potential $V(\phi, \rho_S)$, which satisfies these requirements is

$$V(\phi, \rho_S) = (1/2)\,(1 + \rho_S)(\phi^2 - 1)^2 + K_s(1/2)\,(1 - \rho_S)(\phi - A)^2 \ , \tag{7.13}$$

where the meaning of the constant K_s will be discussed in Sect. 7.3. Clearly, when $\rho_S = +1$, onle the first term on the right is non-zero and the equilibrium values (densities) of the fluid are at $\phi = \pm 1$, corresponding to bulk values of the liquid and gas. When $\rho_S = -1$, only the last term on the right is non-zero fixing the equilibrium value of $\phi = A$ inside the solid phase. Of course, in reality, the fluid cannot go into the solid domain, but the phase-field needs to be defined everywhere as we do not keep track on the spatial location of the phase boundaries at the level of bulk fields. The meaning of A is contemplated in the next section. In Sect. 8.2.2 we will see that field A can be used to fix the values of the surface tensions and the equilibrium contact angles in a three phase system. Thus, the phase-field free energy becomes

$$F = \int dV \tfrac{1}{2}|\nabla\phi|^2 + V(\phi, \rho_S) \ , \tag{7.14}$$

with $V(\phi, \rho_S)$ given by Eq. (7.13). In Sect. 7.3 we show how this particular form of F can be justified from density functional perspective.

As a general rule of thumb of construction of Landau free energies (phase-field free energies), one should use minimal couplings between fields and respect the symmetries of the system, which are known either microscopically or experimentally. For complicated enough systems this type of semi-phenomenological approach might very well be the only sensible option in practice: Direct construction of density functional theory may prove to be too difficult. The disadvantage of the methodology described above is that the parameters of the free energy are not easily related to more microscopic parameters. Also, the symmetry principle guiding the form of the interaction terms in the free energy (couplings, powers of fields etc.) may not be strong enough to fix the form of the terms in the actual evolution equation of the field even though many universal (scaling related) phenomena are not that sensitive to the exact form of F. There are methods to fix the form of the coupling terms approximatively in the evolution equation. We will return to this subject again in Chap. 9.

7.3 Relating phase-field model to density functionals

As the microscopic starting point we consider a Hamiltonian many-body system with Lennard-Jones type of interaction potential between the fluid particles. To solve the static problem, *i.e.* the determination of the free energy functional F we can utilize various techniques discussed in Chap. 6. For example, we could try to calculate

$$\mathrm{Tr'}e^{-\beta\mathcal{H}_N} = e^{-\beta\Omega[\phi]} \propto \tag{7.15}$$

$$\sum_{N=0}^{\infty} \frac{1}{h^{3N}N!}\int d\mathbf{r}_1 \ldots d\mathbf{r}_1 \int d\mathbf{p}_1 \ldots d\mathbf{p}_N \; \delta\Big(\phi(\mathbf{r}) - \langle\hat{\phi}(\mathbf{r})\rangle_b\Big)\, e^{-\beta(\mathcal{H}_N - \mu N)} \; . \tag{7.16}$$

Classical trace in the previous formula is equivalent to integration over all coordinates and momenta, h is the Planck's constant. The 'cell' average of the microscopic exprssion of the total density, $\hat{\phi} \equiv \sum_{n=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$, over a cell of linear size b is denoted by $\langle\hat{\phi}\rangle_b$. For practical purposes it is more convinient to construct Ω using some other technique than doing the multiple integrals in Eq. (7.16). One possibility is to use classical density functional theory [228] a brief account of which is given in Sect. 6.1.2. The generalized grand canonical free energy density functional Ω_D for a fluid interacting with a solid wall is given by

$$\Omega_D[\phi] \equiv \frac{1}{2}\int_D d\mathbf{r} \int_D d\mathbf{r}'\, \tilde{w}(|\mathbf{r} - \mathbf{r}'|)\, \phi(\mathbf{r})\phi(\mathbf{r}') + \int_D d\mathbf{r}\, f_{HS}(\phi(\mathbf{r}), T) + \int_D d\mathbf{r}\, [V_S(\mathbf{r}) - \mu_0]\, \phi(\mathbf{r}) \; , \tag{7.17}$$

where $\phi(\mathbf{r})$ is the inhomogeneous density of the fluid. The solid walls in the present description only appear through the domain restriction D of the volume integration: the support is non-zero only in the region occupied by the fluid. The temperature of the fluid is T and the reference chemical potential is μ_0. Depending on the magnitude of μ_0 we can have coexistence of liquid and gas, or we can make either one of the two phases metastable. The free energy density of hard sphere reference fluid is denoted by f_{HS}. It contains the information on repulsive interactions in the system. The attractive interparticle potential between fluid atoms is $\tilde{w}$. Finally, V_S is the substrate potential. Note that we use the term 'generalized' grand canonical free energy for Ω_D, because it is only by minimizing Ω_D with respect to ϕ that yields the *thermodynamic* grand canonical free energy of the fluid at fixed temperature T and chemical potential μ_0.

The functional Ω_D can be cast into a local form by performing a gradient expansion for the slowly varying density field ϕ. The result is

$$\frac{1}{2}\int_D d\mathbf{r} \int_D d\mathbf{r}'\, \tilde{w}(|\mathbf{r} - \mathbf{r}'|)\, \phi(\mathbf{r})\phi(\mathbf{r}') \approx \frac{1}{2}\int_D d\mathbf{r}\, \varrho_0(\phi_u)|\nabla\phi|^2 + a'(\phi_u)\phi^2(\mathbf{r}) + \ldots \; , \tag{7.18}$$

where ϕ_u is the average uniform value of the density field around which we are expanding and $a'(\phi_u)$ is a constant. As a matter of fact, Eq. (7.18) is the low density limit of a more general gradient expansion which is discussed in Sect. 7.4. The mass matrix $\varrho_0(\phi_u)$ can be expressed in terms of direct pair correlation function $c^{(2)}$ (which is different from ordinary correlation function) as

$$\varrho_0(\phi_u) = \frac{1}{6}kT \int dr\, r^2 c^{(2)}(r, \phi_u) \; . \tag{7.19}$$

When combined with the quadratic terms of the expansion of $\tilde{w}$, the reference free energy density f_{HS} gives rise to the famous double well potential which can be approximated as $\varrho_2\phi^2 + \varrho_4\phi^4$. In order to be able to model a two-phase coexistence with the aid of *local* free energy density one needs to have non-convex potential (see also Sect. A). If non-local quadratic interaction is kept, then the potential part consisting of f_{HS} is convex even for two-phase coexistence. The local free energy density with square-gradient and non-convex potential part will not be able to model the detailed structure of wetting film in the manner of the non-local one, which gives a very reasonable description of both partial and complete wetting films [239, 251]. Of course, the existence of the substrate potential is also crucial for the detailed description of the film. We will show below that the effect of V_S can be generated by other means, too, if only the partial wetting regime is to be described (with finite contact angles) and no attention is paid to the film structure.

Since the solid phase does not appear in Eq. (7.17) except through the definition of the integration domain, we can define a new field ρ_S, which allows us to extend the integration over the whole space, including the solid domain. Let ρ_S be the indicator field (scaled density field) of the solid phase. In other words, $\rho_S = 1$ inside the solid phase ($\mathbf{r} \notin D$) and $\rho_S = 0$ in the fluid phase ($\mathbf{r} \in D$). We can then rewrite Eq. (7.17) as

$$\Omega_D[\phi] \approx \tilde{\Omega}[\phi, \rho_S] \ , \tag{7.20}$$

where the approximative equality follows from the use of the gradient expansion of Eq. (7.18), which enables us to write the new functional

$$\tilde{\Omega}[\phi, \rho_S] \equiv \frac{1}{2} \int d\mathbf{r}\, (1-\rho_S)\, \varrho_0(\phi_u) |\nabla\phi|^2 + \int d\mathbf{r}\, (1-\rho_S)\, \tilde{f}(\phi) + \int d\mathbf{r}\, (1-\rho_S)\, [V_S(\mathbf{r}) - \mu_0]\, \phi \ . \tag{7.21}$$

The effective double well potential is denoted by $\tilde{f}$. Because of the factors $(1 - \rho_S)$ the integrands are zero when we go outside of the original integration domain D. Therefore, in principle, we do not have to worry about the indefinite values of the ϕ field inside the solid domain as far as numerics goes. However, since the physical interpretation of the density functional theory requires that the values of both fields ϕ and ρ_S should be unambigiously given at all spatial points according to the physical values of the density there, we should assign the value $\phi(\mathbf{r}) = 0$ to the points $\mathbf{r} \notin D$, because the fluid density vanishes inside the solid. To enforce the vanishing fluid density inside the solid domain, we define

$$\Omega[\phi, \rho_S] \equiv \tilde{\Omega}[\phi, \rho_S] + \int d\mathbf{r}\, \rho_S \phi^2 \ . \tag{7.22}$$

The second term on the right is zero in the fluid phase, since $\rho_S = 0$ there. In the solid phase, the free energy functional $\Omega[\phi, \rho_S]$ clearly has a single parabolic well with minimum at $\phi = 0$. Thus, if we replace ϕ by its minimum value (which should be realized in the equilibrium) and substitute it into $\int d\mathbf{r}\, \rho_S \phi^2$, we notice that the thermodynamics should be unaffected as we have merely added a constant (zero) to the free energy.

Next, we argue that we can simplify the appearance of the functional Ω further by leaving out the term $\int d\mathbf{r}\, (1-\rho_S)(V_S - \mu_0)\phi$ by allowing the field ϕ be replaced with a new field $\tilde{\phi}$, which takes non-zero values even inside the solid phase. The new field $\tilde{\phi}$ cannot be interpreted as a density field any more. Rather, it becomes a *phase-field*, which takes a different value inside each of the phases (solid/liquid/gas). We define

$$\tilde{\phi}(\mathbf{r}) = \begin{cases} \phi(\mathbf{r}) \ , \ \text{for } \mathbf{r} \in D \ ; \\ A(\mathbf{r}) \ , \ \text{for } \mathbf{r} \notin D \ ; \ . \end{cases} \tag{7.23}$$

The new field A is constant in time but can possibly depend on spatial location within its domain. The field A can be interpreted as a 'wall potential' that gives rise to spatially dependent wetting properties of the solid walls. Its action is equivalent to the potential of the solid wall V_S, which makes partial wetting and metastable coexistance possible (V_S can be taken to contain the constant off-set $-\mu_0$). Hence, we obtain

$$\Omega[\phi, \rho_S] \doteq \Omega_A[\tilde{\phi}, \rho_S] \equiv \int d\mathbf{r} \, \left\{ (1-\rho_S)\left[\tfrac{m}{2} |\nabla\tilde{\phi}|^2 + \tilde{f}(\tilde{\phi}) \right] + \rho_S(\tilde{\phi} - A)^2 \right\} \; , \tag{7.24}$$

where the relational symbol $\doteq$ says that the two expressions of free energy have the same physical content: only the way the interaction between the fluid and solid phases is *controlled* has been changed, not the effect itself. According to Eq. (7.23), the field $\tilde{\phi}$ is identical to ϕ in the fluid phases and takes the *exact* value of $A(\mathbf{r})$ in the solid phase. With definition of Eq. (7.23), it is exactly true that $\int d\mathbf{r}\, \rho_S \phi^2 = \int d\mathbf{r}\, \rho_S (\tilde{\phi} - A)^2$. Even if we drop the requirement that $\tilde{\phi} = A$ in the solid phase, it still holds approximatively that $\int d\mathbf{r}\, \rho_S \phi^2 \approx \int d\mathbf{r}\, \rho_S (\tilde{\phi} - A)^2$. This is because the relaxational dynamics to be introduced below, drives the phase-field configuration towards such a state where $\tilde{\phi} \approx A$. In particular, well within the solid phase we expect the equality to hold. Small violations appear close to phase boundaries but their magnitude can be controlled by introducing a 'stiffness' parameter K_s such that instead of the free energy contribution $\int d\mathbf{r}\, \rho_S (\tilde{\phi} - A)^2$ we write (for unconstrained field $\tilde{\phi}$) $\int d\mathbf{r}\, K_s \rho_S (\tilde{\phi} - A)^2$. When K_s is large enough, the approximation $\tilde{\phi} \approx A$ becomes better and better even under non-equilibrium conditions, because the dynamics quickly relaxes any non-equilibrium configuration of the phase-field to its equilibrium value A, which is the minimum of the potential $(\tilde{\phi} - A)^2$. As a conclusion, we argue that the term $\int d\mathbf{r}\, K_s \rho_S (\tilde{\phi} - A)^2$ mimics the effect of the substrate potential on scales where $V_S(\mathbf{r}) \approx 0$. It is important to notice that if we extended the domain of the field A into the fluid domain, spatially varying thickness of the fluid film under complete wetting conditions could be modeled as well. With the current model we can only control only the contact angle. For more discussion on the role of the substrate potential consult Sect. 6.4.

Finally, we can define a shifted density field in such away that instead of the characteristic values of ρ_S being zero and one, we make them plus and minus one. The full free energy is now of the form

$$F = \int d^3r \, \left[(m/2)|\nabla\phi|^2 + (1/2)(1+\rho_S)\tilde{f}(\phi) + (K_s/2)(1-\rho_S)(\phi - A)^2 \right] \; . \tag{7.25}$$

Thus, we have ended up with the same expression as in Eq. (7.14), which obtained using the experimentally known phase diagram and structure factor! In the expression above we have allowed the gradients $\nabla\tilde{\phi}$ to vary in all space, so the factor $(1 - \rho_S)$ of the gradient term from Eq. (7.21) has been removed. The only effect, which is easy to estimate analytically, of the removal is that the magnitudes of the surface tensions are changed. This free energy will be utilized in Chap. 8 to derive explicit equations of motion for phase boundaries present under phase coexistence. Before doing that, we apply the cook book recipe presented in the beginning of the chapter to fix the dynamics. The solid density field ρ_S needs no equation of motion since we treat it as inert spectator phase in the current approximation. When momentum conservation is left out of the description of the problem, the Poisson brackets producing reactive couplings vanish completely in Eq. (7.7). The remaing term R has to have the structure

$$R = M\nabla^2 \frac{\delta F}{\delta\phi} + \eta \; , \tag{7.26}$$

where η is stochastic conserved noise with correlations

$$\langle \eta(x,t)\eta(x',t') \rangle = T\, M \nabla^2 \delta(x - x')\, \delta(t - t') \; . \tag{7.27}$$

The presence of the Laplacians (∇^2) is dictated by the fact that the fluid mass is conserved. The equation of motion for ϕ is

$$\partial_t \phi = R \ , \tag{7.28}$$

where the form of R guarantees relaxation to the equilibrium probability density $e^{-\beta F}$. Neglecting the noise means that we are cutting off the connection to the equilibriating heat bath. Since the fluctuations can be added later on, we wil first study the properties the model with no thermal noise and with no convective hydrodynamic modes. The generalization of the model to cover these important features is presented in Ch. (9)

7.4 Remarks on density correlations and gradient expansion

Let us try to see fit together the language of the density functional theory with the phase-field formalism by studying the two-point density correlation function. First, we note that the free energy, which the phase-field formalism utilizes is related to the grand potential Ω by the Legendre transformation with *constant* chemical potential μ:

$$F = \Omega - \mu N \ , \tag{7.29}$$

where $N = \int d\mathbf{x}\, \rho(\mathbf{x})$. Therefore, by leaving out the contribution of constant chemical potential we can use F instead of Ω. The Legendre trasformation that the classical density functional theory utilizes is with respect to external one-body potential $V_{ext}(\mathbf{x})$, which can be taken to be part of the total chemical potential. However, traditionally one separates these contributions and calls the constant part of μ the chemical potential and the varying part $V_{ext}(\mathbf{x})$ external field (potential). To make contact with the density functional literature, we divide

$$F_V[\phi] = F[\phi] + \int d\mathbf{x}\, V_{ext}(\mathbf{x})\phi(\mathbf{x}) \ , \tag{7.30}$$

where F_V can be seen as the functional Legendre transformation of F. To be more exact, we should write $F_V[V_{ext}] = F[\phi] + \int d\mathbf{x}\, V_{ext}(\mathbf{x})\phi(\mathbf{x})$ to make it explicity that the variable V_{ext} is replaced by the expectation value $\phi = \langle\hat{\phi}\rangle$ the brackets denoting average over equilibrium Gibb's distribution.

In Sect. 7.2 we showed hot the structure function gives rise to the gradient term in the free energy. Let us see now what kind of density correlation function (structure factor) is generated if we use the non-local density functional F derived in Sect. 6.1.2 as the phase-field free energy.

$$F[\phi] = F^0 + \frac{1}{2}\int_0^1 d\alpha \int d\mathbf{x}_1 \int d\mathbf{x}_2\ \rho_\alpha^{(2)}(\mathbf{x}_1, \mathbf{x}_2) U_1(r_{12}) \ , \tag{7.31}$$

where the interaction potential of the system U has been divided into the reference potential U_0 residing in the reference free energy F^0 and the two-body interaction U_1 as explained in Sect. 6.1.2. To compute the two-body function in the phase-field representation we make use of the following results from density funtional theory:

$$\frac{\delta \Omega}{\delta U(x_{12})} = \frac{\delta F}{\delta U(x_{12})} = \frac{1}{2}\rho^{(2)}(\mathbf{x}_1, \mathbf{x}_2) \ . \tag{7.32}$$

As shown in [229] (p. 158), these relations hold exactly. Treating the thermodynamic free energy F_T as a functional of the interaction potential, the phase-field formalism tells us that

$$\frac{\delta F_T}{\delta U(\mathbf{x}_{12})} = \frac{\delta}{\delta U(\mathbf{x}_{12})}(-\beta^{-1}) \ln Z \approx -\frac{\beta}{Z}\frac{\delta}{\delta U(\mathbf{x}_{12})}\int \mathcal{D}\phi\ e^{-\beta F} \tag{7.33}$$

$$= \frac{1}{Z}\int \mathcal{D}\phi\ \frac{\delta F}{\delta U(\mathbf{x}_{12})}\, e^{-\beta F} \approx \frac{1}{2}\rho^{(2)}(\mathbf{x}_1,\mathbf{x}_2)\,\frac{1}{Z}\int \mathcal{D}\phi\ e^{-\beta F} = \frac{1}{2}\rho^{(2)}(\mathbf{x}_1,\mathbf{x}_2)\ . \qquad (7.34)$$

So, Eq. (7.32) is confirmed as far as we can consider replacement of F by F_T as a reasonable approximation. However, it would be inconsistent to write $\delta F/\delta U(\mathbf{x}_{12}) \propto \langle\phi(\mathbf{x}_1)\phi(\mathbf{x}_2)\rangle$ because the functional F is not of the form $\int d\mathbf{x}' \int d\mathbf{x}'\ \phi(\mathbf{x})U(\mathbf{x},\mathbf{x}')\phi(\mathbf{x}')$ as $\rho^{(2)}$ is a non-linear functional of ϕ. In the low density approximation the quadratic form appears, but even then, it is not the full interaction potential U, which is sandwidched between ϕ's but $U_1 = U - U_0$.

To extract the quadratic approximation of F we Taylor expand it around a constant homogeneous density ϕ_u and consider fluctuations only to second order in $\Delta\phi(\mathbf{x}) \equiv \phi(\mathbf{x}) - \phi_u \ll \phi_u$. The free energy becomes ([231], p.99)

$$F[\phi] \approx F[\phi_u] + \frac{1}{2}k_B T \int d\mathbf{x}_1 \int d\mathbf{x}_2\ \Delta\phi(\mathbf{x}_1)\Big(\frac{\delta(\mathbf{x}_1-\mathbf{x}_2)}{\phi_u} - c(|\mathbf{x}_1-\mathbf{x}_2|,\phi_u)\Big)\Delta\phi(\mathbf{x}_2)\ , \qquad (7.35)$$

where c is the direct correlation function of the system. The direct correlation function (minus the delta function) is related to the inverse of the pair correlation function as we will see soon. In the Fourier space

$$F[\phi] \approx F[\phi_u] + \frac{1}{2}k_B T \int d\mathbf{q}\ \Delta\phi(\mathbf{q})\Big(\frac{1}{\phi_u} - c(q,\phi_u)\Big)\Delta\phi(-\mathbf{q})\ . \qquad (7.36)$$

Direct computation yields

$$G(\mathbf{k},\mathbf{k}') = \langle\Delta\phi(\mathbf{k})\Delta\phi(\mathbf{k}')\rangle = \Big(\frac{1}{\phi_u} - c(q,\phi_u)\Big)^{-1} = \ \chi(\mathbf{k})/\beta \propto S(\mathbf{k})\ , \qquad (7.37)$$

where $\chi(\mathbf{k})$ is the static density response function and the last relation follows from the definition of the structure factor S. A more cumbersome way of seeing this is to operate in real space. We define a matrix

$$K_S(\mathbf{x},\mathbf{x}') \equiv \frac{\delta(\mathbf{x}-\mathbf{x}')}{\phi_u} - c(|\mathbf{x}-\mathbf{x}'|,\phi_u) \qquad (7.38)$$

The path integration $\int\mathcal{D}\phi\,\phi(\mathbf{x})\phi(\mathbf{x}')\exp(-\beta F) = K_S^{-1}(\mathbf{x},\mathbf{x}') = G(\mathbf{x},\mathbf{x}')$ gives the inverse kernel. It should be kept in mind that $K_S^{-1}(\mathbf{x}_1,\mathbf{x}_2) \neq 1/G(\mathbf{x}_1,\mathbf{x}_2)$ but

$$\int d\mathbf{x}_3\, K_S^{-1}(\mathbf{x}_1,\mathbf{x}_3)G(\mathbf{x}_3,\mathbf{x}_2) = \delta(\mathbf{x}_1-\mathbf{x}_2)\ . \qquad (7.39)$$

Strictly speaking, K_S is determined as a function of a space dependent equilibrium density $\phi_0(\mathbf{x})$ as shown in Ref. [228]. Correspondingly, the correlation function is also defined as $G = \langle(\phi(\mathbf{x})-\phi_0(\mathbf{x}))(\phi(\mathbf{x})-\phi_0(\mathbf{x}))\rangle$ and $c(k,\phi_u)$ is replaced with $c^{(2)}(k,\phi_0)$. We have simply evaluated the functional Taylor series expansion of $F[\phi]$ around the point $\phi_u = const.$

We can continue simplifying the non-local functional (7.35) further. Usually, the direct correlation function of a uniform fluid is short-ranged [231]. Hence, we can write

$$\Delta\phi(\mathbf{x}_2) \approx \Delta\phi(\mathbf{x}_1) + (\mathbf{x}_{12}\cdot\nabla)\Delta\phi(\mathbf{x}_1) + \tfrac{1}{2}(\mathbf{x}_{12}\cdot\nabla)^2\Delta\phi(\mathbf{x}_1) + \dots\ . \qquad (7.40)$$

Expansions utilizing of derivatives of density are realistic only in situations where the spatial variation of the density ϕ is slow over atomic distances, e.g. close to spinoidal (p. 15, Ref. [233]). However, the full non-local form of the quadratic interaction term should be used when the inhomogeneities are steeply varying [252]. By choosing the order-parameters cleverly (Fourier coefficients of the density profile instead of densities) even the nucleation of crystal out of the melt has been considered [253] using square-gradient approximation. Substitution of the expansion (7.40) into Eq. (7.35) yields [231, 228]

$$F[\phi] = \int d\mathbf{x}\ \tfrac{1}{2}\varrho_0(\phi_u)|\nabla\phi(\mathbf{x})|^2 + f^0(\phi(\mathbf{x})) + \dots\ . \tag{7.41}$$

where the prefactor function $\varrho_0(\phi_u) = (k_b T/6) \int d\mathbf{x}\, c(r, \phi_u)$. Moreover, it has been assumed that we can replace the argument ϕ_u of the reference free energy density f^0 of the homogeneous fluid by $\phi(\mathbf{x})$.

The important physics can be read off from the lowest order terms of the expansion. The density and temperature dependent value of ϱ_0 affects the surface tension of the system as well as on the bulk correlation length especially in the critical region. Moreover, the prefactor function of the quadratic term $\phi^2(\mathbf{x})$ is

$$\varrho_2 \equiv -k_B T\left(c_a(\phi_u) - \frac{1}{\phi_u}\right)\ , \tag{7.42}$$

where $c_a(\phi_u)$ is the k-independent term of the expansion $c(k, \phi_u) \approx c_a(\phi_u) + c_b(\phi_u)k^2$. The fluid is stable against fluctuations whose wavevectors satisfy $\varrho_2 > 0$. Spinodal decomposition takes place in the negative compressibility region $\varrho_2 < 0$. Of course, there are higher order terms which provide a cut-off for unstable modes.

Chapter 8

Phase boundary dynamics in liquid-gas-solid system

Having described the coarse-graining formalism in practice for macroscopic quantum phenomena, we are now ready to move onto another application, which has to do with the dynamics of classical fluids in contact with solid phase. Our goal is to model both the bulk and interfacial dynamics of a liquid-gas system confined by solid wall(s). In particular, we want to derive the equations of motion for the meniscus (two dimensional liquid-gas phase boundary) and the contact line (one dimensional line, where all the three phases meet) starting from the 3D bulk equations of motion. The formalism flexible enough to allow for the description of considerabley more complicated set-ups but for concreteness sake we present in glory detail the calculations for the following system:

A column of liquid is confined between two vertical straight walls situated at $y = 0$ and $y = L$. Both finite and infinite wall separations will be considered. The liquid rises spontaneously under the action of capillary forces. It is connected with an infinite reservoir which fills the lower half-space $z \leq 0$. The reservoir is not explictly modeled and its presence will be felt only through boundary conditions to be discussed later. The walls are assumed to be smooth but they can contain chemical impurites, which alter the local wetting properties: The advancing contact line wants to visit the more easily wettable (energetically more favourable) regions of the walls and avoid others. Of course, the surface tension takes care of the fact that a section of the triple line slowly traversing through a hard to wet region cannot fall too much behind from the more rapidly advancing parts giving rise to an avalanche type of motion [4]. Because the contact line roughens in the course of time, it also affects the morphology of the meniscus and vice versa.

Why should on be interested in the dynamics of lines and interfaces in the first place? Because they are a natural part of the coarse-graining chain. First of all, as lower dimensional subsets of slow variables they are relevant macroscopic variables themselves. In the present context they can be interpreted as Goldstone modes of the bulk system, which have long life times. Another fact, which justifies their study, has to do with reduction of information content. Because many physically relevant processes take place on interfaces such as phase and grain boundaries [18] the bulk degrees of freedom are not directly relevant or their effect can be taken into account indirecetly through suitable boundary conditions, for example. In

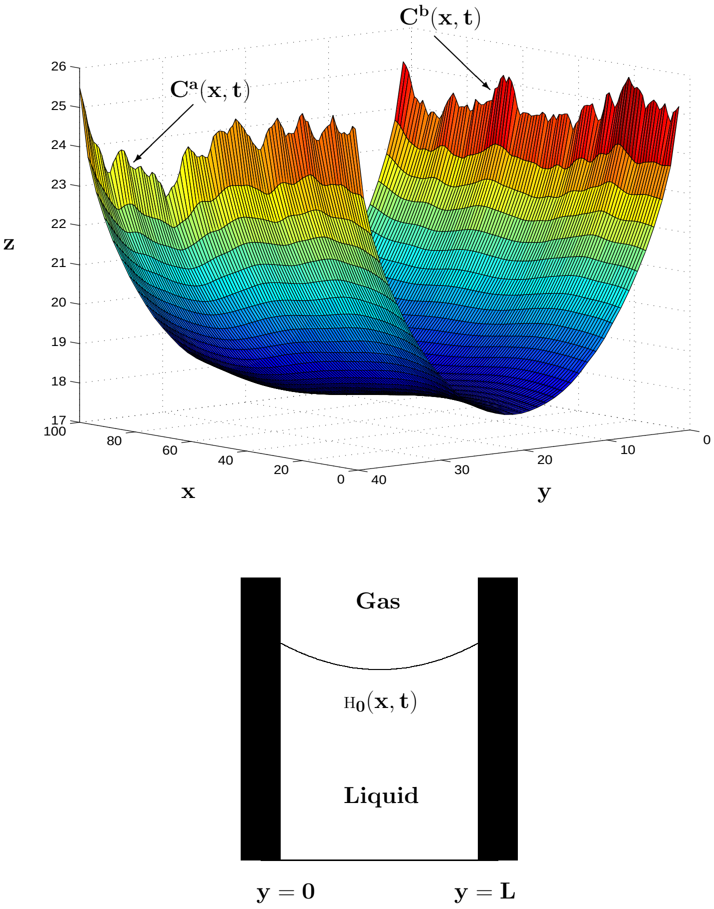

Figure 8.1: Top view shows the meniscus $\mathrm{H}(x, y, t)$ rising between two chemically inhomogenous walls, which cause the contact lines $\mathrm{C}^s(x, t)$ $(s = a, b)$ to roughen. The lower figure provides a side view of the parabolic meniscus profile $\mathrm{H}_0(y, t)$.

this sense the bulk can be sometimes seen to act as a kind of a heat bath on the subsystem (=interface) degrees of freedom. Integrating, or more appropriately for the purposes of this chapter, projecting out the bulk can considerably simplify the computational task of finding out what happens at phase boundaries. Of course, there are limitations just like in the many-particle models where one tries to obtain an effective model for fewer degrees of freedom by 'integrating out' the effect of some particles (degrees of freedom). A blind elimination of uninteresting degrees of freedom, when continued far enough, results in a intractable model with very complicated effective interactions between the remaining degrees of freedom. The complication present in the huge number of constituents with simple interactions transforms into the not-so-simple (≈ hopelessly difficult) interaction between the surviving constituents.

A distant indication of this can already be seen in App. C.14.6 where the coupled equations of motion are given for the interaction of two contact lines in the double wall set-up. These equations are approaching the limit where analytic work is still feasible.

8.1 Where do we stand in the coarse-graining chain?

At this point it is good to remind ourselves of our current location in the big scheme of things. To establish a link of the material to be presented in this chapter to the general theme of coarse-graining, go back to Sect. 7.1.1 where we tried to justify the general form the time evolution equation that any macroscopically relevant quantum observable should have. As far as the expectation values of the observables can be considered classical, and the limit (action of generating functional)/$\hbar \to \infty$ can be taken, the equation of motion (7.4) for conserved classical fields ψ_μ reads

$$\partial_t \psi_\mu = -\int d\mathbf{x}' \int dt' \; \{\psi_\mu(\mathbf{x},t), \psi_\nu(\mathbf{x}',t')\} \frac{\delta F[\psi]}{\delta \psi_\nu(\mathbf{x}',t')} + M\nabla^2 \frac{\delta F[\psi]}{\delta \psi_\mu(\mathbf{x},t)} + \eta_\mu \; , \tag{8.1}$$

where we have set $\hat{\Gamma}_{\mu\nu} = -M\nabla^2 \delta_{\mu\nu}$. First, we should determine the physical meaning of the fields ψ_μ. Conserved, and thus slow variables of the three-phase system consist of the mass, momentum and energy densities of the fluids given that the solid can be regarded as an inert spectator phase. For simplicity we only consider the total mass density of the fluids here. Inclusion of the momentum and energy densities will be considered in the next chapter. The next step is the determination of the free energy F_{3D}. Classical density functional theory introduced in Chap. 6 allows us to bridge the length scale gap between the molecular fluid and the macroscopic density representation. Thus, F_{3D} has the form given in Eq. (7.25). Hence, supposing that the mass density of the fluid is the only relevant macrovariable, $\psi_\mu = \phi(\mathbf{x},t)$ and the Poisson bracket term on the right of Eq. (8.1) vanishes. If we also drop the stochastic term η for simplicity, Eq. (8.1) reduces to a nonlinear diffusion type of equation of motion for the bulk field ϕ:

$$\partial_t \phi(\mathbf{x},t) = M\nabla^2 \frac{\delta F_{3D}[\phi]}{\delta \phi(\mathbf{x},t)} \; . \tag{8.2}$$

This result could have been obtained right away using physical intuition. Because ϕ is conserved, it should follow a continuity type of equation, $\partial_t \phi + \nabla \cdot \mathbf{j}_\phi = 0$. The conserved current can in first approximation to be the gradient of the driving chemical potential according to Fick's law: $\mathbf{j}_\phi = -M\nabla\mu$ and by definition $\mu = \delta F_{3D}/\delta\phi$. Combining all this leads immediately to Eq. (8.2).

There are regimes for physical parameters where the dropping of the momentum density can be justified in the dimentional analysis sense as will be shown in Sect. 10.4. Of course, in reality, leaving out momentum conservation will not be a good approximation which holds in all space points $\mathbf{x}$. The dimensional analysis argument holds only in spatial average sense over suitable chosen scales. It turns out that the dynamics induced by the equation of motion (8.2) is rather boring far a way from the phase boundaries: The density field ϕ simply relaxes to its constant bulk equilibrium value and does not change after a while. The interesting dynamics takes place only in the vicinity of the boundaries where multiple phases meet. Therefore, we will project out the uninteresting bulk degrees of freedom and concentrate on studying the evolution of the lower dimensional structures, which include two dimensional phase boundaries and one dimensional triple lines (contact lines).

The main theoretical findings of Chap. 8 consist of the coupled set of equations of motion for the meniscus and the contact lines in the geometry depicted in Fig. 8.1. The linearized equation of motion for the fluctuations $h(\mathbf{k},t)$ of the meniscus will be presented in Eq. (8.65) for single wall set-up:

$$g_1(k,t)\,\partial_t h(\mathbf{k},t) + g_2(k,t)\,h(\mathbf{k},t) = -\frac{M\sigma}{4}k^2\,h(\mathbf{k},t)\ . \tag{8.3}$$

This equation tells us how the local velocity (term $g_1\partial_t h(\mathbf{k},t)$) of the meniscus depends on the local (and nonlocal) features of the geometry. The prefactor functions g_1 and g_2 contain important physics. All the relevant time and length scales of the problem can be extracted from them as will be explained in Sect. 8.3. The contact line equation, which acts as boundary condition for the meniscus equation, is given in Eq. (8.58) and Eq. (8.61). Combining them yields the following equation for the fluctuations $c(\mathbf{k},t)$:

$$|k|^{-2}f_1(\mathrm{c}_0|k|)\,\partial_t c(k,t) + \frac{\partial_t \mathrm{c}_0}{|k|}f_2(\mathrm{c}_0|k|)\,c(k,t) = M\Gamma(k)\,c(k,t) + MA_k[\mathrm{c}_0,c] \tag{8.4}$$

The structure of this equation is the same as Eq. (8.3). On the right hand side we have a deterministic restoring force $\Gamma(k)$, which counteracts the stochastic pinning force A_k stemming from the chemical inhomogeneity of the walls. It is the stochastic force, which makes the contact line rough and the meniscus crumbled. In moving from the Molecular Dynamics description to the large scale physics given by Eq. (8.4) the span of the time and lenght scales is huge: From molecular collision times and mean-free paths to features visible to bare eye!

The next step in making the model more realistic is to take into account the momentum conservation of the fluid particles. This leads to a fully hydrodynamic description of the three phase model which is the focus of Chap. 9. The reason why we have not talked about the momentum conservation in this chapter is that the general methods applied in the derivation of the hydrodynamic equations of motion in Chap. 9 are not restricted to the contact line problem in any way. We will briefly touch on the generalization of the evolution equation (8.2) in Sect. 10.2 at the Stokes' flow level, where the inertial terms of the momentum balance equation disappear. The projection formalism given in this chapter then produces new terms in the meniscus and contact line equations. The derivation and study of them is left for future work.

8.2 Coarse-graining model parameters from microscopics

8.2.1 Crossing quantum-classical boundary: van der Waals forces

In the Born-Oppenheimer approximation one can try to form the effective many-body force fields between nuclei, which can thereafter be treated as classical 'atoms' (or ions). It is then, in principle, possible to go on developing classical Molecular Dynamics based approach for the coarse-grained degrees of freedom, which calls for more approximations and causes accumulation of errors. Even though we are never free from approximations, it is sometimes more convenient not to introduce intermediate coarse-graining steps, but take one bigger leap instead. This approach works nicely for determination of macroscopic surface tensions from the quantum mechanics.

Simplifying things a bit, one can say that the surface tensions are produced by van der Waals forces, which depend on the electronic structure of the materials in contact. To put it in another way, the electronic structure determines the optical properties of materials, which give rise to the London dispersion forces, the most significant element of the van der Waals force. The importance of optical properties can be understood by the fact that quantum fluctuations induce dipole-dipole interactions most efficiently in the spectral range varying from visible to vacuum ultraviolet spectrum [254]. Thus, even completely neutral surfaces can attract each other thorough quantum fluctuation induced forces. One of the well-known examples of this phenomenon is the Casimir effect [255]

To accomplish the calculation of the surface energies one now resort to either analytic or computational techniques. On the analytical side, one can use finite temperature Green's function formalism [256] (to which our generating functional formalism reduces in equilibrium) to compute effective interaction between macroscopic bodies as a function of their separation. On the computational side one can perform a first-principles calculation using the quantum density functional theory discussed in the previous chapter 6. In practice, one computes the interface energy per unit area (surface tension) for a system comprised of a thin film of material of type B between slabs of material A and C. Depending on the surface tension one wishes to calculate, some of the materials can be the same or vacuum. One obtains $E_{AC}(L_f, \varepsilon)$, where L_f is the thickness of the intercalating film. The expression for $E_{AC}(L_f, \varepsilon)$ makes also use of the London dispersion spectra of the materials [257] (dielectric constant ε), which can be obtained from experimental data or first-principles calculations [254]. More precisely, the surface tension σ_{AC} is related to $E_{AC}(L_f, \varepsilon)$ through

$$\sigma_{AC} = -\frac{1}{2} E_{AC}(L_f, \varepsilon_A, \varepsilon_B, \varepsilon_C) \ , \tag{8.5}$$

because there are two interphases in the three slab system (ABC) where the intercalating layer B is the vacuum. Moreover, L_f cannot be taken to zero: It is of the order of interatomic bond length. It is also important to notice that another coarse-grained quantity, namely the dielectric constant ε has entered our hierarchical construction. Microscopically, ε tells how the interaction of two charged objects embedded in polarizable material change due to polarization effects, which are of many-body nature: interaction with phonons leads to screening of charges [258]. Macroscopically, ε binds together the (macroscopic) eletric field $\mathbf{E}$ and the (macroscopic) electric displacement field $\mathbf{D}$:

$$\mathbf{D} = \varepsilon \mathbf{E} \tag{8.6}$$

in homogenous medium. These macro fields have been obtained by spatially coarse-graining (averaging over semi-macroscopic cells) the microscopic Maxwell's equations [259]. Since Eq. (8.6) can also be written as $\mathbf{D} = \varepsilon_0(1 + \chi_E)\mathbf{E}$, where

$$\chi_E \equiv \frac{1}{\varepsilon_0} \frac{\partial \mathbf{P}}{\partial \mathbf{E}} \tag{8.7}$$

is the electric susceptibility and $\mathbf{P}$ is the polarizability, we see that ε represents a generalized susceptibility. Thus, it is not a transport coefficient, because it does not bind a field to a current but it mediates a linear response between two macroscopic fields just like the transport coefficients do, and so its expression can be coarse-grained in a similar way from microscopics. Using ε, we can express the surface tension as a function of parameters belonging to different levels of effective descriptions:

$$\sigma = \sigma(\varepsilon(\hbar, e, m_e)) \ . \tag{8.8}$$

Electron's mass m_e and charge e represent the dependence on the quantum mechanical degrees of freedom, which themselves can be functions of more microscopic parameters, in principle at least. We should keep in mind, though, that crossing of scales in cases, which are not as well known as the present example, will not be easy. Here we have had the luxury to bypass many pitfalls by utilizing knowledge, which has accumulated over several decades of research in the area.

This section will finish with a remark on the disjoining pressure, which also arises do to van der Waals forces, and plays an important role in the hydrodynamics of wetting. The surface tensions only capture the short-range effect of the van der Waals-London forces as seen from the definition (8.5): The distance L_f is of the order of the bond length, so the energy E_{AC} contains effects such as covalent bonding. But the van der Waals forces are long-ranged. For two dipoles the force decays like r^{-7} as a function of the distance. For two macroscopic surfaces separated by distance ζ, combining the effect of all individual dipoles leads to a long range force F_{vdW}, which follows another power law: $F_{vdW} \sim \zeta^{-3}$. The corresponding interaction energy [254],

$$E_{vdW}(\zeta) = -\frac{A^H}{12\pi\zeta^2} \ . \tag{8.9}$$

The constant A^H is called Hamaker's constant, and its value dependes on the matrials, whose interaction energy is being evaluated as well as on the the shape of the bodies. Hamaker's constant can be postive or negative. When negative, it produces a repulsive force between solid surface and the liquid-gas boundary of the wetting layer, which corresponds to the material B sandwidched between the solid A and gas C using our earlier nomenclature. The disjoining pressure $\Pi(\zeta)$, which tends to thicken the wetting layer, is then defined as $\Pi \equiv -dE_{vdW}/d\zeta$. Inversely, $E_{vdW}(\zeta) = \int_\zeta^\infty d\zeta' \, \Pi(\zeta')$. In deriving the equation of motion of the contact line, one must then include the disjoining pressure (long range van der Waals energy) in the free energy functional F_{1D} [260]:

$$F_{1D} = F_0 + \int_{x_{min}}^{x_{max}} dx \left(-S + \tfrac{1}{2}\sigma(d\zeta/dx)^2 + E_{vdW}(\zeta) + G(\zeta) \right) \ . \tag{8.10}$$

The reference free energy is F_0, S is the spreading coefficient and G describes the gravitational and hydrostatic effects. The domain covered by the liquid is confined between x_{min} and x_{max}. This is essentially the form of the free energy ($\zeta = c$) which we will be using in later sections apart from the term E_{vdW}. As we are not intrested in the microscopic motion of the precursor film, we drop the van der Waals energy. Taking E_{vdW} into account would bring about a new term on the right hand side of Eq. (8.89), for example.

8.2.2 Surface tensions from classical Density Functional Theory

Another possibility of determining the macroscopic surface tensions is to introduce an intermediate coarse-graining stage, which is the classical Molecular Dynamics level. In terms of the effective two-body (and higher) interaction forces one can derive the classical free energy density functional which can then be used for determination of the surface energies in terms of the parameters of the free energy. This has been done in Refs. [261, 239]. First, the liquid-gas surface tension,

$$\sigma = \frac{1}{2}(\Delta\rho)^2 \int_0^\infty dz \ t(z) \ , \tag{8.11}$$

where $\Delta\rho$ is the liquid-gas density difference and z-direction is opposite to the solid substrate surface. The potential of the fluid particle interacting with the other fluid particles filling the upper half space is denoted by $t(z)$:

$$t(z) \equiv \int_z^\infty dz' \int_{-\infty}^\infty dx' \int_{-\infty}^\infty dy' \ \tilde{w}(r') \ , \tag{8.12}$$

with $r' = \sqrt{x'^2 + y'^2 + z'^2}$. The attractive part of the effective two-body potential $\tilde{w}$ has been given in Eq. (6.81). The solid-liquid surface tension reads,

$$\sigma_{sl} = -\frac{1}{2}\rho_l^2 \int_0^\infty dz \ t(z) + \rho_l \int_{d_w}^\infty dz \, V_S(z) \ . \tag{8.13}$$

The interaction between the solid and the fluid particles leads to a formation of the narrow depletion layer whose width is d_w [239]. This is of the order of the interatomic bond length, as discussed in Sect. 8.2.1. The origin of the substrate potential V_S has been explained in Sect. 6.4.1. Finally, the solid-gas surface tension

$$\sigma_{sg} = \Omega_s(l_0) \ , \tag{8.14}$$

where Ω_s is the effective interface potential (free energy) which can be extracted from the free energy (7.17) by substituting the sharp-interface ansatz,

$$\phi_l(z) = \theta(z - d_w)\Big(\theta(l - z)\rho_l + \theta(z - l)\rho_g\Big) \ , \tag{8.15}$$

and collecting the terms which are proprotional to the interfacial area. The bulk densities of the liquid and gas have been denoted by ρ_l and ρ_g in Eq. (8.15) and the width of the liquid layer is l. The value l_0 of l which minimizes Ω_s appears on the right hand side of Eq. (8.14). Finally, θ stands for the Heaviside step function above.

Having now extracted the values of the surface tensions from the classical density functional theory, let us do the same thing using our phase-field formulation, which has been explained in Sect. 7.3. The procedure is well-known [231] and follows the same lines as in the density functional case. One of the main differences is that the phase-field free energy (7.25) is local in its argument fields and therefore the sharp kink approximation used in Eq. (8.15) is not a good one any more. Instead, to get analogous results from the phase-field theory, one should substitute an ansatz like

$$\phi(z) \approx \tanh((z - l)/\xi) \ , \tag{8.16}$$

where we have assumed that ρ_g ρ_l have been shifted to values ± 1 in dimensionless units. The bulk correlation lenghth ξ is a function of the parameters of the phase-field free energy, and when it goes to zero, we recover Eq. (8.15). Using this type of approach combined, the surface tensions have been calculated in Ref. [262]. We get

$$\sigma = 2\sqrt{2}/3 \tag{8.17}$$

in our dimensionless unit system where the liquid and gas densities have been shifted to $\phi = \pm 1$. The solid-liquid surface tension will have a more interesting dependence of the parameters of the (phase-field) free energy (7.25):

$$\sigma_{sl}(\bar{A}, K_s) = \frac{\phi_1^3 - 3\phi_1 + 2}{3\sqrt{2}} + \frac{\sqrt{K_s}}{2}(\bar{A} - \phi_1)^2 \ , \tag{8.18}$$

where the auxiliary function

$$\phi_1 \equiv -\sqrt{\frac{K_s}{2}} + \sqrt{\frac{K_s}{2} + \bar{A}\sqrt{2K_s} + 1}\ . \tag{8.19}$$

Finally, the solid-gas interface energy, which looks very similar to σ_{sl} except for the signs of the terms:

$$\sigma_{sg}(\bar{A}, K_s) = \frac{-\phi_2^3 + 3\phi_2 + 2}{3\sqrt{2}} + \frac{\sqrt{K_s}}{2}(\bar{A} - \phi_2)^2\ , \tag{8.20}$$

with

$$\phi_2 \equiv \sqrt{\frac{K_s}{2}} - \sqrt{\frac{K_s}{2} - \bar{A}\sqrt{2K_s} + 1}\ . \tag{8.21}$$

We should keep in mind that we only made the form of the phase-field free energy (7.25) plausible. We did not not tell what the values of the parameters K_s and the mean value of $\bar{A}$ one should use (noise correlation function was fixed through fluctuation-dissipation therem, which does not say anything about $\bar{A}$). However, knowing the values of the surface tensions from density functional theory, we are now in a position to fix the parameters K_s and $\bar{A}$ (which we will encounter again in Sect. 8.3.1). They can be solved from the set of equations obtained by setting the phase field surface tensions equal to the values computed from density functional theory. Corresponding to Eq. (8.8) we now have

$$\sigma_{sg} = \sigma_{sg}\Big(\bar{A}(\tilde{w}, V_S),\ K_s(\tilde{w}, V_S)\Big)\ , \tag{8.22}$$

and similarly for σ_{sl}. The difference is that now the chain of effective descriptions ends at the level of classical Molecular Dynamics parametrization. Of course, we could express $\tilde{w}$ and V_S in terms of quantum mechanical parameters, which would make Eq. (8.22) the same as Eq. (8.8) if not too much pile-up of error would have been induced by introduction of the Molecular Dynamics coarse-graining level. This problem will be discussed in the next section 8.2.3.

8.2.3 Breakdown of classical Density Functional Theory

There are two main assumptions which must not be violated in order for the results of Sect. 8.2.2 to be trusted. The first assumption concerns the mean-field nature of the density profile ansatz (Eq. 8.15 or Eq. (8.16)). The mean-field density profile given in Eq. (8.16) can be found by solving the extremal of the phase-field free energy via Euler-Lagrange equation corresponds to a situation where the translational invariance has been broken in one spatial direction only. When substituted back into the expression of free energy to compute the surface tension, we do not get a correct result which would be valid in finite temperature, rather the zero temperature approximation. This is because the thermal fluctuations roughen the phase boundary and the straight interface profile $\phi(z) = \tanh((z-l)/\xi)$ does not take this into account: Starting at $z = -\infty$ the liquid bulk density becomes $\phi(-\infty) = -1$. The profile changes sign at plane $z = l$ and assumes the gas bulk density far a way from the interface: $\phi(\infty) = +1$.

To take into account the temperature effects, one should estimate the entropic effects, which must be done perturbatively in most cases [263]. For simple enough toy models $\sigma(T)$ can be found exactly [264] What is quite surprising, though, is that when the mean-field surface tension is used (despite its approximative nature) in the evolution equations of the interface such as the dynamics of the meniscus, which is going to be discussed in Sect. 8.4, the dynamics seems not to be affected by the fact that temperature renormalization of σ has not been taken into account. This seems to indicate that the zero temperature fixed point controls the dynamic situtation at least as far as the correctness is measured by comparing numerical results of scaling of the correlation functions with those calculated using dynamic renormalization group [246]. It is an interesting question whether this phenomenon has something in common with the competition of quenched and thermal noises, which renders temparature as dangerous irrelevant variable to be briefly discussed in Sect. 8.3.1. Even if there is no quenched noise component to begin with, it might be generated when projecting lower dimensional interfactial evolution equations out of the bulk dynamics (Sect. 12.3).

Another factor which is missing from the analysis of the surface tensions so far is the effect of curved (global) geometry. Because the meniscus in a capillary tube is curved, the usual thermodynamic relations do not hold any more. It turns out that the radius of curvature should be introduced as a new thermodynamic variable. When the radius of curvature goes to infinity, the corrections to surface energy goes like

$$\sigma \approx \sigma_\infty (1 - 2\delta/R_e + \ldots) \ , \tag{8.23}$$

where σ_∞ is the limit of the surface tension when radius of curvature $R_e \to \infty$ and δ is roughly a constant. For more information the reader is referred to Refs. [262, 265, 266]. The effect of curved geometry is clearly visible in the value of the contact angle θ_{eq} which is a function of the surface tensions. For small enough curvatures (which is the limit our theory should work) this correction vanishes and will not be taken into account in the rest of the text.

Despite the usefulness of the density functional theory, there is another problem associated with it, which is more fundamental than the mean-field approximations addressed above. This has to do with the breakdown of the pairwise additivity of interactions. As we have indicated in Sect. 6.4.1, the total interaction energy of two macroscopic bodies occupying volumes V_1 and V_2 is given by

$$\int_{V_1} dV_1 \int_{V_2} dV_2 \ \rho_1(\mathbf{r}_1)\, w(\mathbf{r}_1 - \mathbf{r}_2)\, \rho_2(\mathbf{r}_2) \ . \tag{8.24}$$

As explained in Chap. 6 w is the interaction potential between atoms of type one and two in the lowest order approximation of density functional theory. Using effective dipole-dipole interaction in Eq. (8.24) reproduces Eq. (8.9). The problem is that if the density of the macroscopic objets 1 and 2 is high, their atoms loose their identity as their electronic structure becomes more bulk like. Lifshitz [267] has shown that as far as the medium between the two materials is vacuum, the interaction still obeys pairwise additivity and is attractive. However, if the interlayer medium is not vacuum, the pairwise additivity breaks down and the density functional theory presented above does not hold. If it turns out, that taking into account some higher (finite) order many-body interactions is sufficient (which does not have to be the case), the classical density functional theory can be generalized to inclued these effects. Thus, the quantum mechanical approach presented in Sect. 8.2.1 is safer as it takes into account the full many-body nature of the van der Waals interaction, which becomes important when there is a thin layer of third material in-between two others.

All in all, if we are not focusing on two microscopic details the classical density functional theory should be a reasonable approximation for the quantities of interest. Numerics seems to indicate that in the dynamic situations the zero-temperature approximation used in the mean-field calculation of the surface tensions does not seem to affect many of the universal properties such as statistical measures of roughness of the phase boundary.

8.3 Experimentally measurable parameters

In Sect. 8.1 we advertized that the relevant time and length scales, which are hidden in the three dimensional bulk evolution equation (8.2), can be read off from the parameters of equations of motion of the meniscus and the contact line. The macroscopic parameters appearing in Eq. (8.3) and Eq. (8.4) are functions of the more microscopic parameters of underlying levels of the hierarchy as explained in Sect. 8.2. More specifically, the parameters of our effective theory can all be expressed in terms of the surface tensions, which in turn can be given in terms of more microscopic (known) parameters. The mobility M is the only exception to the rule: It is expressible with the aid of more microscopic parameters of the theory, which are not directly related to the surface tensions. Knowing the values of the parameters of the model is one of the great advantages of the systematic coarse-graining procedure. The final stages of the procedure, projecting out the bulk dynamics, works for many inhomogeneous systems, where the bulk phases are separated by thin interfaces. For simple enough systems [268, 269] it is possible to deduce the correct form of the interface equation without any intercourse to systematic coarse-graining approach. The family of models which start directly with the interfacial description of the problem are called sharp interface models. The problem of this approach is, though more time-saving than the systematic coarse-graining derivation, the fact that the parameters of the sharp interface model have to be guessed or fitted. As shown in Ref. [270] the projection method allows the *determination* of the sharp-interface model parameters in terms of the parameters of the bulk free energy F_{3D} in more general cases than the contact line problem, too. It should be kept in mind that usually it is very difficult to guess the right form of the effective interface equation without deriving it through the projection technique. The 'first principles' derivation of the contact line dynamics clearly rules out some popular choices for effective description of triple line [4] at least in the case of smooth walls. Among others, local equations such as Quenched-Edwards-Wilkinson (QEW) equation [271] have been suggested to describe roughening of the contact line. In contrast, Eq. (8.4) is non-local in real space, which is evident from factors $|k|$. Non-local Fourier space forms of evolution equations have been derived using slightly different methods in Ref. [272].

As not just the form of the equations but also the values of the parameters are fixed through coarse-graining, we should explain the relation of the most important parameters of the theory to the experimentally measurable observables. That is what we will do next. Let us concentrate on the contact line equation (8.4) as it contains in addition to the parameters of the meniscus equation also the stochastic term which needs two extra parameters for its quantification. Expanding the coefficient functions we get the result (App. C.15.2),

$$\frac{1 - e^{-2\mathrm{C}_0|k|}}{4k^2}\,\partial_t c(k,t) + \frac{\partial_t \mathrm{C}_0}{4|k|}\left(1 + e^{-2\mathrm{C}_0|k|}\right) c(k,t) = -2M\sigma|k|\,c(k,t) + MA_k(c)\ , \qquad (8.25)$$

where the stochastic noise originates from the contribution of the stochastic properties of the solid walls to the projected free energy. According to our variational prescription of the projection (App. C.1) the random part of the equation of motion is generated from

(App. C.14.6)

$$\frac{\delta}{\delta c(x,t)} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dx \int_{0}^{\mathrm{C}(x,t)} dz \, (\sigma_{sl}(x,z) - \sigma_{sg}(x,z)) = A(x, 0, \mathrm{C}_0(t) + c(x,t)) \ , \tag{8.26}$$

where $A(x,0,z) \equiv \sigma_{sl}(x,z) - \sigma_{sg}(x,z)$ is the projection of the bulk field $A(x,y,z)$ on the wall $y = 0$. It should kept in mind that the Fourier transform,

$$A_k(c) \equiv \int dx \, e^{\imath kx} A(x, 0, \mathrm{C}_0(t) + c(x,t)) \ , \tag{8.27}$$

cannot be carried out explicitly because the random field A depends on the fluctuating contact line profile c, which additionally also appears in the equation of motion (8.25) linearily on both sides. Thus, even though the deterministic part of the evolution equation has been linearized the stochastic part has not. In fact, more care should be exercized when linearizing non-linear stochastic equations [273]. Here we are simply guided by the physical intuition that in the limit of vanishing surface randomness the linearized theory should provide a reasonable approximation. Even with non-vanishing noise the corresponding linearized stochastic evolution equation for a similar system has been numerically shown to give consistent results [4] for many observables of interest.

8.3.1 Noise parameters

The local wetting properties of the solid walls can be altered in two ways. We are focusing on perfectly flat walls with chemical impurites randomly distributed over the surface. We also briefly consider regular distributions in Sect. 8.8. Instead of altering the local surface tensions, the local wetting properties can also effectively be changed by making the side walls rough e.g. be etching or lapping with coarse sapphire powder [274]. It turns out that formalism we are developing here for smooth solid walls can also be used for the rough ones. However, since the noise enter is a somewhat different way in the latter case, we refrain from applying our results to such cases and leave it for future work.

By definition the field A_k depends on the random solid-liquid and solid-gas surface tensions both of which are known functions of more microcopic parameters. What has to be fixed experimentally, is the distribution and the local amplitude of the noise inside the wetting patches on the solid walls. For simplicity, $A(x,0,z)$ is assumed to be Gaussian white noise with

$$\langle A(x,0,z) \rangle = \bar{A} \ . \tag{8.28}$$

$$\langle A(x,0,z) A(x',0,z') \rangle = D\delta(x - x')\, \delta(z - z') \ . \tag{8.29}$$

Gaussianity is not a serious limitation and can be dropped. For simplicity, let us concentrate now on the case where the distribution of local wetting sites is characterized by a single parameter, the noise strength D appearing in the noise correlation function. If it can be experimentally shown that the adjacent wetting sites (corresponding to a chosen resolution) are not correlated (consistent with delta distribution), it remains to determine the spread of the local noise amplitudes a. One realization of the random variable a can be defined as $a \equiv A(x,0,z)$ for $x, z \in S$, where the set S determines the Sth patch area. In other words, the parameter D is the half-width of the Gaussian peak, $P(a) \propto exp(-Da^2)$, where a is the local noise amplitude. The position of the peak determines the mean value of $\bar{A}$ and its width D can fixed by binning the local fluctuation of the contact line within a given time window τ [275]:

$$a(x,t) \equiv \Delta c(x, \tau + t) - \Delta c(x,t) \ , \tag{8.30}$$

where $\Delta c(x,t) \equiv c(x,t) - \langle c(x,t) \rangle$. Typically, the larger τ is, the more Gaussian the distribution becomes. This type of noise extraction method seems to work well in practice, and it has been successfully applied to two-phase fluid flow [276] and slow combustion fronts in paper [277].

The frozen side wall noise is not the only noise which appears in the problem. So far we have neglected the thermal noise which comes into play through the requirement that the fluid should go to Gibb's equilibrium in the long time limit (see Sect. 7). In this chapter we are leaving out the thermal noise both for simplicity and because the quenched noise A_k is expected to dominate many of the universal scaling properties as compared to thermal noise. Using renormalization language, it is not obvious, though, that the zero temperature fixed point should dominate. The competition of the thermal and quenched noise has been studied e.g. in the context of creep in elastic systems [278], where the authors showed that the dimensionless temperature flows to zero. Yet, temperature turns out to be a dangerously irrelevant variable (thermal disturbance being the *only* noise present, makes temperature normally relevant variable!).

Including thermal noise furnishes us with an experimental method to determine the value of the mobility M. This can be done via the Fluctuation-Dissipation theorem [8]. By performing a measurement of the fluctuations through e.g. scattering radiation into the two-phase system produces the structure function, which is essentially the correlation function $C(x)$ of total density fluctuations in the system. Extracting the mobility from the dimensionfull prefactor of $C(x)$ gives in principle the value of M. Unfortunately, the Poisson bracket formalism, which we are using does not give any means to fix dissipative transport coefficients such as M theoretically. We have to do it by other means. For example, one can use Mori's projection technique [27].

8.3.2 Important length scales

As is clear from Eq. (8.25), all length scales can be expressed in terms of the surface tensions, mobility and noise parameters explained above. The mean contact line height in a pure system c_0 will be derived in App. C.12.2:

$$\mathrm{c}_0(t) = \sqrt{\frac{M\sigma K t}{u} + c_i^2} \ , \tag{8.31}$$

which for zero initial height, $c_i = 0$ follows a diffusive-like $t^{1/2}$-growth law. This result has been experimentally verified in a number of different systems [279, 280]. Taking into account gravity and evaporation [281], for example, limit the validity range of the simple form given in Eq. (8.31).

The contact line height c_0 thus depends on the mobility, liquid-gas surface tension σ and the curvature K of the meniscus (u is just a numerical constant). When $K \neq 0$, the meniscus in the pure system is assumed to have a parabolic shape in the double wall set-up:

$$\mathrm{H}_0 \approx \mathrm{c}_0 + K(y^2 - Ly) \ , \tag{8.32}$$

where we have assumed that the two walls are situated at $y = 0$ and $y = L$. This ansatz holds very well both numerically and analytically [262]. Since the curvature can be expressed as a function of the contact angle for parabolic meniscus and because the contact angles are functions of the mean value $\bar{A}$ of the noise at the wall, we have

$$K = K(\bar{A}) \ . \tag{8.33}$$

This holds to a good approximation even when the interface is moving because the dynamic contact angle $\theta_d(t)$, which actually should be used to fix K does not deviate from the equilibrium value θ_0 significantly the higher the meniscus rises. For a driven system, where fluid is forced to flow between the plates with the aid of a pressure or chemical potential gradient this does not hold any more: $\theta_d \neq \theta_0$ [262]. Also, since the average value $\langle A \rangle = \bar{A}$ has been included in the dynamics of the pure system (8.32), it should be removed from Eq. (8.25). Multiplying both sides by a factor $|k|$ will effectively take care of this as explained in App. C.15.2.

There are also other internal scales hidden in Eq. (8.25), which manifest themselves in certain statistical measures of the contact line such as its two-point correlation function. The cross-over length,

$$\xi_\times(t) \equiv \sqrt{M\sigma/\dot{\mathrm{c}}_0} \sim \sqrt{\mathrm{c}_0/K} \ , \tag{8.34}$$

can be obtained by comparing the strengths of the second term on the left to the restoring force (first term on the right) in Eq. (8.25). The correlation length $\xi_\times$ separtes two different types of regimes: On scales $k\xi_\times \ll 1$ the contact line fluctuations are damped by the interfacial tension σ whereas for $k\xi_\times \gg 1$ the damping is due to the mass flow from the reservoir. The interesting thing is that $\xi_\times$ is given by the same expression in a simpler model of spontaneous imbibition in disordered medium [4] given that one makes the identification $K = \bar{\alpha}/(M\sigma)$. Thus, the average disorder $\bar{\alpha}$ corresponds to the curvature of the meniscus in the contact line problem. As we will show later in App. C.8, in deriving the contact line evolution equation, we have made use of the fact that the curvature is small: $KL^2/\mathrm{c}_0 \ll 1$. Together with Eq. (8.34) this means that

$$\xi_\times \gg L \ . \tag{8.35}$$

In other words, the dimensions of the experimental set-up have to be such that the separtion of the walls in y-direction must be much smaller than the extent of the walls in the x-direction in order for there to be enough room for the correlations to reach the cross-over scale $\xi_\times$. To get some idea of the magnitude of the numbers we plug in a plate separation $L \sim 50\,\mu m$ which satisfies inequality (8.35) when $\xi_\times \approx 1mm$. Supposing the mean contact line height is also of the order of $1mm$, the curvature should be $\mathcal{O}(10^3 m^{-1})$.

Finally, we note that the computationally convinient boundary condition of the chemical potential $\mu(x, y, 0) = 0$, which establishes the connection to the reservoir, is not the best possible for direct experimental comparison. Rather, the theory should be formulated in terms of the mass flux $(\partial_z \mu|_{z=0})$ which is easier to measure experimentally. This is possible even for non-driven mass flows if one can self-consistently find the flux which gives rise to the same flow which would arise in spontaneous capillary rise with no forcing. For driven systems there is no problem, as the flux is a given quantity.

8.4 Projection of the 3D bulk model

We will now start deriving the equations of motion for the meniscus and the contact line. The remaining sections from now on utilize heavily the material presented in the App. C. The appendices can be read through in the order they appear to get a more detailed justification of the results presented below.

We start with the 3D bulk evolution equation for the conserved order parameter field $\phi(x)$, whose values determine in which phase the system is sitting at any particular spatial location x. In Sect. 7.3 we have argued that the following bulk evolution of motion should be used for a conserved density field (phase-field) ϕ:

$$\partial_t \phi(x,t) = M \nabla^2 \mu(x,t) \ , \tag{8.36}$$

where the chemical potential density $\mu \equiv \delta F/\delta\phi$, and M denotes mobility. The free energy functional through which the chemical potential is defined is of the Ginzburg-Landau form:

$$F = \int dx \int dt \left[\frac{1}{2} |\nabla \phi|^2 + V(\phi, \rho, A) \right] \ . \tag{8.37}$$

The gradient term punishes for spatial fluctuations in the value of the order parameter ϕ when moving from one phase to the other. The potential,

$$V = (1/2)(1+\rho)(\phi^2 - 1)^2 + (1/2)(1-\rho)(\phi - A)^2, \tag{8.38}$$

has three minima corresponding to three different (equilibrium) phases. Field ρ represents the 'density' of the solid phase: in the spatial regions where $\rho(x) = -1$ the factor $(1+\rho) = 0$ and the potential V has a single minimum at $\phi = A$, which is fixed to be the value of the phase field in the solid phase. Where $\rho(x) = +1$ the factor $(1-\rho) = 0$ and the potential V has two minima ($\phi = \pm 1$) signifying the coexistence of two fluid phases. We can interpret $\phi = +1$ as the characteristic value of the phase field in the liquid phase, and $\phi = -1$ characterizes the gas phase.

In order to utilize standard techniques to eliminate bulk degrees of freedom from the formulation, we need to invert the Laplacian opertor appearing on the right hand side of Eq. (8.36). Therefore, we have to determine the boundary conditions for the chemical potential. The solid phase studied in this work will comprise two vertical walls separated by distance L. Obviously, in the limit if $L \to \infty$ it suffices to study just the effect of a single wall. We will assume that there is no mass flux through the solid boundaries, *i.e.* $\partial_n \mu|_0 = \partial_n \mu|_L = 0$. At the reservoir boundary ($z = 0$) we establish a connection to the fluid reservoir via a Dirichlet boundary condition $\mu_{z=0} = 0$. These requirements allow us to find G_{3D} explicitly. The actual construction of the Green function is performed in App. C.6 and other choices for the boundary conditions are discussed in App. C.7. Invertion of the Laplacian yields

$$M^{-1} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dy_1 \int_{0}^{\infty} dz_1 \, G_{3D}(x,y,z : x_1,y_1,z_1) \, \partial_t \phi(x_1,y_1,z_1,t) = \mu(x,y,z,t) \ . \tag{8.39}$$

To derive the effective equation of motion for lower dimensional objects such as the meniscus ($\textsc{h}(x,y,t)$) and the contact line ($\textsc{c}(x,t)$), it is useful to think of Eq. (8.36) as arising from minimization of a free energy functional (see [282]) containing both driving potential (μ) and the Rayleigh dissipation functional ($\int (\partial_t \phi)^2$) such that the Euler-Lagrange equation corresponds to the bulk equation of motion (Eq. (8.36)). The three dimensional nonlinear evolution equation for the bulk order parameter field ϕ, which has to be supplemented with proper boundary conditions, is very hard to solve analytically. Further progress can be made by approximating the smoothly varying true solution ϕ with a function which is the characteristic function of the phases changing discontinuously from one bulk value to the other right at the phase boundary. Specifically, we will choose

$$\phi \approx -1 + 2\,\theta(\mathrm{H}(x,y,t) - z) \ . \tag{8.40}$$

The factor of two is the so called miscibility gap and it is given by the separation of the potential wells of the free energy, which for the current choice of model parameters is 2. Matters simplify substantially since we only have to know the position of the phase boundary (given by $z = \mathrm{H}(x,y,t)$) to be able to tell with the aid of Eq. (8.40) what the approximate 3D bulk solution is. The dynamics of the phase boundary H is obtained by projecting out the bulk degrees of freedom. Mathematically this means that both sides of Eq. (8.39) will be operated on by the projection operator

$$P(\cdot) \equiv \int dz\, (\partial_z \phi)\, (\cdot) \approx \int dz\, (-2\delta(\mathrm{H} - z))\, (\cdot) \ . \tag{8.41}$$

Differentiation of the approximative solution of ϕ in Eq. (8.40) with respect to time gives us something simple

$$\partial_t \phi \approx 2\delta(\mathrm{H} - z) v_z \approx 2\delta(\mathrm{H} - z)\, \partial_t \mathrm{H} \ , \tag{8.42}$$

where we discarded some nonlinearities by setting $v_z \approx \partial_t \mathrm{H}$. Using these results we can cast Eq. (8.39) into the following form (NB: should be checked if v_n is really the normal velocity also for model B):

$$\begin{aligned} \frac{4}{M} \int dx_1 \int dy_1\, G_{3D}(x, y, \mathrm{H_C}(x,y,t) : x_1, y_1, \mathrm{H_C}(x_1,y_1,t))\, \partial_t \mathrm{H_C}(x_1,y_1,t) \\ = -\frac{\delta F_{2D}[\mathrm{H_C}]}{\delta \mathrm{H_C}(x,y,t)} = \sigma \nabla \cdot \frac{\nabla \mathrm{H_C}}{\sqrt{1 + |\nabla \mathrm{H_C}|^2}} \ . \end{aligned} \tag{8.43}$$

We have written $\mathrm{H} = \mathrm{H_C}$ to stress the fact that the current equation of motion (8.43) has to be supplemented with a fixed (unknown) boundary condition $\mathrm{C}(x,t)$ determining the contact line.

In the set-up we have in mind there will be multiple phase boundaries: with one vertical plate immersed in the liquid reservoir there will be a gas-solid phase boundary above the meniscus and a liquid-solid boundary below the meniscus. The projection operator defined in Eq. (8.41) only projects onto the liquid-gas phase boundary and thus only yields the meniscus equation of motion. In principle, we should also perform a similar projection for the gas-solid and liquid-solid boundaries and generate their equations of motion as well. To avoid this complication we are assuming that both these boundaries are completely determined through knowledge of the position of the three-phase contact line $\mathrm{H}(x, y = 0, t) \equiv \mathrm{C}(x,t)$. In the sharp phase boundary approximation the liquid-solid interface will be those point in the plane $y = 0$ of the vertical wall which satisfy $z \leq \mathrm{C}(x,t)$. The remaining area, $z > \mathrm{C}(x,t)$ in the same plane determines the gas-solid boundary.

To get an evolution equation for the contact line itself, we would like to simply set $y = 0$ in Eq. (8.43) and use the fact that $\mathrm{H}(x,0,t) = \mathrm{C}(x,t)$ Doing so, we don't gain any new information because we would have to know what the expression $\nabla^2 \mathrm{H}|_{y=0}$ on the right hand side of the projected equation means. In order to understand how to obtain the contact line equation systematically requires that we take a couple of steps back and returnd to our fundamental evolution equation for the phase field, Eq. (8.39) which hasn't been projected yet. The way to proceed is to treat the problem as an functional extremization problem (validity of this interpretation depends on the boundary conditions of μ). The functionals to be extremized are called Rayleigh's dissipation functional R and the free energy functional F. In the normal Lagrangian mechanics the dissipation function is a positive definite function quadratic in the velocity v whereas the free energy is a function of the spatial position variable q. Since we are dealing with a field theory, the corresponding objects in our case will be the velocity of the phase field $\partial_t\phi(x, y, z, t)$ and its 'conjugate', $\phi(x, y, z, t)$. Both of these objects live in the three dimensional space. As will be explained below, we aim at constructing Lagrange's equation of motion for the pair $\partial_t\phi$ and ϕ by 'differentiating' (taking variations) of the Lagrangian with respect to them. Our next assumption is that we will obtain the correct equation of motion for the liquid-gas boundary, which lives in two dimensional space, by restricting the bulk variations $\delta\phi$ to this lower dimensional subspace, where they will become related to variation $\delta\textsc{h}$ as explained in App. C.1. Finally, at the bottom of the hierarchy we have the contact line which is a one dimensional object. To obtain its dynamics we have to restrict the variations of $\delta\textsc{h}$ to one dimensional domain of the contact line given by $\delta\textsc{c}$. All in all, we are assuming that the higher dimensional variation always contains all the information of the lower dimensional one, and once we take the restricted variation of the functionals, we obtain the relevant information concerning the dynamics of lower dimensional collective coordinates (meniscus and contact line in this case). Applying the familiar means of Lagrangian mechanics [283]: we exactly reproduce the fundamental evolution equation of the phase field (Eq. (8.39)):

$$\frac{\delta R_{3D}[\partial_t\phi]}{\delta(\partial_t\phi(x, y, z, t))} = -\frac{\delta F_{3D}[\phi]}{\delta\phi(x, y, z, t)} \ . \tag{8.44}$$

More information about the technique is provided in App. C.1. Replacing ϕ with its approximation given in Eq. (8.40) and $\partial_t\phi$ with the form given in Eq. (8.42) in the functionals and performing the integration over z-coordinate yields new functionals $R_{2D}[\partial_t h]$ and $F_{2D}[h]$. The projected equation of motion for the meniscus, Eq. (8.43) is reproduced by taking functional derivatives with respect to the projected degrees of freedom

$$\frac{\delta R_{2D}[\partial_t\textsc{h}]}{\delta(\partial_t\textsc{h}(x, y, t))} = -\frac{\delta F_{2D}[\textsc{h}]}{\delta\textsc{h}(x, y, t)} \ . \tag{8.45}$$

As explained in the App. C.1 the variation of the meniscus in the previous equation should be performed in such a manner that the contact line profile $\textsc{c}$ stays fixed. Solving Eq. (8.45) in terms of the unknown (fixed) $\textsc{c}$, substituting back and integrating out the y-coordinate finally produces again two new functionals $R_{1D}[\partial_t\textsc{c}]$ and $F_{1D}[\textsc{c}]$. The contact line equation results after taking variations of the new functionals with respect to projected degrees of freedom $\partial_t\textsc{h}(x, 0, t) \equiv \partial_t\textsc{c}(x, t)$ and $\textsc{h}(x, 0, t) \equiv \textsc{c}(x, t)$, analogously to the meniscus equation of motion:

$$\frac{\delta R_{1D}[\partial_t\textsc{c}]}{\delta(\partial_t\textsc{c}(x, t))} = -\frac{\delta F_{1D}[\textsc{c}]}{\delta\textsc{c}(x, t)} \ . \tag{8.46}$$

Eq. (8.46) together with Eq. (8.45) constitute a pair of equations to be solved simultaneously. The contact line equation acts as a boundary condition for the meniscus equation, which in turn is needed to determine the form of the contact line equation. The problem is fully analogous to Stefan type diffusion problem relevant *e.g.* for crystal growth on vicinal surfaces [284] in which the diffusion equation for density ρ is to be solved subject to boundary condition which depends on the bulk field ρ. In other words, the boundary conditions affects the bulk solution whose derivatives are needed to fix the boundary condition. If time variations are neglected the equilibrium problem is analogous to the two-step minimization procedure used in the context of critical wetting theory [285].

Finally, assuming that contact angle at solid wall(s) is close to $\pi/2$ it follows that $|\nabla \mathrm{H}|^2 \ll 1$ and the coupled equations of motion for the meniscus and the contact line are in the single wall case without memory effects can be written in the following form. First, the meniscus equation is obtained from Eq. (8.45) by forming the correct functionals R_{2D} and F_{2D} (App. C.5), taking the variations:

$$\begin{aligned} M^{-1}\int_{-\infty}^{\infty}dx_1\int_{0}^{\infty}dy_1\, G_{3D}(x,y,\mathrm{H}(x,y,t);x_1,y_1,\mathrm{H}(x_1,y_1,t))\,\partial_t\mathrm{H}(x_1,y_1,t) \\ = -\frac{\delta F_{2D}[\mathrm{H}_\mathrm{C}]}{\delta \mathrm{H}_\mathrm{C}(x,y,t)} \approx (\sigma/4)\,\nabla^2\mathrm{H}(x,y,t)\ . \end{aligned} \tag{8.47}$$

Then, the contact line equation, which acts as a boundary condition for the previous equation, is given by Eq. (8.46)

$$\begin{aligned} 2M^{-1}\int_{-\infty}^{\infty}dx_1\int_{0}^{\infty}dy_1\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dx_2\int_{0}^{\infty}dy_2\int_{-\infty}^{\infty}dt_2\,\frac{\delta(\partial_{t_1}\mathrm{H}_\mathrm{C}(x_1,y_1,t_1))}{\delta(\partial_t\mathrm{C}(x,t))} \\ \times\, G_{3D}(x_1,y_1,\mathrm{H}_\mathrm{C}(x_1,y_1,t_1);x_2,y_2,\mathrm{H}_\mathrm{C}(x_2,y_2,t_2))\,\delta(t_1-t_2)\,\partial_{t_2}\mathrm{H}_\mathrm{C}(x_2,y_2,t_2) \\ = -\frac{\delta F_{1D}[\mathrm{C}]}{\delta\mathrm{C}(x,t)} = f_{restoring} + f_{random}(\mathrm{C})\ . \end{aligned} \tag{8.48}$$

We have purposefully written the left hand side in a lenghty format to make it clearer how on actually goes from Eq. (8.45) (equivalently, Eq. (8.47)) to Eq. (8.46) (equivalently, Eq. (8.48)). One simply solves the linearized version of Eq. (8.47) and substitutes the solution H_C back into the dissipation functional R_2D to produce $R_{1D}[\partial_t\mathrm{C}]$. It is the variation of this functional with respect to velocity $\partial_t\mathrm{C}(x,t)$ which constitutes the left hand side of Eq. (8.48). Of course, most of the integrals can be done and the deterministic part of the linearized equation motion becomes local in the Fourier space. On the right hand side of Eq. (8.48) we do exatly the same thing: We substitute H_C into F_{2D} and integrate out the y-dependence thus producing $F_{1D}[\mathrm{C}]$ for the contact line which lives in a lower dimensional space than the meniscus. Since the procedure is exactly the same on both sides, we have not expanded the variational derivative $\delta F_{1D}/\delta\mathrm{C}(x,t)$ explicitly. Instead, we have said that it consists of two pieces: The deterministic restoring force is denoted by $f_{restoring}$ and the random pinnig force is f_{random}. The latter force appears because of the chemical composition is not homogeneous on the wall and its specific form is derived in App. C.1. In next section we will see what these equations look like in the Fourier representation after linearizing their deterministic parts.

8.5 Partially linearized equation of motion for contact line

To progress analytically further, we linearize the deterministic parts of the equations of motion, that is the Green functions appearing in Eq. (8.47) and Eq. (8.48). Linearization is performed around the mean meniscus profile $\mathrm{H}_0(y,t)$ (the detailed derivation is given in

App. C.5). We assume that without any *random* inhomogeneities on the wall(s), the meniscus assumes the shape H_0, which we sometimes call the zeroeth order solution for the meniscus. It can be a funtion of both spatial coordinates x and y, but assuming that the wall is completely homogeneous, $\mathrm{H}_0 = \mathrm{H}_0(y,t)$, *i.e.* the zeroeth order solution only dependes on the coordinate perpendicular to the wall. The fluctuations of the meniscus induced by random distribution of more or less wettable regions of the solid wall are denoted by $h = h(x,y,t)$. Let the full solution of the meniscus be denoted with H. Then,

$$\mathrm{H}(x,y,t) = \mathrm{H}_0(y,t) + h(x,y,t) \ \ ; \ \ \mathrm{C}(x,t) = \mathrm{C}_0(t) + c(x,t)\ . \tag{8.49}$$

where we have also defined the corresponding elements of the full contact line profile C. It consists of the height of the contact line on the pure wall C_0 and the fluctuating part c arising from the randomness in the local wetting properties. It is convinient to assume that the zeroeth order solutions and the fluctuating contributions are tied together through

$$\mathrm{H}_0(0,t) = \mathrm{C}_0(t) \ \ ; \ \ h(x,0,t) = c(x,t)\ . \tag{8.50}$$

These choices suffice to respect the definition $\mathrm{H}(x,0,t) \equiv \mathrm{C}(x,t)$. In the simplest case of one vertical wall one obtains,

$$\begin{aligned} \mathrm{H}_0(y,t) &\approx \mathrm{C}_0 - \alpha y\ , & (8.51)\\ h(x,y,t) &\approx \int dk\, e^{\imath kx}\, g_{qs}(k,y)\, c(k,t) & (8.52) \end{aligned}$$

The magnitude of the coefficient α is fixed by the contact angle θ, which is a known function of the parameters of the free energy. The dependence of h on c as given in Eq. (8.52) holds only in the so called quasi-stationary approximation only, which is derived in App. C.11.1. Thus, in the single wall case we define the quasi stationary kernel function $g_{qs}(k,y) \equiv \exp(-|k|y)$. For double wall set-up with solid walls at $y = 0$ (a-wall) and $y = L$ (b-wall),

$$\begin{aligned} \mathrm{H}_0(y,t) &\approx \mathrm{C}_0 + K(y^2 - Ly)\ , & (8.53)\\ h(x,y,t) &\approx \int dk\, e^{\imath kx}\, g^a_{qs}(k,y)\, c^a(k,t) + \int dk\, e^{\imath kx}\, g^b_{qs}(k,y)\, c^b(k,t) & (8.54) \end{aligned}$$

The quasi stationary kernel for double wall system, $g^a_{qs}(k,y) = \sinh(|k|(L-y))/\sinh(|k|L)$ reduces to $e^{-|k|y}$ in the single wall limit $L \to \infty$. The other kernel, $g^b_{qs} = \sinh(|k|y)/\sinh(|k|L)$ vanishes as the b-wall recedes to infinity. The explicit representations of the kernel functions g^a_{qs} and g^b_{qs} in Fourier and real space have given in App. C.11.1.

In the rest of this section we will concentrate on the evolution equation of the contact line in the single wall case. As we have seen, the real space form of the evolution equation (8.47) is a lengthy one. Linearization of the Green's function G_{3D} given in App. C.3 makes it even lenghtier giving rise to three distinct pieces on the left hand side. Substitution of

$$\mathrm{H}_\mathrm{C} = \mathrm{H}_0 + h_\mathrm{C} = \mathrm{H}_0 + \int dx'\, g_{qs}(x-x'.y)\, c(x',t)\ , \tag{8.55}$$

and separating out the deterministic terms, which are functions of C_0 but not c, we get a nested convolution chain on the left hand side:

$$\frac{1}{M}\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \int_0^{\infty} dy_1 \int_0^{\infty} dy_2\ g_{qs}(x-x_1,y_1)\times$$

$$
\begin{aligned}
&\Big\{ G_{3D}(x_1, y_1, \textsc{h}_0(y_1,t); x_2, y_2, \textsc{h}_0(y_2,t)) \int_{-\infty}^{\infty} dx_2'\, g_{qs}(x_2 - x_2', y_2)\, \partial_t c(x_2', t) \\
&+ \partial_{z_1} G_{3D}(x_1, y_1, z_1; x_2, y_2, \textsc{h}_0(y_2,t))|_{\textsc{h}_0} \int_{-\infty}^{\infty} dx_1'\, g_{qs}(x_1 - x_1', y_1)\, c(x_1', t)\, \partial_t \textsc{h}_0(y_2, t) \\
&+ \partial_{z_2} G_{3D}(x_1, y_1, \textsc{h}_0(y_1,t); x_2, y_2, z_2)|_{\textsc{h}_0} \int_{-\infty}^{\infty} dx_2'\, g_{qs}(x_2 - x_2', y_2)\, c(x_2', t)\, \partial_t \textsc{h}_0(y_2, t) \Big\} \\
&\qquad = f_{restoring} + f_{random}(\textsc{c}) \ . \qquad (8.56)
\end{aligned}
$$

On the third line the substitution symbol $|_{\textsc{h}_0} \equiv |_{\textsc{h}_0(y_1,t)}$ because the derivative is taken with respect to z_1. On the fourth line $|_{\textsc{h}_0} \equiv |_{\textsc{h}_0(y_2,t)}$ since the Green's function is differentiated with respect to z_2. Though not obvious immediately, even after linearization of the Green's function, Eq. (8.56) will still be strongly nonlinear since the random fluctuations of the surface tension term f_{random} will be dependent on the contact line position $\textsc{c}(x,t)$. The (linearized) non-local restoring force derived in App. C.18 on the contact line can be expressed in the following form subject to same approximations mentioned above:

$$
\begin{aligned}
f_{restoring} = -2 \int_{-\infty}^{\infty} dx_1 \int_{0}^{\infty} dy_1 \int_{-\infty}^{\infty} dx_1' \,\{ [\, \partial_{x_1} g_{qs}(x - x_1, y_1) \partial_{x_1} g_{qs}(x - x_1', y_1) \\
+ \partial_{y_1} g_{qs}(x - x_1, y_1) \partial_{y_1} g_{qs}(x - x_1', y_1)] \ c(x_1', t)\} \ . \qquad (8.57)
\end{aligned}
$$

As said above, the explicit form of the Green functions G_{3D} and g_{qs}, which depend on the geometery of the set-up, will be derived later. In this section will state the results for the single wall case, which is the simplest.

Collecting the results presented fully in App. C.3 and App. C.15.2 yields the following equation of motion for fluctuating Fourier modes of the contact line:

$$
|k|^{-2} f_1(\textsc{c}_0|k|)\, \partial_t c(k,t) + \frac{\partial_t \textsc{c}_0}{|k|} f_2(\textsc{c}_0|k|)\, c(k,t) = -M \frac{\delta F_{1D}[c]}{\delta c(k,t)} \ . \qquad (8.58)
$$

The scaling function f_1 is related to the contribution originating from expression PI_D. It scales like $f_1 \sim |k|\textsc{c}_0$ for $|k|\textsc{c}_0 \ll 1$; for $|k|\textsc{c}_0 \gg 1$ f_1 approaches a constant. The other scaling function f_2 goes to different constants at these limits. In later calculations of the dynamic critical properties we have used the following approximations of the functions f_1 and f_2:

$$
f_1 \approx 1 - \exp(-2\textsc{c}_0|k|) \ \ ; \ \ f_2 \approx 1 + \exp(-2\textsc{c}_0|k|) \ . \qquad (8.59)
$$

For comparison, the equation of motion of an imbibition front [4] reads

$$
|k|^{-1} f_{I1}(\textsc{c}_0|k|)\, \partial_t c_k(t) + \partial_t \textsc{c}_0 f_{I2}(\textsc{c}_0|k|)\, c(k,t) = -M \frac{\delta F_{1D}[c]}{\delta c(k,t)} \ , \qquad (8.60)
$$

where $\textsc{c}_0$ is the mean position of the fluid front and $c(k,t)$ denotes the Fourier modes of the fluctuations around $\textsc{c}_0$. As seen from the definitions of the functions [4] f_{I1} and f_{I2} are the same as the *approximations* used for f_1 and f_2. The only difference between the left hand sides of the equation of motion of imbibition and contact line problems is the 'extra' factor of $|k|$ in the latter. Its originates from the functional dependence of h on c.

The driving force originating from the functional derivative on the right hand side of the equation of motion (8.58) is given by

$$
\frac{\delta F_{1D}[c]}{\delta c(k,t)} = \Gamma(k)\, c(k,t) + A_k(c) \ , \qquad (8.61)
$$

where the restoring force is denoted by Γ and A_k is the projection of the wall potential to the solid-fluid phase boundary. Correlations of the stochastic force have been discussed in Sect. 8.3. Specific forms of the restoring force will be considered in Sect. 8.8.

8.6 Approach of equilibrium

As seen from Eq. (8.47) the Laplacian appearing on the right hand side of the evolution equation of the meniscus, makes it necessary to impose a boundary condition to be satisfied at the wall $y = 0$ (in the case of a single wall). In general we can either say that the height of the contact line is given at the wall (i) or that the gradient of H is given (ii). The full model for the meniscus dynamics is then given by

(i) Meniscus equation of motion + Dirichlet boundary condition (8.62)
$\mathrm{H}(x, 0, t) = \mathrm{C}(x, t)$.
(ii) Meniscus equation of motion + von Neumann boundary condition (8.63)
$\nabla_n \mathrm{H}(x, y, t)|_{y=0} = \tan\theta(x, t)$.

Both choices (i) and (ii) should lead to the same result. In other words, the bulk evolution equation for the phase field ϕ also determines how the phase boundaries move. The boundary condition for H must be so chosen that the behaviour of $\phi(x, y, \mathrm{H}(x, y, t), t) = 0$ fixed by Eq. (8.36) is faithfully reproduced. We will show in Sect. 8.7 how the dynamic contact angle can be expressed in terms of the contact line position or vice versa.

Equilibriation takes place when the meniscus reaches the equilibrium contact angle $\theta_0(x)$, which is a (known) function of the chemical surface structure of the wall. If the wetting properties of the wall are homogeneous, the equilibrium contact angle will not depend on the spatial position x measured along the wall. For a set-up with single vertical wall the equilibrium meniscus shape should be given by $\mathrm{H} = \mathrm{C}_0 - \alpha_0 y$, i.e it is a straight plane with contact angle $\theta_0 = \pi/2 - \alpha_0$ crossing the solid wall at height C_0. The value of θ_0 is a function of the the surface tensions as discussed in Sect. 8.2. When there are two vertical walls present equilibriation without gravity takes place when $\alpha = 0$, *i.e.* when the meniscus becomes a straight horizontal plane with no curvature. With zero curvature there cannot be any pressure difference (or chemical potential difference in this version of our model which has no hydrodynamics and therefore no real pressure field) across it unlike in the case of a curved meniscus.

In equilibrium we assume that Eq. (C.207), which determines the behaviour of the mean meniscus position $\mathrm{H}_0(y, t)$, is satisfied. In other words,

$$I_A(y, t) = \frac{M\sigma}{4} \partial_y^2 \mathrm{H}_0(y, t) + \tilde{\Lambda}_{\mathrm{H}_0}(y, t) \ , \tag{8.64}$$

where the projected surface contribution of pure walls is denoted by $\tilde{\Lambda}_{\mathrm{H}_0}$. In equilibrium $I_A \propto \partial_t \mathrm{H}_0 = 0$ from which it follows that $\partial_y^2 \mathrm{H}_0 = -(4M/\sigma)\tilde{\Lambda}_{\mathrm{H}_0}$. If we have supplied the boundary conditions in such a form (see discussion above) which gives rise to a non-zero $\tilde{\Lambda}_{\mathrm{H}_0}$ independent of y, we get a parabolic equilibrium profile. There can be other mechanisms, too, which give rise to equilibrium curvature of the meniscus. For example, modeling a stripe defect (App. 8.8) would give rise an additional constant contribution to the curvature due to the Lagrange's multiplier guaranteeing the conservation of the fluid volume.

Next, we discuss the flucttutations around the equilibrium profile $\textsc{h}_0$, which is assumed to be reached in one of the cases mentioned above. In App. C.9 we derived the following equation for the fluctuation modes $h_{\mathbf{k}}$ of the meniscus:

$$g_1(k,t)\,\partial_t h_{\mathbf{k}}(t) + g_2(k,t)\,h_{\mathbf{k}}(t) = -\frac{M\sigma}{4}k^2\,h_{\mathbf{k}}(t)\ . \tag{8.65}$$

Let us study now how the zero mode of Eq. (8.65) behaves if the contact line has stopped moving: Eq. (8.64) is satisfied by $\textsc{h}_0 = \mathit{const}$ when boundary conditions are such that $\tilde{\Lambda}_{\textsc{h}_0}(y,t) = 0$. Furthermore, since $\partial_t\textsc{h}_0 = \partial_t\textsc{c}_0 = 0$ and because $g_2(k,t) \propto \partial_t\textsc{c}_0$, it must be that $g_2 = 0$. The linearized meniscus equation of motion reduces to $g_1(k,t)\,\partial_t h_{\mathbf{k}}(t) = -(\sigma/4)k^2 h_{\mathbf{k}}(t)$. For $k \to 0$ the right hand side of previous equation goes to zero and therefore the zero mode of the fluctuations becomes zero for suitably chosen initial condition. In fact, this is required by self-consistency of our assumption given in Eq. (8.49): If $h_{k=0} \neq 0$ it has to be included in the deterministic $\textsc{h}_0$. It should be noted that even after the average position of the contact line has become stationary ($\partial_t\textsc{c}_0 = 0$), locally the contact line is still searching for minimum energy configuration and the non-zero modes become static only after the local equilibrium contact angles fixed by the wall impurities have been attained. The decay time constant can be estimated from

$$h_{\mathbf{k}}(t) \sim \exp\left(-\int_0^t d\tau\frac{M\sigma k^2}{4g_1(k,\tau)}\right)\,h^i_{\mathbf{k}}\ , \tag{8.66}$$

which is the solution of the fluctuating meniscus modes in the case of fixed mean contact line position determined by $\partial_t\textsc{c}_0 = 0$. The 'initial' condition $h^i_{\mathbf{k}}$ is given by the meniscus shape at the moment when $\partial_t\textsc{c}_0$ becomes zero. In reality the approach of pinning height can very slow. Using the results of Sect. 8.7 we can obtain a rough estimate of the life time τ_k of perturbations:

$$\tau_k \approx \frac{\textsc{c}_0}{M\sigma k^2}\ . \tag{8.67}$$

The result holds only for modes in the local regime where $\textsc{c}_0 k \ll 1$.

8.7 Equation of motion for the meniscus: memory effects

In this section we study the equation of motion for the liquid-gas interface and show that the combined system (contact line and meniscus) has a memory, i.e. the changes in the morphology of the contact line will affect the motion of the meniscus for some time, not just instantaneously. We will show this by demonstrating that the evolution equation of the meniscus starts resembling a diffusion equation on certain time and length scales.

In the following we will concentrate on modes satisfying the constraint $\textsc{c}_0(t)k \ll 1$, which determines the so called local regime. In this regime the equation of motion will be local in real space; in Fourier space only even powers of wave vectors will appear. From Eq. (8.65) we obtain

$$\partial_t h_{\mathbf{k}}(t) = -\tilde{\sigma}k^2\,h_{\mathbf{k}}(t)\ , \tag{8.68}$$

where $\tilde{\sigma} \equiv M\sigma/(4\tilde{g}_1)$. In real space we have the following equivalent boundary value problem

$$\left\{\begin{array}{l}\partial_t h(x,y,t) = \tilde{\sigma}\nabla^2 h(x,y,t)\ .\\ h(x,0,t) = c(x,t)\ .\end{array}\right. \tag{8.69}$$

Strictly speaking, one should be more carefull with going from Fourier to real space because Eq. (8.68) is only valid for wave vectors $\mathrm{c}_0(t)k \ll 1$. For larger values of k one should take into account the full k-dependence of the functions g_1 and g_2 appearing in Eq. (8.65). The correction terms arising from the inclusion of the full k-dependence will be neglected in the following.

The full solution of the boundary value problem of the type $(\partial_t - \tilde{\sigma}\nabla^2)\psi = \rho$ with Dirichlet, von Neumann or mixed boundary conditions is given by [286]:

$$\begin{aligned}\psi(\mathbf{r},t) \;=\; & \int_{t_0}^{t} dt' \int_V dV'\, G^H(\mathbf{r},t;\mathbf{r}',t')\,\rho(\mathbf{r}',t') + \tilde{\sigma}\int_{t_0}^{t} dt' \int_S dS' \,\Big[G^H(\mathbf{r},t;\mathbf{r}',t')\,\partial_{n'}\psi_S(\mathbf{r}',t') \\ & - \partial_{n'}G^H(\mathbf{r},t;\mathbf{r}',t')\,\psi_S(\mathbf{r}',t')\Big] + \int_V dV'\, G^H(\mathbf{r},t;\mathbf{r}',t_0)\,\psi(\mathbf{r}',t_0)\;, \end{aligned} \tag{8.70}$$

where G^H is the Green function of the diffusion equation (heat kernel) respecting the boundary conditions and $\tilde{\sigma}$ plays the role of the diffusion constant. The source term is denoted by ρ and the initial condition by $\psi(\mathbf{r},t_0)$. Naturally it is assumed that $t > t_0$. The boundary of domain V is S; $\psi_S(\mathbf{r},t)$ denotes the point $\mathbf{r}$ on S and $\partial_n\psi_S$ the component of $\nabla\psi$ along the outward normal $d\mathbf{S}$. Depending on whether we choose to use Dirichlet or von Neumann boundary data, only one of the two boundary data terms on the right hand side of Eq. (8.70) will survive, because the Green function G^H_{2D} is assumed to fulfil *homogeneous* boundary conditions.

If t_0 would be taken to be the time when the initial meniscus was a flat plane, dropping the last term of Eq. (8.70) would be rigorously justified. However, since Eq. (8.69) becomes valid only when the terms proportional to the velocity of the contact line $\partial_t\mathrm{c}_0$ can be neglected, the meniscus has had enough time to assume some non-flat shape. For the discussion of memory effects the last term is not important in the sense that it doesn't contain any information on the configurations at the intermediate times $t' \in (t,t_0)$ unlike the second term in Eq. (8.70). Forgetting the initial condition and source terms we can now write down the solution. For von Neumann data we get

$$h(\mathbf{r},t) = \tilde{\sigma}\int_{t_0}^{t} dt' \int_{-\infty}^{\infty} dx'\, G^H_{2D}(x,y,t;x',0,t')\,\alpha(x',t')\;. \tag{8.71}$$

Above we utilized the assumption of small α: $\partial_y h|_0 = \tan\alpha \approx \alpha$. For the Dirichlet problem posed in Eq. (8.69) we obtain:

$$h(\mathbf{r},t) = -\tilde{\sigma}\int_{t_0}^{t} dt' \int_{-\infty}^{\infty} dx'\, \partial_{y'} G^H_{2D}(x,y,t;x',y',t')|_{y'=0}\, c(x',t') \tag{8.72}$$

Choosing the Dirichlet boundary data we see that for $\partial_t\mathrm{c}_0 \approx 0$ both the *fluctuations* of the local contact angle $\theta(x,t) = \pi/2 - \alpha(x,t)$ and the *fluctuations* of the meniscus $h(x,y,t)$ can be expressed with the aid of a memory kernel:

$$h(x,y,t) = \int_{t_0}^{t} dt' \int_{-\infty}^{\infty} dx'\, K_h(x-x',y,t-t')\,c(x',t') + h_i(x,y,t)\;; \tag{8.73}$$

$$\alpha(x,t) = \int_{t_0}^{t} dt' \int_{-\infty}^{\infty} dx'\, K_\alpha(x-x',t-t')\,c(x',t') + \alpha_i(x,t)\;, \tag{8.74}$$

where we have also taken into account the modifications due to the initial conditions h_i and α_i at time t_0. They can be easily worked out from Eq. (8.73). Explicitly,

$$K_h(x-x',y,t-t') \equiv -\tilde{\sigma}\frac{\partial}{\partial y'} G^H_{2D}(x,y,t;x',y',t')|_{y'=0}\;; \tag{8.75}$$

$$K_\alpha(x-x',t-t') \equiv -\tilde{\sigma}\frac{\partial^2}{\partial y \partial y'} G^H_{2D}(x,y,t;x',y',t')|_{\substack{y=0\\ y'=0}} \ . \tag{8.76}$$

First of all, it should be remembered the only *constant* solution of Eqs. (8.73) and (8.74) is the trivial one: $h = 0$, $\alpha = 0$. These equations describe the fluctuations and any constant contribution has been included in the zeroeth order term H_0. Secondly, we note that it doesn't suffice to set $y = 0$ in Eq. (8.72) or in Eq. (8.73) to generate an integral equation for the contact line c, since both these formulae were derived under the assumption that the mean height C_0 has already become almost stationary. Eq. (8.73) doesn't say anything about how the flucutations of the meniscus (or the contact line) evolved while the mean interface height was traversing towards its initial position at $t = t_0$. This information is buried in the term $h_i(x,y,t)$. To take into account the time developement as well as the random fluctuations of the wetting properties of the wall, one should use Eq. (8.58). Similar criticism applies to the formula for the dynamic contact angle which was derived for $\alpha \ll 1$ by differentiating Eq. (8.73) with respect to y. To get an expression for the dynamic contact angle *during* movement of the average contact line position $\mathrm{C}_0(t)$ (say, as a function of driving chemical potential gradient) one has to resort to different solution scheme because the Green function formula above only works for operators of the type ∇^2.

By substituting Eq. (8.73) into the evolution equation of the contact line (Eq. (8.48)) we can formally cast the contact line dynamics into a form of the generalized Langevin equation which in the Fourier space reads

$$\partial_t c_k(t) + \int_{t_0}^{t} dt' S_{kk'}(t-t')\, c_{k'}(t') = f_r \ , \tag{8.77}$$

where $S_{kk'}$ is the memory kernel matrix (App. C.16). Summation is implied over the entry $\mathbf{k}'$. The random noise term f_r is not thermal but quenched so the full equation is nonlinear, after all. The emergence of memory terms is, of course, immediately clear from the full equation of motion of the meniscus (Eq. (8.47)) after one replaces the fluctuation part of the terms H with h given in Eq. (8.73). Drastic approximations are needed, though, to unravel the physics.

8.8 Stripe defects and restoring force

Restoring force is the (deterministic) force opposing the bending of the contact line. The line is being bent either by geometric properties (roughness of the solid walls) or by different local wetting properties arising from the chemical composition of the walls. These two effects result in different types of terms in the equation of motion of the contact line and hence, one cannot be replaced fully by the other in some effective sense. As stated in the beginning of Chap. 8 we will only concentrate on chemically inhomogeneous but completely smooth solid surfaces. The chemical composition such as that of a polycrystalline material is said to give rise to a regular defect, when the local wetting properties of a region having a simple well defined geometric shape is different from the rest of the wall. For example, take the wall to be situated on plane $y = 0$, which means that its surface of the wall is spanned by coordinates x and z. If the local wetting properties of a stripe like region ($-L_d/2 \leq x \leq L_d/2$, $-\infty < z < \infty$) are homogeneous and different from the rest of the wall, we call it a stripe defect with defect width L_d. From our results it is clear that the form of the force is independent of the precise form of the defect geometry. In contrary, the force is dependent on the overall geometry (whether there are two walls or just one, for instance).

Let us now see how the physical set-up affects the form of the restoring force per unit lenght, $\Gamma(k)$. The first derivation was presented by Joanny and de Gennes (JdG) who obtained a linear wave vector dependence:

$$\Gamma_{JdG}(k) = \theta_0^2 \sigma |k| \ . \tag{8.78}$$

In the previous equation σ denotes the liquid-gas surface tension and θ_0 is the contact angle. A similar derivation was presented by Pomeau and Vannimenus in Ref.[287]. The authors included the effect of gravity which was neglected in the derivation of Eq. (8.78). The result in the units of capillary length $\sigma/(g\rho)$ is

$$\Gamma_{PV}(k) = \vartheta^{-\frac{3}{4}} \left(1 + \vartheta^{-\frac{1}{2}} k^2\right)^{\frac{1}{2}} \ , \tag{8.79}$$

where the geometric factor $\vartheta \equiv 1 + (\tan\theta_0)^{-2}$. The contact angle $\theta_0 = \arctan \partial_y \mathrm{H}_0|_{y=0}$. Eq. (8.79) is a slight generalization of Pomeau and Vannimenus which interpolates correctly between the small and large values of distance y as compared to capillary length. Equivalently, in Fourier space one can reproduce the JdG result by considering wave vectors $k/\vartheta^{1/4} \gg 1$ for $\theta_0 \ll 1$. In this chapter we are studying a set-up where there are two walls instead of just one and no gravity. Inclusion of gravity is discussed in Sect. 10.2 This change in the global geometry changes the form of the kernel Γ changes again. In the units of L, the wall separation, we get

$$\Gamma_{2W}(k) = \sigma |k| \coth(|k| L) \tag{8.80}$$

All of these three kernels become similar for large enough values of the wave vector $|k|$. To get a nonzero value for the kernel one needs either gravity or a finite system (finite wall separation for the two wall set-up). The detailed derivation of the restoring force Γ_{2W} has been presented in App. C.17. It should be noted that the factor θ_0^2 present in Eq. (8.78) is missing from our result due to the different choice of coordinates better suited for contact angles close to $\pi/2$. Even when the liquid-gas surface is exactly perpendicular to the solid wall, there is a finite restoring force resisting bending of the line.

Based on the form of the restoring force for the two-wall set-up, it is straightforward to write down the relationship existing in equilibrium between the contact line profile ($\mathrm{C}(x,t)$) and the local wetting properties of the solid wall (Γ):

$$\mathrm{C}(x) = \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dq \, \frac{\kappa(x, \mathrm{C}(x)) \, \cos(q(x - x_1))}{\Gamma_{2W}(q)} \ . \tag{8.81}$$

The local surface tension fluctuations have been denoted by $\kappa(x,z) \equiv (\sigma_{sl}(x,z) - \sigma_{sg}(x,z))/\sigma$, where σ is the liquid-gas surface tension. The restoring force kernel Γ_{2W} is given in Eq. (8.80). Clearly more complicated defect geometries can be considered with the aid of Eq. (8.81) than just a single stripe defects. For example, we can easily find out the emerging contact line profile for an array of stripe defects by making $\kappa(x,z)$ a periodic function in x. When considering defects which have unlimited extension in the z-direction, the non-linearity present in Eq. (8.81) vanishes and we have

$$\mathrm{C}(x) = \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dq \, \frac{\kappa(x) \, \cos(q(x - x_1))}{\Gamma_{2W}(q)} \ . \tag{8.82}$$

For a single stripe defect $\kappa = k_2 = const$ when $|x| < L_d$ and otherwise $\kappa = k_1$, where k_1 is another constant. The width of the defect is L_d. As pointed out at the end of App. (C.18), in order for the integral to exist, it is important that $\Gamma_{2W}(q)$ does not go to zero too fast (or at all). Thus, we see that one does not even have to introduce gravity to have the desired property $\lim_{k\to 0} \Gamma(k) \to const$: Confinement of the fluid between two walls suffices.

8.9 Dissipation channels

Wetting of defects having regular geometry is just application among many others. Using the formalism presented it is possible to study the dynamics of these effects, not just in thermal equilibrium properties. Another dynamics related application has to do with the foundations of dissipation channels close the moving contact line. Ref. [288] utilizes a variational formalism similar to ours. They study the spreading dynamics of a sessile droplet, which relaxes from the initial nonequilibrium configuration to equilibrium its shape obeyin the following equation of motion:

$$\frac{\delta R_{1D}[r,\dot{r}]}{\delta \dot{r}(t)} = -\frac{F_{1D}[r]}{\delta r(t)} \ . \tag{8.83}$$

The radius of the droplet is $r(t)$. The free energy is just the surface free energy of the droplet, which can be parametrized in terms of the height ξ of the droplet from solid:

$$F_{1D}[r] = \pi r^2(t)(\sigma_{sl} - \sigma_{sg}) + 2\pi\sigma \int_0^{r(t)} d\rho\, \rho \sqrt{1 + (d\xi/d\rho)^2} \ . \tag{8.84}$$

Owing to the volume conservation of the liquid, there is a functional relationship between the height and the radius, which must be taken into account when taking the variational derivative of F_{1D} with respect to r.

The dissipation functional is not constructed through projections as in our approach. Instead, the authors make use Ref. [260], where the dissipative contributions to the contact line motion are divided into three channels:

$$R_{1D} = R_l + R_w + R_f \ . \tag{8.85}$$

The origin of the first term on the right hand side of Eq. (8.85) lies in the asymmetric hopping of the liquid molecules between the adsorbtion sites of the solid surface as they are pushed away by the advancing liquid edge [288]. This term has the form

$$R_l = 2\pi r \, \frac{\zeta_0 \dot{r}^2}{2} \ , \tag{8.86}$$

where ζ_0 is a friction coefficient. The second term, R_w, accounts for the dissipation due to viscous fluid flow inside the droplet:

$$R_w \propto r\eta\dot{r}^2 \ln(r/a) \ , \tag{8.87}$$

with a microscopic cut-off a. The viscosity of the fluid is η. Finally, the last channel, R_f, is due to the dissipation in the precursor film:

$$R_f \propto \frac{\eta\dot{r}^2}{\theta_a} \ , \tag{8.88}$$

where θ_a is the apparent contact angle. Even though all these terms (R_l, R_w, R_f) are proportional to the square of the velocity, they cannot be derived from our Rayleigh dissipation functional, which, dispate being proprotional to the square of the velocity, only conveys the effects of fluid's mass conservation. After all, the nontrivial kernel G_{3D} results from the inversion of the ∇^2-operator on the right hand side of the fundamental bulk equation of motion (8.36).

How to derive the dissipation channels more rigorously, without resorting to a semi-phenomenological contact line equation (8.83)? As all the channels result from the effect of hydrodynamics of the fluid molecules, we cannot rely on an entirly diffusive mass transport model used in this chapter. The motion of the fluid molecules have to be taken into account by proper coarse-graining of the hydrodynamic degrees of freedom combined with the diffusive phase-field model given by Eq. (8.36) This is the subject of Chap. 9. However, in the current context we do not take the modeling as far as to be able dexcribe processes giving rise to the term R_l. We only show how to systematically derive an equation of motion for a system where the conservation of the momentum of the fluid is to be accounted for. It remains as a future project to try to justify at least the terms R_w and R_f through a two stage projection process which we have described in this chapter. When properly done, it may be possible that the conservation of the fluid volume will affect the form of the dissipative terms above. It will be especially interesting to compare with theories which are based on solid physics principles but which use less systematic procedure to derive the time evolution of triple line. For example, Ref. [289] gives the following dynamics for the contact line motion on a heterogeneous surface:

$$\frac{3\eta l}{\theta_0}\frac{\partial c}{\partial t} = -\sigma\theta_0^2 \int dx' \, \Gamma_{PV} c(x',t) - H(c(x,t) + \mathrm{c}_0, z) \ . \ , \tag{8.89}$$

The equilibrium contact angle is θ_0 and l is a numerical constant originating from elimination of divergence of the viscous stress at the contact line. The random field $H(x,z)$ corresponds to our random wetting force A_k. The right hand side coincides exactly with our result of Eq. (8.61) when the restoring force takes into account the effect of gravity: $\Gamma = \Gamma_{PV}$ given in Eq. (8.79) and contact angle θ_0 is assumed to approach zero. When the projection formalism is applied to the fully hydrodynamical model (which will be briefly discussed in Sect. 10.2 for non-fluctuating contact line) we expect the friction term on the left of Eq. (8.89) to be modified due to the presence of the Green's function G_{3D}, which takes care of the volume conservation. Similar comments apply to a recent proposition [290] to model the contact line motion with the aid of Model A type of non-conserved phase-field technique coupled with hydrodynamics. In contrast, the conservation of the fluid has been properly taken into account in Ref. [291], where contact line dynamics of a diffuse fluid interface is studied using phase-field description. However, no clear meaning is associated with the order parameter field ϕ, which is just referred to as "measure of the phase". When the coarse-graining from microscopics is possible, as is the case here, there will be no uncertanity about the physical interpretation of the macroscopic fields, such as ϕ. We have already considered some possible interpretations in Sect. 6.4.2, where mass density and concentration representations are compared. The discussion is continued in Sect. 9.5.3.

Chapter 9

The route to classical hydrodynamics

9.1 Density functional of solid-fluid system

The interpretation and derivation of the components of the free energy functional are presented in Chap. 6. There the tools for deriving the effective action (free energy) are discussed in more detail. The proper derivation based on density functional theory reveals the precise for F_t should have when expressed in terms of the set of relevant macroscopic variables which consists of the mass density and momentum densities (velocity) of the fluid as well as the mass density of the solid. The total free energy F_t of the solid-fluid system can be decomposed into three parts as

$$F_t = F_k + F_f + F_S \ . \tag{9.1}$$

As we are going to utilize a variational principle in most of this work work, we customarily include also a time integral in the expression of the free energy so that the units of F_t are actually those of action: $[F_t] = [E]s$, where unit of energy is denoted by $[E]$. For more details on the units of F_t the reader is referred to App. D.1. The first term in Eq. (9.1) is the energy of the moving fluid elements, which are being constantly kicked by the equilibrium thermal fluctutations in addition to being subject to macroscopic fluxes imposed through boundary conditions:

$$F_k = \int dV \int dt \ \tfrac{1}{2}\phi \, \mathbf{v}^2 \ . \tag{9.2}$$

The form of the kinetic part of the free energy density can be justified in many ways, for example by Galilean invariance. Another derivation presented in Ref. [240] is based on a direct cellular coarse-graining technique, which is also discussed in Chap. 6. There we have also derived the free energy of the inhomogeneous stationary fluid F (Eq. (???)), which we now split into two pieces: $F = F_f + F_S$.

$$F_f = \int dV \int dt \ \left[\tfrac{1}{2}|\nabla\phi|^2 + V(\phi) \right] \ , \tag{9.3}$$

where ϕ is the density field. For a liquid-gas system the potential has a double well form: $V(\phi) = a\phi^2 + b\phi^4$ as discussed earlier. The remaining piece

$$F_S = \int dV \int dt \ (V_S - \mu_0)\phi \ . \tag{9.4}$$

The potential V_S of the solid wall felt by the fluid particles is called the substrate potential. The constant (auxiliary) chemical potential μ_0 doesn't play a role in what follows and will be dropped from further analysis.

The substrate potential V_S also enables the modeling of the variable thickness of the absorbed liquid film under complete wetting conditions in the direction normal to the solid surface. As this was not relevant for the applications we considered in Chap. 8, we used there another (analytically simpler) form of the fluid-solid free energy, which also allowed us to establish the connection between the phase-field and density functional theories. As argued in Sect. 7.3, the physics remains the same if we replace the sum $F_f + F_S$ given above with the functional (Sect. 7.3)

$$F = \int dV \int dt \, \left[\tfrac{1}{2} |\nabla \phi|^2 + V(\phi, \rho, A) \right] \ , \tag{9.5}$$

where ρ is the density field of the solid and A is the wall potential, which plays a role similar to the substrate potential V_S as far as the local surface tensions are considered even though its *effects* are macroscopically relevant. The wall potential A is thus not a macroscopic relevant variable in the same sense as ρ, ϕ and $\mathbf{v}$. Setting the value of $\phi = A$ in D' (= domain of the solid), where A is a given local function, determines the local wetting properties of the solid surfaces in the system. Alternatively, one can choose to change the substrate potential V_S in order to change the local surface tensions. As shown in Ref. [262], the wall potential, which vanishes in the fluid phase, is sufficient to reproduce Young's law governing equilibrium contact angle formation.

In the next section we will derive the evolution equations of the coarse-grained, macroscopically relevant variables (*e.g.* mass and momentum densities). The form of these equations is dictated by the form of the free energy, which we have been able to derive from microscopics. An important related issue is to what extent can the boundary conditions of the evolution equations of the relevant variables be *derived from* the microscopics. This question is not commonly pondered in the literature: the boundary conditions are usually imposed in such a way that the problem becomes mathematically well-posed and respects the experimentally observed facts. In the forthcoming chapters we will demonstrate that the effective boundary conditions on a macroscopic level are readable from the form of the free energy. Indeed, in Ch. 11 we demonstrate that a substrate potential, which does not vanish in the fluid phase, does play a role in the emergence of the solid-fluid boundary condition for the velocity of the fluid elements. This effect is not accounted for by a wall potential A which vanishes in the fluid domain. To model the interaction between the fluid and the solid at this level can be done by letting $A = A(x, y, z) \neq 0$, even when $z \in D$ (D = fluid domain) in the vicinity of the solid boundaries. This extention is not used, however, in any of the current applictions of this work.

9.2 Evolution of coarse-grained fields

Corresponding to the splitting of the free energy, we will denote the chemical potentials arising from taking the variation with respect to ϕ with the same subscripts. Thus,

$$\mu_k \equiv \frac{\delta F_k}{\delta \phi} = \frac{1}{2} v^2 \ \ ; \ \ \mu_f \equiv \frac{\delta F_f}{\delta \phi} \ \ ; \ \ \mu_S \equiv \frac{\delta F_S}{\delta \phi} = V_S \ . \tag{9.6}$$

We note that μ_f is the same chemical potential μ which we used in Sect. 8.4. The total chemical potential is obviously

$$\mu_t \equiv \frac{\delta F_t}{\delta \phi} = \mu_k + \mu_f + \mu_S \ . \tag{9.7}$$

This information will be used to derive the Poisson bracket terms in the equation of motion for the velocity (momentum) field $\mathbf{v}$. We denote the contribution to $\partial_t v_i$ due to the nonlinear coupling between the velocity and the order parameter field ϕ as $Q_{\mu\nu}$, where μ and ν refer to the labeling of the components of the order parameter. The order parameter ψ is a column vector whose transpose is below denoted by row vector ψ^{T}:

$$\psi^{\mathrm{T}} \equiv [\psi_0, \psi_1, \psi_2, \psi_3]^{\mathrm{T}} = [\phi(\mathbf{x},t), v_x(\mathbf{x},t), v_y(\mathbf{x},t), v_z(\mathbf{x},t)]^{\mathrm{T}} \ . \tag{9.8}$$

In our hydrodynamic formulation, we have four dynamically relevant components ψ_μ: the density field ϕ is the zeroeth component of ψ; the three remaining components of ψ consist of the three components of velocity (momentum density) v_s ($s = x, y, z$, or $s = 1, 2, 3$). As will be discussed at the end of this section and in Sect. D.2.2 we should really use the momentum density as the order parameter and write instead of Eq. (9.8),

$$\psi^{\mathrm{T}} \equiv [\psi_0, \psi_1, \psi_2, \psi_3]^{\mathrm{T}} = [\phi(\mathbf{x},t), j_x(\mathbf{x},t), j_y(\mathbf{x},t), j_z(\mathbf{x},t)]^{\mathrm{T}} \ . \tag{9.9}$$

However, since the equations of motion appear more familiar in the velocity representation we can use the variable $\mathbf{v}$ directly for the purposes of Sect. 9.3 and Sect. 9.4.

The simplest possible form of the equation of motion for the order parameter field, which guarantees relaxation to Gibbs equilibrium characterized by F_t and which incorporates the macroscopic Poisson bracket in an intuitive way, is given below:

$$\boxed{\partial_t \psi_\mu(\mathbf{x},t) = N_\mu - \Gamma_{\mu\nu} \frac{\delta F_t[\psi]}{\delta \psi_\nu} + \eta_\mu(\mathbf{x},t) \ .} \tag{9.10}$$

Einstein summation convention for repeated indices is used. The various quantities appearing in the previous formula are defined as follows: $\Gamma_{\mu\nu}$ is the dissipative coefficient ($\propto \nabla^2$ for conserved dynamics) and η_μ is the thermal noise field, whose correlations depend on $\Gamma_{\mu\nu}$. For conserved dynamics the noise is conserved, which means that the thermal average $\langle \eta(\mathbf{x},t)\eta(\mathbf{x}',t')\rangle \propto \nabla^2 \delta(\mathbf{x}-\mathbf{x}')\delta(t-t')$. More complicated forms of the noise correlator are encountered in Sect. 9.5.2. Finally, N_μ is the Poisson bracket term producing couplings between different component fields. Its exact form will be derived in App. D.4:

$$N_\mu = -\int d\mathbf{x}' \left(Q_{\mu\nu}(\mathbf{x},\mathbf{x}') \frac{\delta F_t[\psi]}{\delta \psi_\mu(\mathbf{x}')} - T \frac{\delta Q_{\mu\nu}}{\delta \psi_\mu(\mathbf{x}')} \right) \ . \tag{9.11}$$

To get N_μ we need to compute $Q_{\mu\nu}$, which is defined to be the Poisson bracket of the macroscopic component fields:

$$Q_{\mu\nu}(\mathbf{x},\mathbf{x}') \equiv \{\psi_\mu(\mathbf{x}), \psi_\nu(\mathbf{x}')\} \ . \tag{9.12}$$

Typically the latter term in Eq. (9.11) turns out to be zero or negligible for other reason. In the current construction it is equal to zero as shown below. Since all Poisson brackets

$Q_{\mu\nu}$ are proportional to a derivative of the delta function, it suffices to study just the case $Q_{\mu\nu} = \{v_s(\mathbf{x}), \phi(\mathbf{x}')\}$ ($\mu = s = 1, 2, 3$ and $\nu = 0$). We obtain,

$$\begin{aligned} \int d\mathbf{x}'\, T \frac{\delta Q_{\mu\nu}}{\delta\psi_\mu(\mathbf{x}')} &= T \int d\mathbf{x}'\, \frac{\delta}{\delta\phi(\mathbf{x}')} \left(\phi(\mathbf{x}) \frac{\partial\delta(x_s - x'_s)}{\partial x_s} \prod_{r\neq s} \delta(x_r - x'_r) \right) \qquad (9.13) \\ &= T\, V^{2/3} \int dx'_s\, \delta(x_s - x'_s) \frac{\partial\delta(x_s - x'_s)}{\partial x_s} = 0 \; . \qquad (9.14) \end{aligned}$$

We have normalized the delta functions at zero equal to the linear size L of the system $\delta(\mathbf{0}) = V = L^3$, where V is the total volume. The last integral is zero because we are integration an odd function over the symmetric interval. Similiar argumentation holds for the Poisson brakets of the momentum densities, as well. If one treats $\mathbf{v}$ as the fundamental variable and relates it to the momentum density the latter term on the right hand side of Eq. (9.11) can become non-zero. This is another indication that it is really the momentum field which should be considered more fundamental than the velocity field.

9.3 Momentum balance

We first derive the equation of motion of the momentum field $\mathbf{j}$ of the fluid, which can be recast in a little bit different but more familiar form in terms of the velocity field $\mathbf{v}$. As argued above, we can drop the second term on the right hand side of Eq. (9.11) yielding

$$N_s = -\int d\mathbf{x}'\, Q_{\mu s}(\mathbf{x}, \mathbf{x}') \frac{\delta F_t[\psi]}{\delta\psi_\mu(\mathbf{x}')} \qquad (9.15)$$

$$= -\int d\mathbf{x}'\, \{v_s(\mathbf{x}), \phi(\mathbf{x}')\} \frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}'\, \{v_s(\mathbf{x}), v_j(\mathbf{x}')\} \frac{\delta F_t}{\delta v_j(\mathbf{x}')} \; . \qquad (9.16)$$

The number of spatial dimensions is three and the time dependence of the fields has been suppressed. It should be noted that the couplings mediated by the Poisson bracket terms lead to renormalization of both reactive and dissipative coefficients [5]. In other words, Poisson bracket terms contain both reactive and dissipative terms. The brackets are evaluated in App. D.1. We obtain

$$\{v_s(\mathbf{x}), \phi(\mathbf{x}')\} = \partial_s \delta(\mathbf{x} - \mathbf{x}') \; ; \qquad (9.17)$$

$$\{v_s(\mathbf{x}), v_j(\mathbf{x}')\} = \frac{(v_s(\mathbf{x}') - v_s(\mathbf{x}))}{\phi(\mathbf{x})} \partial_j \delta(\mathbf{x} - \mathbf{x}') + \frac{(v_j(\mathbf{x}') - v_j(\mathbf{x}))}{\phi(\mathbf{x}')} \partial_s{}' \delta(\mathbf{x}' - \mathbf{x}) \; . \qquad (9.18)$$

The abbreviatation ∂_i denotes differentiation with respect to x_i, and $\partial_i{}'$ denotes differentiation with respect to the primed coordinate x'_i.

The result of applying the kernels defined in Eq. (9.17) and Eq. (9.18) on an arbitrary function $f(x)$ is seen by partial integration which allows us to get rid of the derivatives of the delta functions:

$$\int d\mathbf{x}'\, \{v_s(\mathbf{x}), \phi(\mathbf{x}')\}\, f(\mathbf{x}') = \partial_s f(\mathbf{x}) \; ; \qquad (9.19)$$

$$\begin{aligned} \int d\mathbf{x}'\, \{v_s(\mathbf{x}), v_j(\mathbf{x}')\}\, f(\mathbf{x}') = &-v_s(\mathbf{x})\phi^{-1}(\mathbf{x})\partial_j f(\mathbf{x}) - \partial_s \Big[v_j(\mathbf{x})\phi^{-1}(\mathbf{x}) f(\mathbf{x}) \Big] \\ &+ v_j(\mathbf{x})\partial_s \Big[\phi^{-1}(\mathbf{x}) f(\mathbf{x}) \Big] + \phi^{-1}(\mathbf{x})\partial_j \Big[v_s(\mathbf{x}) f(\mathbf{x}) \Big] \; . \qquad (9.20) \end{aligned}$$

After replacing the function with an appropriate functional derivative of the total free energy, the Poisson bracket contribution to the equation of motion of the velocity field reads

$$\int d\mathbf{x}' \left\{v_s(\mathbf{x}), \phi(\mathbf{x}')\right\} \frac{\delta F_t}{\delta \phi(\mathbf{x}')} = \partial_s \mu_t = \partial_s \mu_k + \partial_s \mu_f + \partial_s \mu_S \ ; \tag{9.21}$$

$$\int d\mathbf{x}' \left\{v_s(\mathbf{x}), v_j(\mathbf{x}')\right\} \frac{\delta F_t}{\delta v_j(\mathbf{x}')} = (\mathbf{v} \cdot \nabla)\, \mathbf{v} - \frac{1}{2} \nabla v^2 \ , \tag{9.22}$$

where $v^2 \equiv v_1^2 + v_2^2 + v_3^2$. The velocity dependent term $\nabla v^2/2$ present in the expression of $\nabla \mu_k$ cancels out the last term on the right hand side of Eq. (9.22) when the two Poisson brakcet expressions of Eq. (9.21) and Eq. (9.22) are summed up. Thus, substituting the values of $\nabla \mu_k$ and $\nabla \mu_S$ into Eq. (9.16) and grouping similar terms together yields

$$\mathbf{N} = -\left[\, \nabla \mu_f + \nabla V_S + (\mathbf{v} \cdot \nabla)\, \mathbf{v} \,\right] \ . \tag{9.23}$$

The last term in the expression of $\mathbf{N}$ is the usual convective term of the Navier-Stokes equation. The second and third force terms are new. They will be shown to give rise to boundary conditions at solid-fluid and fluid-fluid boundaries. The full form of the momentum balance equation is

$$\phi \left(\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla)\, \mathbf{v} \right) = -\nabla p + \eta_d \nabla^2 \mathbf{v} + \tilde{\mathbf{f}}_b + \eta \ , \tag{9.24}$$

where we have defined a driving force term $\tilde{\mathbf{f}}_b$, which is a sum of the new terms mentioned above:

$$\tilde{\mathbf{f}}_b \equiv -\phi \nabla \mu_f - \phi \nabla V_S \ . \tag{9.25}$$

The final term on the right hand side of Eq. (9.24) describes the stochastic momentum exchange between fluid elements by thermal fluctuations. The emergence of the pressure term p is explained in Sect. 10.1. Depending on our preferences, different representations of this equation are possible. Also, the way the boundary conditions of the momentum balance equation has to be supplemented with, can change its appearance through additional terms. Some of the choices regarding boundary conditions are discussed in Sect. 11. With reference to Sect. 10.2 we can rewrite Eq. (9.24) as

$$\phi \left(\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla)\, \mathbf{v} \right) = -\nabla p_2 + \eta_d \nabla^2 \mathbf{v} + \mathbf{f}_b + \eta \ , \tag{9.26}$$

where, in addition to a new pressure field $p_2 \equiv p + \phi \mu_f$, we have used a new bulk force density

$$\mathbf{f}_b \equiv \mathbf{f}_{cap} + \mathbf{f}_{wall} \ , \tag{9.27}$$

whose effect on the dynamics of the flow will be made clear in the subsequent chapters. Specifically,

$$\mathbf{f}_{cap} \equiv \mu_f \nabla \phi \quad ; \quad \mathbf{f}_{wall} \equiv -\phi \nabla V_S \ . \tag{9.28}$$

Even though both terms have been expressed in terms of the bulk fields (μ_f, ϕ and V_S), their range of action is limited as can be easily seen from the form of the forces. The capillary force is active close to fluid-fluid boundaries where the density field experiences a sudden jump making $\nabla \phi$ a sharply peaked function there. By construction, the same mechanism is active at the fluid-solid boundary, because the gradient of ϕ changes there rapidly. However, it should be remembered, that in this work we do not make any claims about the actual form of the solid-fluid capillary stress which can be generalized from the more familiar fluid-fluid capillary stress [292] As will be shown in Chap. 11, $\mathbf{f}_{cap}$ will correctly reproduce the the well-know Laplace pressure drop across curved phase boundaries. The second term $\mathbf{f}_{wall}$ is active only in the vicinity of the solid walls due to the short range of the substrate potential V_S. Its effects, which are related to the emergence of the no-slip boundary condition of the fluid elements are discussed Sect. 11.3. There we also briefly discuss how V_S effects the magnitudes of the equilibrium contact angles in a three phase system. It should be remembered, that when the equilirium contact angle formation is concerned, one should either use the wall potential A, which we have introduced in Sect. 9.1, or the substrate potential V_S since their effect is the same.

9.4 Mass balance

In this section we derive the equation of motion of the mass density field ϕ, which turns out to take the form of the Model B of critical dynamics with an extra convective term. In Sect. 10.2 we study the consequencies of the convective term in the equation of motion of the phase-field ϕ. Proceeding in a similar manner as previously, Eq. (9.10) gives

$$\partial_t \phi(\mathbf{x}) = -\Gamma_{00} \frac{\delta F_t[\phi]}{\delta \phi} - \int d\mathbf{x}' \, \{\phi(\mathbf{x}), v_s(\mathbf{x}')\} \, \frac{\delta F_t}{\delta v_s(\mathbf{x}')} + \eta_0 \ . \tag{9.29}$$

The stochasitic *conserved* noise is denoted by η_0. Thus, the conservation law of mass determines the correlation function of the noise through the fluctuation–dissipation theorem and fixes the kinetic coefficient $\Gamma_{00} = -M\nabla^2$. The rest of the couplings are zeroes: $\Gamma_{0\nu} = 0$ for $\nu = 1, 2, 3$. The Poisson bracket gives

$$\{\phi(\mathbf{x}), v_s(\mathbf{x}')\} = \partial_s \delta(\mathbf{x} - \mathbf{x}') \ . \tag{9.30}$$

Applying it to an arbitrary function $f(\mathbf{x})$ gives

$$\int d\mathbf{x}' \, \{\phi(\mathbf{x}), v_s(\mathbf{x}')\} \, f(\mathbf{x}') = \partial_s f(\mathbf{x}) \ . \tag{9.31}$$

Substitution of $\delta F_t / \delta v_s = \phi \, v_s$ for f in Eq. (9.31) gives the explicit form of the Poisson bracket term:

$$\int d\mathbf{x}' \, \{\phi(\mathbf{x}), v_s(\mathbf{x}')\} \, \frac{\delta F_t}{\delta v_s(\mathbf{x}')} = \nabla \cdot (\phi \, \mathbf{v}) \ . \tag{9.32}$$

Placing the previous result on the left hand side of the equation gives the following equation of motion for the order parameter field ϕ:

$$\partial_t \phi + \nabla \cdot (\phi \, \mathbf{v}) = -\Gamma_{00} \frac{\delta F_t[\phi]}{\delta \phi} + \eta_0 \ . \tag{9.33}$$

Using the incompressibility, $\nabla \cdot \mathbf{v} = 0$ and the kinetic coefficient $\Gamma_{00} = -M\nabla^2$ gives

$$\partial_t \phi + \mathbf{v} \cdot \nabla \phi = M \nabla^2 \mu_t + \eta_0 \ , \tag{9.34}$$

where $\mu_t = \delta F_t[\phi] / \delta \phi$. The phase-field model, which we studied previously can be obtained by leaving out the convective term $\mathbf{v} \cdot \nabla \phi$ as well as the noise term η_0. In this approximation the density field ϕ obeys just the equation of continuity. There is also no connection with the heat bath. It should also be noted that the incompressibility condition is an extra restriction imposed on the velocity field. It is not deriveable from the present formalism. For a single homogeneous (constant density everywhere in space) fluid component the mass conservation equation reduces to the incompressibility condition since the diffusive mass flux vanishes and by the same token one should also remove the thermal noise to respect the fluctuation-dissipation theorem. Of course, in reality thermal noise is always present.

It is appropriate to point out that the incompressibility condition really means that the comoving density (following the fluid) is constant $d\phi/dt = \partial_t\phi + \mathbf{v}\cdot\nabla\phi = 0$. If the continuity equation holds (no sources or sinks), together with $d\phi/dt = 0$ it *follows* that $\nabla\cdot\mathbf{v} = 0$. Even gases can be taken effectively incompressible over sufficiently small distances, if the flow velocity is small enough (p.59, prob.6, Ref. [293]). From microscopic simulation point of view, when the particle velocities $\mathbf{u}_p$ are much smaller than the velocity of sound c_s, $\mathbf{u}_p \ll c_s$ the incompressibility result $\nabla\cdot\mathbf{v} = 0$ holds to a good approximation [294]. Compressibility of *mixtures* made of two incompressible components is discussed in Ref. [295].

9.5 Analysis of the equations of motion

In the following two subsections we analyze the equations of motion of single and two–component fluids more thoroughly. For compliteness sake we have also included the energy density, even though we have not derived any explicit representation of the dependence of the free energy density on the (internal) energy density $\mathcal{E}$. The temperature dependence of $f(\mathcal{E})$ is discussed in Sect. 6.5. Here we settle for contemplating on the zero temperature behaviour were appropriate.

9.5.1 Single component fluid, two phases

Relevant set of coarse-grained variables of a single component 2-phase fluid is $\psi \equiv (\phi, \mathbf{j}, \mathcal{E})$, where the index assignment goes as $\psi_0 \equiv \phi$, $\psi_i \equiv j_i$ $(i = 1, 2, 3)$, and $\psi_4 \equiv \mathcal{E}$. Instead of the momentum density one can use velocity. The internal energy density $\mathcal{E}$ can be replaced with entropy s (or $\mathcal{E}_p$ defined in App. D.1.4). The equations of motion are

$$\begin{aligned}
\partial_t\phi &= -\int d\mathbf{x}' \boxed{\{\phi(\mathbf{x}), \phi(\mathbf{x}')\}} \frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}' \{\phi(\mathbf{x}), j_s(\mathbf{x}')\} \frac{\delta F_t}{\delta j_s(\mathbf{x}')} && (9.35)\\
&\quad -\int d\mathbf{x}' \{\phi(\mathbf{x}), \mathcal{E}(\mathbf{x}')\} \frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \Gamma_{0\nu}\nabla^2 \frac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_0 \; . \\
\partial_t j_i &= -\int d\mathbf{x}' \{j_i(\mathbf{x}), \phi(\mathbf{x}')\} \frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}' \{j_i(\mathbf{x}), j_s(\mathbf{x}')\} \frac{\delta F_t}{\delta j_s(\mathbf{x}')} && (9.36)\\
&\quad -\int d\mathbf{x}' \{j_i(\mathbf{x}), \mathcal{E}(\mathbf{x}')\} \frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \Gamma_{i\nu}\nabla^2 \frac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_i \; . \\
\partial_t\mathcal{E} &= -\int d\mathbf{x}' \{\mathcal{E}(\mathbf{x}), \phi(\mathbf{x}')\} \frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}' \{\mathcal{E}(\mathbf{x}), j_s(\mathbf{x}')\} \frac{\delta F_t}{\delta j_s(\mathbf{x}')} && (9.37)\\
&\quad -\int d\mathbf{x}' \{\mathcal{E}(\mathbf{x}), \mathcal{E}(\mathbf{x}')\} \frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \Gamma_{4\nu}\nabla^2 \frac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_4 \; .
\end{aligned}$$

In Eq. (9.36) the index i takes values in the set $\{1, 2, 3\}$ correponding the to three momentum currents. The structure of all equations is the same: on the right hand side there are first the reactive terms which give couplings between the different coarse-grained variables. The last two terms describe dissipation of (free) energy and thermal fluctuations, which quarantee the relaxation to Gibb's equilibrium state. All dissipative terms are of 'conservation type' indicated by the presence of the operator $\Gamma_{\mu\nu}\nabla^2$. This is necessary to respect the conserved nature of the relevant coarse-grained variables. Other choices of dissipative coefficients are discussed in Sect. 9.5.2. Had some other (non-conserved) variable been used instead, it would not have been *a priori* clear what kind of dissipative coefficient one should use. Of course, the theory still does not say anything about the numerical value of $\Gamma_{\mu\nu}$, which can also be chosen to be zero.

We begin to analyze the set of equations above by a few observations on Eq. (9.35). The first (framed) Poisson bracket on the right is zero, it has just been written down for more symmetric appearance. The next term on the right, $\int d\mathbf{x}' \, \{\phi(\mathbf{x}), j_s(\mathbf{x}')\} \, \delta F_t/\delta j_s(\mathbf{x}') = \nabla \cdot \mathbf{j}$, is the familiar convective term (derived in Eq. (D.57)). The third term describes a coupling with the energy density and is not present in conventional mass balance equation. Also the last two terms, which describe dissipation ($\Gamma_{0\nu}\nabla^2\delta F_t/\delta\psi_\nu$) and noise ($\eta_\phi$) caused by thermal fluctuations, are absent in the conventional hydrodynamics. However, these terms are automatically generated through when applying Eq. (9.10). Thus, the formalism described in the beginning of Sect. 9.4 gives rise to both fluctuation (noise) and dissipation in the mass balance equation. Noise and dissipation go hand in hand: either they are both present or absent. Otherwise we have to accept the violation of the fluctuation-dissipation theorem. We should remember, though, that equations of the form of Eq. (9.35) without thermal noise, have been studied in other contexts. For example, in Ref. [4] a *phenomenological* evolution equation of the Cahn-Hillard type was taken to describe diffusive motion of fluid penetrating a porous medium. The dissipative term gives also rise to additional nonlinear momentum dependence due to the kinetic energy term present in F_t: $\Gamma_{00}\nabla^2\delta F_t/\delta\phi = \Gamma_{00}\nabla^2(-j^2/(2\phi^2)+\mu_f+\mu_S)$ and $\Gamma_{0\nu}\nabla^2\delta F_t/\delta\psi_\nu = \Gamma_{0\nu}\nabla^2(j_\nu/\phi)$ ($\nu = 1, 2, 3$). In traditional model H of critical dynamics this problem is avoided by scaling away the dependence of the order parameter ϕ such that the kinetic energy does not couple mass density with the momentum field. Some consequencies of this assumption are discussed at the end of App. D.1.2. For small flow velocities it seems appropriate to disregard the quadratic term in momentum density in the same way as the nonlinear convective term of the momentum balance equation can be left out.

If strict mass conservation is required the last two terms of Eq. (9.35) have to be left out and it reduces to the continuity equation of standard form. In case the extra terms are kept, we have to find a physical interpretation for them. The dissipative term $\Gamma_{00}\nabla^2\delta F_t/\delta\phi$ (which is the heart of the phase-field formalism without momentum and energy conservation) describes the interchange of mass between the liquid and gas phases. Without it the numerical solution of the pure mass balance equation cannot preserve a phase boundary of fixed internal width indefinitely. Leaving out the diffusive flux, means that we only have transport through the convective flux, $\mathbf{j} = \phi\mathbf{v}$, arising from the Poisson bracket between ϕ and $\mathbf{j}$. The stochastic terms (η_ϕ, $\eta_{\mathbf{v}}$, $\eta_{\mathcal{E}}$) describe the effect of coarse-graining: the thermal fluctuations in the mass balance formula are caused by uncontrolled 'leakage' through the walls of the differential fluid elements by microscopic motion of molecules [293]. Since mass cannot be generated out nothing, in the context of Eq. (9.35) one possibility to interpret η_ϕ is to say that it describes conversion of one phase to the other. Interpreted as a microscopic source/sink term, the noise η_ϕ describes condensation of small gas bubbles in liquid phase, or condensation of liquid droplets in the gas phase. This interpretation has special relevance close to the liquid-vapour critical point, where the coarse-graining cell size of cellular scheme [240] cannot become arbitrarily large. In a single phase fluid only continuity equation emerges (both dissipative and random terms are missing), whereas the momentum and energy balance equations may still contain noise [293].

The first two Poisson bracket terms on the right hand side of Eq. (9.36) produce the sum $-(1/\phi)\nabla p + \nabla \cdot \mathbf{P} + \tilde{\mathbf{f}}_b$ where p is the pressure and $\mathbf{P}_{ij} = (1/\phi)j_i j_j$ is the usual convective term of the momentum balance equation. For the free energy functional of Eq. (9.1) the force term $\tilde{\mathbf{f}}_b = -\nabla V_S - \nabla \mu_f$, where V_S is the solid wall potential and μ_f is the chemical potential of the fluid. Even though the third term on the right hand side of the momentum balance equation (9.36) gives a sensible contribution, when F_t is replaced with the microscopic Hamiltonian (App. D.3), the macroscopic contribution will be non-standard. This, of course, requires that we are able to find a sensible dependence of F_t on the macroscopic energy density $\mathcal{E}$. This point is further discussed in Sect. 6.5. The choice of the coefficient operator of the dissipation term of the momentum equation and the properties of the noise are presented in Sect. 9.5.2.

Finally, we make a few remarks on the reactive contribution to the energy balance equation (9.37). As shown in App. D.2.1 the convective terms $\nabla \cdot \mathbf{j}$ in the mass balance equation and $\nabla \cdot [(1/\phi)\,\mathbf{jj}] = \nabla \cdot \mathbf{P}$ in the momentum balance equation are correctly produced if one uses just the kinetic energy part $F_k[\phi, \mathbf{j}]$ of the full free energy functional F_t. These convective flux terms can also be motivated based on Galilean invariance of the equations of motion. In conventional hydrodynamics the Galilean invariant part of the energy flux tensor, $\mathbf{j}_G^{\mathcal{E}} \equiv \mathcal{E} + p$, contains both energy and the pressure field. Without knowing the explicit form of $F_t[\phi, \mathbf{j}, \mathcal{E}]$ in the total energy density $\mathcal{E}$, we cannot evaluate the Poisson bracket terms of Eq. (9.37). However, if we drop the internal energy contribution and evaluate on the flux of the kinetic energy density $\mathcal{E}_k \equiv j^2/(2\phi)$, we obtain

$$\begin{aligned}\partial_t \mathcal{E}_k &= -\int d\mathbf{x}'\,[-\mathbf{j}(\mathbf{x}) \cdot \nabla' \delta(\mathbf{x}' - \mathbf{x})]\,\frac{\delta F_t[\phi, \mathbf{j}]}{\delta \phi(\mathbf{x}')} \\ &\quad - \int d\mathbf{x}'\,\left[-\partial_j' \delta(\mathbf{x}' - \mathbf{x})\mathbf{P}_{ji}(\mathbf{x}) + \mathcal{E}_k(\mathbf{x}')\,\partial_i \delta(\mathbf{x} - \mathbf{x}')\right] \frac{\delta F_t[\phi, \mathbf{j}]}{\delta j_i(\mathbf{x}')}\ .\end{aligned} \tag{9.38}$$

The first term on the right hand side of previous equation is the contribution from the Poisson bracket $\{\mathcal{E}_k(\mathbf{x}), \phi(\mathbf{x}')\}$, which has been evaluated in Eq. (D.45). The second term on the right comes from evaluating the bracket $\{\mathcal{E}_k(\mathbf{x}), j_i(\mathbf{x}')\}$ (Eq. (D.49)). It should be noted that there is no term $\int d\mathbf{x}'\,\{\mathcal{E}_k(\mathbf{x}), \mathcal{E}_k(\mathbf{x}')\}\,\delta F_t/\delta \mathcal{E}_k(\mathbf{x}')$ appearing on the right hand side of Eq. (9.38). This is because $\mathcal{E}_k$ is not an independent variable but expressible in terms of ϕ and $\mathbf{j}$. If the substrate contribution to the free energy F_t is left out, then $\delta F_t[\phi, \mathbf{j}]/\delta \phi(\mathbf{x}') = -j^2(\mathbf{x}')/(2\phi^2(\mathbf{x}')) + \delta F_f/\delta \phi(\mathbf{x}')$. Substitution of this result together with $\delta F_t[\phi, \mathbf{j}]/\delta j_i(\mathbf{x}') = j_i(\mathbf{x}')/\phi(\mathbf{x}')$ into Eq. (9.38) gives

$$\partial_t \mathcal{E}_k = -\mathbf{j} \cdot \nabla \frac{\delta F_f}{\delta \phi} - \nabla \cdot \left(\mathcal{E}_k \frac{\mathbf{j}}{\phi}\right) = -\mathbf{v} \cdot (\nabla p + \nabla \cdot \mathbf{p}_{cap}) - \mathbf{v} \cdot \left(\mathbf{v}\,\frac{1}{2}\phi v^2\right)\ , \tag{9.39}$$

where we have utilized $\mathbf{j} = \phi \mathbf{v}$, and the relation $\phi \delta F_f/\delta \phi = \nabla p + \nabla \cdot \mathbf{p}_{cap}$ to be derived in Sect. 10.1.1. Moreover, the microscopic momentum flux density tensor $\mathbf{P}^{\ddagger}$ appearing in Eq. (D.54) has been replaced with the macroscopic one, which corresponds to taking averages of both sides of equation of motion. It is this term which is responsible for cancelling out the nonlinear momentum dependence of the first term on the right hand side of Eq. (9.38): $\int d\mathbf{x}'\,\nabla' \delta(\mathbf{x}' - \mathbf{x}) \cdot \mathbf{P}(\mathbf{x}) \cdot (\mathbf{j}(\mathbf{x}')/\phi(\mathbf{x}')) = -\mathbf{j}(\mathbf{x}) \cdot \nabla[j^2(\mathbf{x})/(2\phi^2(\mathbf{x}))]$. Let us compare the results to those of conventional hydrodynamics, which yields the following relation:

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\phi v^2\right) = \frac{1}{2}v^2 \partial_t \phi + \phi \mathbf{v} \cdot \frac{\partial \mathbf{v}}{\partial t} = -\mathbf{v} \cdot \nabla p - \mathbf{v} \cdot \left(\mathbf{v}\,\frac{1}{2}\phi v^2\right)\ , \tag{9.40}$$

which reduces to our result when capillary pressure $\mathbf{p}_{cap}$ is neglected. When the time variation of the kinetic energy given above is combined with the time variation of the internal energy u (per unit mass) we obtain [293]

$$\frac{\partial \mathcal{E}}{\partial t} = \frac{\partial}{\partial t}\left(\frac{1}{2}\phi v^2 + \phi u\right) = -\nabla \cdot \left[\phi \mathbf{v}\Big(\frac{1}{2}v^2 + h_e\Big)\right] = -\nabla \cdot \left[\mathbf{v}\Big(\mathcal{E} + p\Big)\right] \ . \tag{9.41}$$

The last equality follows from the fact that the enthalpy per unit mass $h_e = u + p/\phi$. We have also substituted $\mathcal{E} = \phi v^2/2 + \phi u$. To confirm this result from Poisson bracket formalism, we should compute the time variation of the internal energy. To be able to do that, we need to determine the energy dependence of the free energy F_t, which we have not specified. This point is further discussed in Sect. 6.5.

9.5.2 Fluctuation and dissipation in single component fluid

In Sections 9.5.1 and 9.5.3 the structure of all the dissipative operators was for simplicity taken to be the same: $\Gamma\nabla^2$. This is a perfectly valid choice based on the conservation of the variables. However, such a choice has indications with respect to the physical properties of the fluid, such as its ability to sustain shear stress. We will make this more transparent below by using a single component, two-phase fluid as an example. For simplicity we will only concentrate on the dynamics of the velocity field as usually the viscous stresses are expressed directly in terms of $\mathbf{v}$, and consequently the fluctuation-dissipation relation is easily seen to hold.

Let us contrast some of the results of Sect. D.2.2 against standard hydrodynamics. First of all, we show below that treating velocity as the fundamental variable in the Poisson bracket formalism will lead to apparance of an 'extra' factor of ϕ in the dissipative term as compared to having the momentum density as the fundamental variable: In Eq. (D.77) the dissipative term reads $\Gamma\nabla^2(j_i/\phi) = \Gamma\nabla^2 v_i$ (momentum density as the fundamental variable) and the dissipative term in Eq. (D.79) is of the form $\hat{\Gamma}\nabla^2(\phi v_i)$ (velocity as the fundamental variable). To make the latter term appear like the the viscous term $\nu\nabla^2 v_i$ in standard hydrodynamics we have to define the use instead of the operator $\hat{\Gamma}\nabla^2$ a more complicated form of the dissipative operator defined below:

$$\hat{\Gamma}(\phi(\mathbf{x})v_i(\mathbf{x})) \equiv \left[\nu\nabla^2\frac{1}{\phi(\mathbf{x})}\right](\phi(\mathbf{x})v_i(\mathbf{x})) = \nu\nabla^2 v_i(\mathbf{x}) \ , \tag{9.42}$$

where we have used the kinematic viscosity $\nu \equiv \eta_d/\phi$ because both sides of the equation of motion (D.79) have been normalized by the density ϕ. In standard hydrodynamics, if the dissipative term is of the form $\nu\nabla^2 v_i$ we know that the fluid must be incompressible. This is because the general requirements on the stress tensor (vanishing under uniform rotation and at rest frame, small velocity gradients) allow us to express the Navier-Stokes equation in the form

$$\phi\Big(\partial_t\mathbf{v} + (\mathbf{v}\cdot\nabla)\mathbf{v}\Big) = -\nabla p + \eta_d\nabla^2\mathbf{v} + (\zeta + \eta_d/3)\nabla(\nabla\cdot\mathbf{v}) \ . \tag{9.43}$$

The shear viscosity is denoted by η_d and the bulk viscosity is ζ. Clearly, if the last term on the right is missing, we must have $\nabla\cdot\mathbf{v} = 0$, since both $\eta_d, \zeta > 0$. It is also assumed in Eq. (9.43) that the viscosities are not strognly dependent on the other thermodynamic fields (p, T), which holds reasonably well for many substances.

Hence, if we wish to allow the appearance of a more general form of the viscous stresses, we have to alter the properties of the stochastic noise terms η_i ($i = 1, 2, 3$) as compared to their properties associated with the simple dissipative term $\Gamma\nabla^2(\phi v_i)$ to fulfil the Fluctuation-Dissipation theorem. We are at liberty of making this choice, since the current Poisson bracket formalism does not fix the form of the coefficient operators. The dissipative operator L_{ij} corresponding to Eq. (9.43) reads instead of $\hat{\Gamma}\nabla^2$

$$L_{ij}(\mathbf{x}) \equiv \Big[\eta_d \delta_{ij}\nabla^2 + (\zeta + \eta_d/3)\nabla_i\nabla_j\Big]\frac{1}{\phi(\mathbf{x})} \ , \tag{9.44}$$

which is consistent with the results of Ref. [296, 297] when the mass density ϕ is taken to be a constant. The noise correlators of the components of the velocity field become

$$\langle \eta_i(\mathbf{x})\eta_j(\mathbf{x}')\rangle = 2TL_{ij}(\mathbf{x})\delta(\mathbf{x}-\mathbf{x}')\delta(t-t') \ . \tag{9.45}$$

When ϕ is not constant, the more general form of dissipative terms implies multiplicative noise terms, which are non-local in Fourier space. Of course, when the momentum density variable is taken to be the fundamental one, this type of non-locality due to the presence of the ϕv_i in the argument of the dissipative operator instead of just v_i, will not be a problem since the extra factor of ϕ vanishes when setting $j_i = \phi v_i$. Another source of non-locality in Fourier space comes about through mode coupling close to critical point. Thus, even though the noise itself would be independent of density or concentration, the transport coefficients, such as viscosity do acquire dependence on the other fields close to criticality as renormalization group procedure shows [298].

9.5.3 Two-component fluid

A relevant set of coarse-grained variables of a two-component single phase fluid is $\{\phi_0, \phi_1, \mathbf{j}, \mathcal{E}\}$, where ϕ_0 and ϕ_1 are the component mass densities. An alternative choice of relevant variables replacing ϕ_0 and ϕ_1 will be discussed later on. As before, the momentum density one can used instead of the velocity. Also, the internal energy density $\mathcal{E}$ can be replaced with entropy s (or $\mathcal{E}_p$ or temperature T). The equations of motion are

$$\begin{aligned}
\partial_t\phi_0 = & -\int d\mathbf{x}' \boxed{\{\phi_0(\mathbf{x}),\phi_0(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta\phi_0(\mathbf{x}')} - \int d\mathbf{x}' \boxed{\{\phi_0(\mathbf{x}),\phi_1(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta\phi_1(\mathbf{x}')} \qquad (9.46)\\
& - \int d\mathbf{x}' \,\{\phi_0(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}' \,\{\phi_0(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \boxed{\Gamma_{0\nu}\nabla^2\tfrac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_0} \ .\\
\partial_t\phi_1 = & -\int d\mathbf{x}' \boxed{\{\phi_1(\mathbf{x}),\phi_1(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta\phi_1(\mathbf{x}')} - \int d\mathbf{x}' \boxed{\{\phi_1(\mathbf{x}),\phi_0(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta\phi_0(\mathbf{x}')} \qquad (9.47)\\
& - \int d\mathbf{x}' \,\{\phi_1(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}' \,\{\phi_1(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \boxed{\Gamma_{1\nu}\nabla^2\tfrac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_1} \ .\\
\partial_t j_i = & -\int d\mathbf{x}' \,\{j_i(\mathbf{x}),\phi_0(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\phi_0(\mathbf{x}')} - \int d\mathbf{x}' \,\{j_i(\mathbf{x}),\phi_1(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\phi_1(\mathbf{x}')} \qquad (9.48)\\
& - \int d\mathbf{x}' \,\{j_i(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}' \,\{j_i(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \Gamma_{i\nu}\nabla^2\frac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_i \ .\\
\partial_t\mathcal{E} = & -\int d\mathbf{x}' \,\{\mathcal{E}(\mathbf{x}),\phi_0(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\phi_0(\mathbf{x}')} - \int d\mathbf{x}' \,\{\mathcal{E}(\mathbf{x}),\phi_1(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\phi_1(\mathbf{x}')} \qquad (9.49)\\
& - \int d\mathbf{x}' \,\{\mathcal{E}(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}' \,\{\mathcal{E}(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \Gamma_{5\nu}\nabla^2\frac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \eta_5 \ .
\end{aligned}$$

Similarily to Sect. 9.5.1, the boxed Poisson brackets are zero because they contain no dependence on microscopic momenta. The mass fluxes should contain no dissipative or stochastic components since they are conserved and cannot transform into each other as contrast to two-phase, single component case. The indices i takes the values $2, 3, 4$ above. The order parameter vector now has six components with the following organization:

$$(\psi_0, \psi_1, \psi_2, \psi_3, \psi_4, \psi_5) \equiv (\phi_0, \phi_1, j_1, j_2, j_3, \mathcal{E}) \ . \tag{9.50}$$

As the microscopic coordinates of different species are independent of each other, the Poisson brackets with the *total* momentum density $\mathbf{j} \equiv \phi \mathbf{v} = \mathbf{j}_0 + \mathbf{j}_1$ are are given by

$$\{\phi_a(\mathbf{x}), \mathbf{j}(\mathbf{x}')\} = \nabla\delta(\mathbf{x} - \mathbf{x}')\phi_a(\mathbf{x}') \ , \tag{9.51}$$

for $a = 0, 1$. In order to evaluate the bracket we used the following definition of the total momentum:

$$\mathbf{j}(\mathbf{x}, t) \equiv \mathbf{j}_0(\mathbf{x}, t) + \mathbf{j}_1(\mathbf{x}, t) = \sum_{\alpha_0} \mathbf{p}^{\alpha_0}(t)\, \delta(\mathbf{x} - \mathbf{x}^{\alpha_0}(t)) + \sum_{\alpha_1} \mathbf{p}^{\alpha_1}(t)\, \delta(\mathbf{x} - \mathbf{x}^{\alpha_1}(t)) \ , \tag{9.52}$$

where the summation index α_0 runs over the indices of particle species 0 and α_1 runs over the indices of species 1. Using Eq. (9.51) it is straightforward to show that the streaming part of Eqs. (9.46) and Eq. (9.47) without the total energy contribution are given by

$$\partial_t \phi_0 = -\nabla \cdot (\phi_0\, \mathbf{v}) \ . \tag{9.53}$$

$$\partial_t \phi_1 = -\nabla \cdot (\phi_1\, \mathbf{v}) \ . \tag{9.54}$$

For two totally immiscible fluids with different viscosities it is possible to use a separate momentum balance equations instead of just one, as we have done. However, whether or not mixing takes place, it is easier to consider suitably 'averaged' quantities such as total pressure ($p \equiv \sum_i p_i$), density ($\phi \equiv \sum_i \phi_i$) and velocity ($\mathbf{v} \equiv \sum_i (\phi_i/\phi)\mathbf{v}_i$) to simplify the mathematical description (p. 154 in Ref. [299]). It should also be noted that when computing Eq. (9.51) we did not have to specify the component velocities $\mathbf{v}_i$ ($i = 0, 1$). In total momentum description the variable viscosities can be taken into account by introducing $\eta_d = \eta_d(\phi)$ which takes values $\eta_0 \equiv \eta_d(\bar{\phi}_0)$ inside the domain of the fluid component 0 and the value $\eta_1 \equiv \eta_d(\bar{\phi}_1)$ within the second components domain. In these formulae $\bar{\phi}_i$ ($i = 0, 1$) are the bulk values of density. Effects of a spatially varying viscosity are discussed in Sect. 11.3.3.

Just like it was possible to use velocity instead of momentum density, we can replace the component mass densities ϕ_0 and ϕ_1 with the total density ϕ and concentration C (which is a useful variable for mixing components) of one of the species:

$$\phi \equiv \phi_0 + \phi_1 \ \ ; \ \ C \equiv \phi_0/(\phi_0 + \phi_1) = \phi_0/\phi \ . \tag{9.55}$$

Consequently, the relevant set of macrosvariables is now given by $\{\phi, C, \mathbf{j}, \mathcal{E}\}$. Owing to the nonlinear relation between the different variables one should keep in mind that in general the equations of motion produced by Poisson bracket formalism can differ depending on whether one first uses the fundamental conserved varibles (such as $\mathbf{j}$ and ϕ as in Sect. D.2.2) and then obtains an equation for a non-conserved variable ($\mathbf{v}$), or if one computes the equation of motion for the non-conserved variable directly. Indeed, in terms of ϕ and C we can replace

Eqs. (9.46) and (9.47) with

$$\begin{aligned}
\partial_t\phi &= -\int d\mathbf{x}'\,\boxed{\{\phi(\mathbf{x}),\phi(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}'\,\boxed{\{\phi(\mathbf{x}),C(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta C(\mathbf{x}')} && (9.56)\\
&\quad -\int d\mathbf{x}'\,\{\phi(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}'\,\{\phi(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \boxed{\tilde\Gamma_{0\nu}\nabla^2\tfrac{\delta F_t}{\delta\psi_\nu(\mathbf{x})}+\tilde\eta_0}\ .\\
\partial_t C &= -\int d\mathbf{x}'\,\boxed{\{C(\mathbf{x}),C(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta C(\mathbf{x}')} - \int d\mathbf{x}'\,\boxed{\{C(\mathbf{x}),\phi(\mathbf{x}')\}}\,\frac{\delta F_t}{\delta\phi(\mathbf{x}')} && (9.57)\\
&\quad -\int d\mathbf{x}'\,\{C(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}'\,\{C(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')} + \tilde\Gamma_{1\nu}\nabla^2\frac{\delta F_t}{\delta\psi_\nu(\mathbf{x})} + \tilde\eta_1\ .
\end{aligned}$$

In Eq. (9.56) we have should explicitly set $\tilde\Gamma_{0\nu} = \tilde\eta_0 = 0$ because the total mass density is a strictly conserved quantity. We have used a tilde symbol above the dissipative coefficients and the noise terms to stress the fact that they are different from the correponding quantities presented in Eqs. (9.46) and (9.47).

Leaving out the Poisson brackets with energy density, the total mass density and concentration evolution equations reduce to the following standard formula in the absense of sources and sinks in the velocity representation:

$$\begin{aligned}
\partial_t\phi &= -\nabla\cdot(\phi\,\mathbf{v})\ . && (9.58)\\
\partial_t C &= -\mathbf{v}\cdot\nabla C\ . && (9.59)
\end{aligned}$$

Eq. (9.58) is a direct consequence of the conservation of mass of both species given by Eqs. (9.53) and (9.54). The second equation can be derived by first formulating the Poisson bracket with concentration in terms of the primary variables ϕ_0 and ϕ_1. Using the chain rule one gets

$$\{C(\mathbf{x}),j_i(\mathbf{x}')\} = \frac{\partial C(\mathbf{x})}{\partial\phi_0}\,\{\phi_0(\mathbf{x}),j_i(\mathbf{x}')\} + \frac{\partial C(\mathbf{x})}{\partial\phi_1}\,\{\phi_1(\mathbf{x}),j_i(\mathbf{x}')\} \qquad (9.60)$$

The first equality follows as the derivative operators with respect to the microscopic position and momentum coordinates are let to act on $C(\phi_0(\{x_0^\alpha\},\{p_0^\alpha\}),\phi_1(\{x_1^\alpha\},\{p_1^\alpha\})$, where the different species are designated by sub indices 0 and 1. The thermodynamic partial derivatives are readily obtained from the defining equation (9.55): $\partial C/\partial\phi_0 = (1-C)/\phi$ and $\partial C/\partial\phi_1 = -C/\phi$. Substitution of Eq. (9.60) and Eq. (9.51) into Eq. (9.57) does indeed produce the result $\partial_t C = -\mathbf{v}\cdot\nabla C$.

Since we can also rewrite the flow equation of the concentration as $dC/dt = 0$, where d/dt is the total derivative (substantial derivative), which means that the composition of any fluid element remains unchanged in the absence of diffusive currents as it moves about. In practice, however, even in immiscible fluids there is limited miscibility between the components, which means that the concentration will not be a step function [300]. This is true even at rather low temperatures [295]. Since partial miscibility implies the presence of diffusive currents we can rewrite Eqs. (9.58) and (9.59) as

$$\begin{aligned}
\partial_t\phi &= -\nabla\cdot(\phi\,\mathbf{v})\ . && (9.61)\\
\partial_t(\phi C) &= -\nabla\cdot(\phi C\mathbf{v})\ . && (9.62)
\end{aligned}$$

Let the diffusive current be denoted by $\mathbf{i}$. When partial mixin takes place the previous equations are replaced with [293]:

$$\begin{aligned}
\partial_t\phi &= -\nabla\cdot(\phi\,\mathbf{v})\ . && (9.63)\\
\partial_t(\phi C) &= -\nabla\cdot(\phi C\mathbf{v}) - \nabla\cdot\mathbf{i}\ . && (9.64)
\end{aligned}$$

These are consistent with (though not equivalent to) the following equations of motion (cf. Ref. [300], where the definition of the total density is different)

$$\begin{aligned} \partial_t(\phi C) &= -\nabla\cdot(\phi C\mathbf{v}) - \nabla\cdot\mathbf{i}\ . \qquad (9.65)\\ \partial_t(\phi(1-C)) &= -\nabla\cdot(\phi(1-C)\mathbf{v}) + \nabla\cdot\mathbf{i}\ . \qquad (9.66) \end{aligned}$$

Instead of ϕC and $\phi(1-C)$ above we could have equally well used ϕ_0 and ϕ_1, respectively. With this replacement we arrive again at Eqs. (9.53) and (9.54) where the diffusive current $\pm\mathbf{i}$ must be added. In the isothermal case we can give an expression for the current $\mathbf{i}$ using Fick's law: $\mathbf{i} = -M\nabla\mu_{mix}$, where μ_{mix} is the chemical potential of the mixture. Eq. (9.66) becomes

$$\phi(\partial_t C + \mathbf{v}\cdot\nabla C) = M\nabla^2\mu\ . \qquad (9.67)$$

This form of the *concentration equation* is very close to the *mass balance equation* of the single component fluid described in Sect. 9.5.1. There are differencies, however. First, the convective term is of the form $\mathbf{v}\cdot\nabla C$ and not $\nabla\cdot(\mathbf{v}C)$ as compared to Eq. (9.33). This makes a difference if the fluids are not incompressible. Second, the chemical potential appearing in the evolution equation of the concentration field is not $\breve{\mu} = \delta F/\delta\phi$ defined in Eq. (9.6) (cf. also Eq. (10.10)) for single species. It is the 'reduced' chemical potential of the fluid mixture [293]:

$$\mu_{mix} \equiv \breve{\mu}_0 - \breve{\mu}_1 = \mu_0/m_0 - \mu_1/m_1\ , \qquad (9.68)$$

where m_0 (m_1) is the mass of the particles in the component 0 (1). The chemical potential of the mixture is obtained by taking the variation of the free energy with respect to concentration, not density as for single component fluid: $\mu_{mix} = \delta F/\delta C$. Because of these differences one should be carefull in interpreting the nature of the order parameter. When the free energy density f ($F = \int d\mathbf{x}\, f(\mathbf{x})$) is expressed as a function of both density and concentration, $f = f(\phi, C)$, it makes a great difference, of course, how the derivatives with respect to arguments are interpreted. For example, without the gradient corrections $\phi^2\partial f/\partial\phi = p$ and $\partial f/\partial C = \mu_{mix}$ as shown in Sect. 10.1.1 and Ref. [295]. It should also be noted that in the single component case we need the phase exchange to take place in order to justify the emergence of the stochastic term. In the two component system we can add a random current $\mathbf{i}'$ on physical grounds, too. Naturally, the Poisson bracket formalism gives rise to stochastic current, as C is not a strictly conserved quantity.

9.6 Comparison with other formalisms

Let us summarize the most important similarities and differences of our derivation of evolution equations of coarse-grained variables, which constitute the hydrodynamical description of simple fluids, compared to the similar theories. Typically, ϕ^4-potential is used in several studies as a prototype free energy. Instead of the double well potential, we use a three-well potential (see Sect. 7.3), whose properties can be mapped onto those of F_t given in Eq. (9.1). It is deriveable via classical density functional theory and provides a direct link between the microscopic and macroscopic worlds. This link allows a direct interpretation of the fields as we know their microscopic origin. The same thing cannot be said about all of the existing work, where the coarse-grained fields are sometimes given names in too loose a manner. Concentrating on mass and momentum balance equation, our model consists of the following equations:

$$\partial_t\phi + \nabla\cdot(\phi\mathbf{v}) = M\nabla^2\mu_t + \eta_0\ . \qquad (9.69)$$

The first term on the right is included since we wish to have a well-defined phase boundary numerically, and allow for diffuse mass exchange through the boundary. The final term describes temperature fluctuations. Since the interpretation based on density functional theory identifies ϕ as the total density field of the system, we should interpret Eq. (9.69) as a description of a two-phase system with a single component. In a two-component system the different components cannot transform into each other via the action of thermal fluctuations. As we have shown in Sect. 9.5.3, for two-component fluid an equation similar to (9.69) emerges, but with different interpretation of the variables: ϕ is analogous to the concentration and μ_t is analogous to the chemical potential of the mixture, which is a linear combination of the chemical potentials of the components.

The second equation of our model is the momentum balance equation. As its name suggests, it takes its simplest form when it is expressed in terms of the momentum density $\mathbf{j}$. However, since most of the work we will be referencing below is formulated in terms of the velocity field $\mathbf{v}$, we have to cast the momentum balance equation into the velocity representation through the substitution $\mathbf{j} = \phi\mathbf{v}$. Unfortunately, the velocity representation looks rather complicated as is explained in App. D.2.2. Therefore we pause here for a moment to shed some light into the appearance of the momentum balance equation leaving more detailed discussion for Appendix. The reason why the velocity representation gives rise to unfamiliar looking terms can be seen by concentrating on the left hand side of the equation of motion (Eq. (D.77)): the time variation of the momentum density can be split into two parts:

$$\partial_t j_i = \partial_t(\phi v_i) = (\partial_t \phi) v_i + \phi(\partial_t v_i) \ . \tag{9.70}$$

We can now solve for $\partial_t \phi$ from the mass balance equation (Eq. (D.75)). Substitution of the result back into Eq. (9.70) and taking the term $(\partial_t \phi) v_i$ to the right hand side gives rise to the form of the momentum balance equation (D.80). To add to the complication, depending on how we choose to represent the driving forces, the final form of the momentum balance equation may look different as will be discussed in Sect. 10.1. Below we express the driving forces in terms of the chemical potential $\mu_2 \equiv \mu_f + V_S$, where μ_f is the chemical potential per unit mass of the fluid and V_S is the substrate potential. The meaning of $\breve{\mu}_f$ will be discussed more thoroughly in the Chap. 10.

Now we are finally ready to reveal the momentum balance equation in the velocity representation. For each component of the velocity ($i = 1, 2, 3$) we get from Eq. (D.80),

$$\phi\Big(\partial_t v_i + (\mathbf{v} \cdot \nabla) v_i\Big) = -\phi \nabla_i \mu_2 + \hat{\Gamma}'_{ij} \frac{\delta F_t}{\delta v_j} + \eta_i + B(\phi, v_i) \ , \tag{9.71}$$

where we have defined a short-hand symbol $B(\phi, v_i) \equiv -\Gamma_{00}[\nabla^2(\mu_k + \mu_2)] v_i - \eta_0 v_i$. The 'kinetic' chemical potential is $\mu_k \equiv -j^2/(2\phi^2)$, and η_0 stands for the noise source of the mass balance equation. In addition, we have used a more general noise term $\hat{\Gamma}'_{ij} \delta F_t / \delta v_j$, where $\hat{\Gamma}'$ can in general be an integral operator as discussed in App. D.2.2. For consistency's sake we differentiate between primed and unprimed operators $\hat{\Gamma}$ depending on whether the functional derivative of the dissipative term is with respect to v_j (in this section) or j_j (as in App. D.2.2). In case we neglect $B(\phi, v_i)$, whose effects have been contemplated in App. D.2.2, we can cast the evolution of the velocity field into the following form:

$$\phi\Big(\partial_t v_i + (\mathbf{v} \cdot \nabla) v_i\Big) = -\nabla p_2 + \mu_f \nabla \phi - \phi \nabla V_S + \hat{\Gamma}'_{ij} \frac{\delta F_t}{\delta v_j} + \eta_i \ , \tag{9.72}$$

We end up with the same result, if we treat $\mathbf{v}$ as the fundamental variable in the Poisson bracket formalism. This was to be expected, of course, since $B(\phi, v_i)$ originates from the dissipative and noise terms of the mass balance equation.

When the dissipation and thermal fluctuations are left out of the mass balance equation it reduces to the continuum equation of standard hydrodynamics [293], which enforces strict mass conservation of a single component single phase fluid:

$$\partial_t \phi + \nabla \cdot (\phi \mathbf{v}) = 0 \ . \tag{9.73}$$

Leaving out the force terms $\mathbf{f}_b \equiv \mu_f \nabla\phi - \phi\nabla V_S$, which are active close to boundaries, together with the noise term η_i from Eq. (9.72), reproduces the standard evolution equation of the velocity. It should be noted that a noisy version correponding to Eq. (9.72) has been presented in (Ref. [293] p. 523) without the force term $\mathbf{f}_b$. If we choose to use only the ϕ^4-potential in F_t instead of the more general form of Eq. (9.3), which gives rise to the extra force $\phi\nabla V_S$, the momentum balance equation (9.72) together with the continuity equation (9.73) reproduce the model of Ref. [301], where momentum density is treated as the fundamental variable instead of velocity. In principle the form of the dissipative *operator* $\hat{\Gamma}'$ is not fixed by the formalism. If we want to generate the viscous stresses of standard hydrodynamics, we have to choose $\hat{\Gamma}'$ as explained in Sect. 9.5.2. This leads to non-vanishing cross correlations between the components η_i of the noise. If we make an additional assumption about the velocity field, and set $\nabla \cdot \mathbf{v} = 0$, we can write $\hat{\Gamma}'_{ij}\delta F_t/\delta v_j = \eta_d \nabla^2 v_i$. Substitution of this into the evolution equation of velocity gives

$$\phi\Big(\partial_t v_i + (\mathbf{v}\cdot\nabla)v_i\Big) = -\nabla p + \mu_f \nabla\phi + \eta_d \nabla^2 v_i \ , \tag{9.74}$$

where the ϕ^4-potential has been used resulting in the missing of the $\phi\nabla V_S$ term. Stochastic terms have been dropped, too. Due to the condition $\nabla \cdot \mathbf{v} = 0$ we do not use p_2 symbol for pressure, as p_2 is a fixed function of the other fields as will be explained in Sect. 10.1. In Eq. (9.74) the pressure p mediates the incompressibility condition and is unknown to be begin with. Together with a fully deterministic mass balance equation,

$$\partial_t \phi + \nabla \cdot (\phi \mathbf{v}) = M \nabla^2 \mu_f \ , \tag{9.75}$$

Eq. (9.74) constitutes the model of Ref. [302]. It should be also noted that the chemical potential in Eq. (9.75) is not the full chemical potential μ_t as in our case but only the ϕ^4-part. Leaving out the solid potential V_S and the noise, for low enough velocities we can approximate $\mu_t = \mu_k + \mu_f \approx \mu_f$ thus reproducing Eq. (9.75).

One of the first models, which coupled the stochastic momentum balance equation and deterministic continuity equation is presented in Ref. [303]. In terms of the velocity,

$$\partial_t \mathbf{v} + (\mathbf{v}\cdot\nabla)\mathbf{v} = -\frac{1}{m}\nabla\mu + \nu\nabla^2\mathbf{v} + \eta \ , \tag{9.76}$$

which should be compared with the representation of the driving force given $\nabla\mu_2$ in Eq. (D.79): μ/m is essentially the chemical potential per mass of molecule just like μ_2 is. Specifically, $m = m_0\phi_0/\phi$, where ϕ is the density, ϕ_0 is the average density and m_0 is the mass unit. The mass balance equation of Ref. [303] reads

$$\partial_t \phi + \nabla \cdot (\phi \mathbf{v}) = 0 \ . \tag{9.77}$$

Assuming that the Laplacian can be replaced with $1/(c_1 L^2)$ ($\nabla^2 \mathbf{v} \approx \mathbf{v}/(c_1 L^2)$), where c_1 is a constant of the order of unity, we can solve Eq. (9.76) and substitute the velocity into the mass balance equation. Even though Eq. (9.77) is deterministic to begin with, it becomes a stochastic equation with dissipation:

$$\partial_t \phi = M \left[\nabla^2 \mu + m \nabla \cdot d\mathbf{v}/dt \right] + \tilde{\eta} \ , \tag{9.78}$$

where $d/dt = \partial_t + \mathbf{v} \cdot \nabla$ and $\tilde{\eta} \equiv -Mm\nabla \cdot \eta$. In App. (D.2.2) we used a converse method: new stochastic and dissipation-like terms appeared in the velocity equation after substitution of the mass balance equation. The effect of these terms are pondered further in Sect. 11.4.

Finally, we note that selecting just the transverse velocity fluctuations in Eq. (9.72) we arrive at the so-called Model H of critical dynamics. In addition we have to drop the solid potential and set $\hat{\Gamma}_{ij} \delta F_t / \delta v_i = \eta_d \nabla^2 \mathbf{v}$. In Model H we interpret ϕ (order parameter) as the entropy density instead of mass density, which is taken to be constant. The evolution of ϕ is given by Eq. (9.69), with μ_t replaced with μ_f. Thus, due to the interpretation of ϕ, its evolution is subject to thermal fluctuations in contrast to the models mentioned above.

It is remarkable that a model similar to Model H can be derived directly based on a projection operator formalism [45]. The complete set of hydrodynamic variables consists of the total mass density and concentration, velocity field and entropy densities. The mass density and the longitudinal velocity components are left out since they are relevant for sound wave mode, which acts on much faster time scale than the diffusive components. Furthermore, entropy variable is assumed to decouple as well, leaving us the velocity and concentration as relevant fields to describe a binary fluid. The velocity equation reads [45]:

$$\frac{\partial v_i(\mathbf{x})}{\partial t} + v_j(\mathbf{x}) \frac{\partial}{\partial x_j} v_i(\mathbf{x}) = -\frac{1}{\overline{\phi}} \frac{\partial p(\mathbf{x})}{\partial x_i} + \eta_d \nabla^2 v_i(\mathbf{x}) + (\zeta + \eta_d/3)) \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} v_j(\mathbf{x}) + f_i^K, \tag{9.79}$$

where $\overline{\phi} = \overline{\phi_1(\mathbf{x})} + \overline{\phi_2(\mathbf{x})}$ is the average density of the fluid. The form of the stress force term f_i^K is fixed by the projection formalism to be

$$\begin{aligned} f_i^K \ &\equiv \ -a_1 \left[\frac{\partial}{\partial x_j} \left(\frac{\partial C}{\partial x_j} \right) \left(\frac{\partial C}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left(\frac{\partial C}{\partial x_j} \right) \left(\frac{\partial C}{\partial x_j} \right) \right] + \ \frac{a_1}{2} \nabla^2 \left[\delta C \, \frac{\partial C}{\partial x_i} \right] \\ &- \ a_2 \frac{\partial}{\partial x_i} \Big([\delta C(\mathbf{x})]^2 - \langle \delta C(\mathbf{x})^2 \rangle \Big) \ , \end{aligned} \tag{9.80}$$

where $\delta C \equiv C(\mathbf{x}) - \overline{C}$ is the deviation from the equilibrium density $\overline{C}$. Both factors, which include correlation functions of the concentration, are inversely proportional to the mean density: $a_1, a_2 \propto 1/\overline{\phi}$. The evolution equation of the concentration becomes [45]

$$\frac{\partial C(\mathbf{x})}{\partial t} + v_j(\mathbf{x}) \frac{\partial}{\partial x_j} C(\mathbf{x}) = D_0 \nabla^2 C(\mathbf{x}) \ . \tag{9.81}$$

Eq. (9.79) and Eq. (9.81) are essentially the same as the equations of motion, which we have presented in Sect. 9.5.3. Only the thermal noise has been dropped. Also the form of the capillary stress term is slightly different than the one which comes out of the Poisson bracket formalism. Namely, if one accepts the arguments of Sect. 6.4.2, in the sharp interface limit we can write

$$F[\phi] \propto F[C] \approx \int d\mathbf{x} \, \frac{1}{2} |\nabla C|^2 + \ldots \ . \tag{9.82}$$

In the Poisson bracket formalism the momentum balance equation will contain a new term, which we call f_i^P. To see this more clearly we use Eq. (9.48) and replace the coordinates ϕ_0 and ϕ_1 with ϕ and C:

$$\begin{aligned} \partial_t j_i &= -\int d\mathbf{x}' \,\{j_i(\mathbf{x}), \phi(\mathbf{x}')\}\, \frac{\delta F}{\delta \phi(\mathbf{x}')} - \int d\mathbf{x}' \,\{j_i(\mathbf{x}), C(\mathbf{x}')\}\, \frac{\delta F}{\delta C(\mathbf{x}')} \\ &\quad - \int d\mathbf{x}' \,\{j_i(\mathbf{x}), j_s(\mathbf{x}')\}\, \frac{\delta F}{\delta j_s(\mathbf{x}')} - \int d\mathbf{x}' \,\{j_i(\mathbf{x}), \mathcal{E}(\mathbf{x}')\}\, \frac{\delta F}{\delta \mathcal{E}(\mathbf{x}')} + \Gamma_{i\nu}\nabla^2 \frac{\delta F}{\delta \psi_\nu(\mathbf{x})} + \eta_i \; . \end{aligned} \tag{9.83}$$

The second term on the right is responsible for generation of the capillary stresses equivalent to f_i^K. Computing the Poisson bracket of C with the aid of the fundamental conserved quantities ϕ_0 and ϕ_1 according to Eq. (9.60), we get

$$f_i^P \equiv -\int d\mathbf{x}' \,\{j_i(\mathbf{x}), C(\mathbf{x}')\}\, \frac{\delta F}{\delta C(\mathbf{x}')} \tag{9.84}$$

$$= -\int d\mathbf{x}' \left[\frac{\partial C(\mathbf{x}')}{\partial \phi_0} \{j_i(\mathbf{x}), \phi_0(\mathbf{x}')\} + \frac{\partial C(\mathbf{x}')}{\partial \phi_1} \{j_i(\mathbf{x}), \phi_1(\mathbf{x}')\} \right] \frac{\delta F}{\delta C(\mathbf{x}')} \; . \tag{9.85}$$

From $C = \phi_0/(\phi_0 + \phi_1)$ we get $\partial C(\mathbf{x}')/\partial \phi_0 = (1 - C(\mathbf{x}'))/\phi(\mathbf{x}')$, and $\partial C(\mathbf{x}')/\partial \phi_1 = -C(\mathbf{x}')/\phi(\mathbf{x}')$. The brackets of momentum with mass densities are readily obtained: for $a = 0, 1$, $\{j_i(\mathbf{x}), \phi_a(\mathbf{x}')\} = -\partial_i' \delta(\mathbf{x}' - \mathbf{x})\phi_a(\mathbf{x})$. Substitution of these results together with Eq. (9.82) into the expression of f_i^P gives

$$f_i^P = \partial_i \Big(C(\mathbf{x}) \frac{\delta F}{\delta C(\mathbf{x})} \Big) = \partial_i [C(\mathbf{x}) \nabla^2 C(\mathbf{x})] \; . \tag{9.86}$$

This is similar to the result of Eq. (9.80) but not exactly the same. In addition to the terms $\partial_i C \nabla^2 C$ and $C \nabla^2 \partial_i C$ there are also other combinations of derivatives appearing in Eq. (9.80). A more quantitative comparison is possible if the two-component density functional $F[\phi_0, \phi_1]$ is derived carefully from first principles and the pair of variables $\{\phi_0, \phi_1\}$ is replaced with $\{\phi, C\}$. If one uses the velocity representation instead of momentum density, the result is $f_i^P = (1/\phi)\partial_i [C(\mathbf{x})\nabla^2 C(\mathbf{x})]$, which is consistent with Kawasaki's result (who also utilized the velocity representation) according to which the thermodynamic prefactors $a_1, a_2 \propto 1/\phi$. We note the similarity to result f_i^{LT} of Ref. [295] who obtains the capillary force $f_i^{LT} \propto -[\nabla \cdot (\rho \nabla C \otimes \nabla C)]_i$, where $\rho(\mathbf{x})$ is the density of the fluid. The difference in the density variable is manifest already in the definition of the pressure tensor, and free energy, which reads [295]: $F \propto \int d\mathbf{x} (\rho/2) |\nabla C|^2$. A similar, but not identical result is also obtained in Ref. [300], where the force term $\mathbf{f}^A$ reads

$$\mathbf{f}^A = \nabla \cdot \left[\rho \frac{\partial e}{\partial \alpha} \Big(|\nabla C|^2 \mathbf{I} - \nabla C \otimes \nabla C \Big) \right] \; , \tag{9.87}$$

where the density factor ρ comes about through the same mechanism as before. The energy of the system is defined as $E = \int d\mathbf{x} \rho e(\mathbf{x})$ where e is the internal energy density per unit mass. Naturally, $e = e(\alpha, C, \rho)$, where $\alpha = |\nabla C|^2/2$. Quasi-thermodynamic arguments used in the two previous in Ref. [295] and Ref. [300] partly explain the differences of the results as compared to each other and the result of Eq. (9.86).

Chapter 10

Bulk forces

10.1 Emergence of pressure

As we have not defined pressure to be one of the primary coarse-grained variables, we should justify its appearance in the momentum balance equation (9.26) by other means. We will show below that the application of the Poisson bracket formalism gives rise to a driving force term, which can be interpreted as pressure field. Naturally, the form of the pressure is fixed by the relevant macrovariables (ϕ, $\mathbf{j}$, $\mathcal{E}$). At the current level of sophistication, it turns out that

$$p = p(\phi) \tag{10.1}$$

analogously to equilibrium thermodynamics. Eq. (10.1) reduces to standard equation of state form when gradient corrections are neglected. This will be shown in Sect. 10.1.2. Sect. 10.1.2 and Sect. 10.1.3 will help us see what kinds of different forms the driving forces of the momentum balance equation can take.

Not only are the driving forces representable in many ways but also the meaning of the pressure term depends on what is assumed to be known of the system. Because the pressure is a known function of the mass density field (Eq. (10.1)), it does not have to be solved unlike in the case where it mediates the incompressibility condition. In other words, using Euler equations as an example, our problem here is analogous to solving the mass and momentum balance equations,

$$\phi \, d\mathbf{v}/dt = -\nabla p + \mathbf{b} \; ; \tag{10.2}$$

$$d\phi/dt + \phi \nabla \cdot \mathbf{v} = 0 \; , \tag{10.3}$$

where $d/dt = \partial_t + \mathbf{v} \cdot \nabla$ is the total derivative, and $\mathbf{b}$ is a bulk force, whose specific form is irrelevant here. Since we have four equations and five unknowns, we have to connect pressure to other fields via equation of state (Eq. (10.1)). It should be noted that other methods such as the Lattice-Boltzmann method described in Ref. [294] and its variants also yield an explicit expression for the pressure in terms of other coarse-grained variables. If the expression of the pressure field is not given, or fixed by the formalism, we need a separate equation to fix its value. Consider, for example the incompressible Euler problem:

$$\phi \, d\mathbf{v}/dt = -\nabla p + \mathbf{b} \; ; \tag{10.4}$$

$$d\phi/dt = 0 \; ; \tag{10.5}$$

$$\nabla \cdot \mathbf{v} = 0 \; . \tag{10.6}$$

Now, the pressure acts as a Lagrange's multiplier, which forces the constraint of Eq. (10.6) on the flow field $\mathbf{v}$. Thus, the role of pressure is conceptually different for compressible and incompressible flows. However, both for inviscid and inviscid incompressible flows the pressure is determined through the condition $\nabla\cdot\mathbf{v} = 0$ (p. 37 of Re. [304]). Our condition 10.1 makes sense in both cases.

10.1.1 Thermodynamic preliminaries

Let us start by writing down some thermodynamic relations involving the pressure, chemical potential and enthalpy. We first make a distincintion between thermodynamic quantities defined per unit mass and unit volume. For example, the total free energy is denoted by F, free energy density per unit mass is $\tilde{f} \equiv F/M$ (M total mass), and free energy density per unit volume is $\rho\tilde{f}$. To make the use of familiar thermodynamic relations easier in Sect. 10.1.1, instead of the symbol ϕ, we use here the symbol $\rho \equiv M/V$ for constant mass density. Thus, the free energy can be written in the following way: $F = \int dV \rho \tilde{f}(\rho) = V(M/V)\tilde{f}(M/V) = M\tilde{f}$. The *static* thermodynamic pressure is defined through

$$p \equiv -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V}\Big(M\tilde{f}(M/V)\Big) = (M/V)^2\tilde{f}(M/V) = \rho^2\frac{\partial\tilde{f}}{\partial\rho} \ . \tag{10.7}$$

In a similar manner, we obtain an expression for the chemical potential per unit mass. Define $M \equiv mN$, where m is the mass of the molecule and N is the total number of molecules in the system. Then,

$$\mu \equiv \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}\Big[mN\tilde{f}\Big(mN/V\Big)\Big] = m\tilde{f}\Big(mN/V\Big) + mN\tilde{f}'\Big(mN/V\Big)\frac{m}{V} \tag{10.8}$$

$$= m\Big[\tilde{f}(\rho) + \rho\tilde{f}'(\rho)\Big] = \frac{M}{N}\frac{\partial}{\partial\rho}\Big(\rho\tilde{f}(\rho)\Big) \ . \tag{10.9}$$

Thus, chemical potential per unit mass, $\tilde{\mu}$ satisfies $N\tilde{\mu} = \partial(\rho\tilde{f})/\partial\rho$. Alternatively, we can define chemical potential per mass of a molecule $\breve{\mu} \equiv \mu/m$: $\breve{\mu} = \partial(\rho\tilde{f})/\partial\rho = \partial f/\partial\rho$, where f is the free energy density per unit volume. When the gradient dependent parts of the free energy density are left out we have

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{x})} = \frac{\partial f(\rho(\mathbf{x}))}{\partial\rho(\mathbf{x})} = \breve{\mu}(\rho(\mathbf{x})) \ . \tag{10.10}$$

That's why it would be consistent to use $\breve{\mu}$ instead of μ but for notational simplicity we use just μ everywhere else but in this section. We just have to keep in mind that μ really means the chemical potential per mass of the single molecule (cf. Ref. [303]) unless otherwise stated. Utilizing the thermodynamic relation ($\mu N = G$) for Gibbs free energy G, we can write $\breve{\mu} = \tilde{f} + \rho\partial\tilde{f}/\partial\rho \equiv \tilde{g}$, where $\tilde{g}$ is the specific Gibbs free energy [295].

To see how the pressure is related to the variation of the free energy, we compute $\nabla(\delta F[\rho]/\delta\rho) = \nabla(\partial f/\partial\rho) = \partial^2 f/(\partial\rho)^2\,\nabla\rho$. On the other hand, using the standard thermodynamic relationship, $p = \rho\partial f/\partial\rho - f$, we obtain

$$\frac{1}{\rho}\nabla p = \frac{1}{\rho}\nabla\left(\rho\frac{\partial f}{\partial\rho} - f\right) = \frac{\partial^2 f}{\partial\rho^2}\nabla\rho = \nabla\frac{\delta F}{\delta\rho} \ . \tag{10.11}$$

Owing to the last relation, we can relate the pressure changes to enthalpy h_e of the system. For an isentropic process conserving particle number it holds that $d\tilde{h}_e = (1/\rho)dp$. Therefore,

$\nabla \tilde{h}_e = (1/\rho)\nabla p$. Even though the *gradient* of the enthalpy in this case is the same as the gradient of $\delta F/\delta\rho = \partial f/\partial\rho = \partial(\rho\tilde{f})/\partial\rho$, it does not follow that $\tilde{h}_e$ would be the same as $\partial(\rho\tilde{f})/\partial\rho$. The correct relation between the free energy and the enthalpy is given by $\tilde{h}_e = \tilde{u} + p/\rho$, where $\tilde{u}$ is the internal energy per unit mass. Thus,

$$h_e = p + (f + Ts) = \rho^2\partial\tilde{f}/\partial\rho + \rho\tilde{f} + Ts = \rho\partial f/\partial\rho + Ts \ , \tag{10.12}$$

where s is the entropy per unit volume. Using the relation $\rho\partial f/\partial\rho = \rho\mu/m = \rho N\tilde{\mu} = N\mu/V$, we obtain the familiar thermodynamic identity for quantities per unit volume, $h_e = N\mu/V + Ts$, or $H_e = N\mu + TS$. For an *isenthalpic* system we can instead of Eq. (10.7) express the pressure also as [304] $p = \rho^2\partial\tilde{u}/\partial\rho$ by assuming that the pressure is a function of ρ only. This is equivalent to $d\tilde{h}_e = (1/\rho)dp$.

10.1.2 Reversible part of the stress tensor

The bottom line is that in the equation of motion for the momentum field $\mathbf{j}$ the first Poisson bracket term on the right hand side of Eq. (9.36) contains a term $-\rho\nabla\delta F_f/\delta\rho(\mathbf{x})$, which we can write as ($\rho = \phi$)

$$-\phi\nabla\delta F_f/\delta\phi(\mathbf{x}) \equiv -\nabla\cdot\sigma^R \ . \tag{10.13}$$

We have defined the reversible stress tensor σ^R, which does not contain viscous stresses generated by the velocity field. Below we will show that the stress tensor can be split into two parts:

$$\sigma^R_{ij} = p_{tot}\,\delta_{ij} + \kappa\,\partial_i\phi\,\partial_j\phi \ , \tag{10.14}$$

The effects of the gradient corrections of the free energy functional, which go beyond standard thermodynamics, are visible both in the non-diagonal part $\kappa\,\partial_i\phi\,\partial_j\phi$ and in the total pressure field p_{tot}, which contains a standard thermodynamic part and a capillary correction:

$$p_{tot} \equiv p + p_{cap} \ . \tag{10.15}$$

The thermodynamic pressure field p and the capillary pressure p_{cap} are defined as:

$$p \equiv \phi\frac{\partial f}{\partial\phi} - f \quad ; \quad p_{cap} \equiv -\phi\,\kappa\nabla^2\phi \ . \tag{10.16}$$

In the special case of dimensionless density field in Eq. (9.3) the constant $\kappa = 1$. In case the free energy functional has a more complicated dependence on the gradients, such that the partial derivative of the free energy density per unit volume with respect to $\partial\phi/\partial x_i \equiv \partial_i\phi$ is not simply $\partial_i\phi$ as above, but

$$\frac{\partial f}{\partial(\partial_i\phi)} = (\partial_i\phi(\mathbf{x}))\,\kappa(\phi(\mathbf{x}),\nabla\phi(\mathbf{x})) \ , \tag{10.17}$$

By construction of the functional derivative, $\delta F_f[\phi]/\delta\phi \equiv \partial f/\partial\phi - \sum_j \partial_j\Big[(\partial_j\phi)\,\kappa(\phi,\nabla\phi)\Big]$, it is easy to show that

$$\phi\,\partial_i\frac{\delta F_f}{\delta\phi} = \partial_i\Big(\phi\frac{\delta F_f}{\delta\phi}\Big) - \frac{\delta F_f}{\delta\phi}\partial_i\phi = \partial_i\Big(\phi\frac{\delta F_f}{\delta\phi}\Big) - \frac{\partial f}{\partial\phi}\partial_i\phi + \sum_j\Big[\partial_j(\kappa\,\partial_j\phi)\Big](\partial_i\phi) \tag{10.18}$$

$$= \partial_i\Big(\phi\frac{\delta F_f}{\delta\phi} - f\Big) + \sum_j \partial_j\Big[\kappa(\phi,\nabla\phi)\,\partial_j\phi\,\partial_i\phi\Big] \ . \tag{10.19}$$

The last relation can be confirmed by rewriting the second and third terms in Eq. (10.18) as

$$\begin{aligned} \frac{\partial f}{\partial \phi}\partial_i \phi &= \partial_i f - \sum_j \frac{\partial f}{\partial(\partial_j \phi)}\partial_i(\partial_j \phi) \ ; && (10.20) \\ \sum_j \Big[\partial_j(\kappa\, \partial_j \phi)\Big](\partial_i \phi) &= \sum_j \partial_j \Big[\kappa\, \partial_j \phi\, \partial_i \phi\Big] - \sum_j \kappa\, \partial_j \phi\, \partial_j(\partial_i \phi) \ . && (10.21) \end{aligned}$$

Using the definition (10.17) and cancelling out some terms yields Eq. (10.19). The first term in the parenthesis on the right hand side of Eq. (10.19) is the total pressure (diagonal part of the stress tensor). After expanding the functional derivative we obtain

$$p_{tot} = \phi \frac{\partial f}{\partial \phi} - f - \phi\, \nabla \cdot [\kappa \nabla \phi] \ . \tag{10.22}$$

Thus, for constant κ we have derived the result of Eq. (10.15). The diagonal part of the stress tensor can also be put into a more symmetric form in the derivatives of the mass density. In the general case of non-constant κ:

$$p_{tot} = \phi \frac{\partial f}{\partial \phi} - f + \kappa \, |\nabla \phi\,|^2 - \tfrac{1}{2} \nabla \cdot \Big[\kappa \nabla \phi^2\Big] \ , \tag{10.23}$$

which is the result to be found in Ref. [301]. The components of the reversible part, which does not contain viscous stresses, of the stress tensor σ^R_{ij} can be written as

$$\sigma^R_{ij} = p_{tot}\, \delta_{ij} + \kappa\, \partial_i \phi\, \partial_j \phi \ , \tag{10.24}$$

where we have also taken into account the non-diagonal contribution represented by the second term in Eq. (10.19). In tensor form we can coviniently express it as

$$\sigma^R = p_{tot} \mathbf{I} + \kappa \nabla \phi \otimes \nabla \phi \ . \tag{10.25}$$

The unit (3×3)-tensor $\mathbf{I} \equiv \sum_j \mathbf{e}_j \otimes \mathbf{e}_j$. Customarily, the indeterminite vector product, which has been used occasionally in the text means the tensor product. For example, in the expression of the flux density tensor we have a term $\mathbf{j}\,\mathbf{j} \equiv \mathbf{j} \otimes \mathbf{j}$.

10.1.3 Driving forces

In the previous sections we have seen how the functional derivative of the fluid's free energy F_f with respect to mass density ϕ gives rise to the diagonal pressure term p_{tot} and an off-diagonal contribution $\kappa \nabla \phi \otimes \nabla \phi$ which together make up the reversible stress tensor σ^R. Its divergence acts as the driving force on the fluid elements. Let us see now how this comes about by using the full form of the momentum balance equation:

$$\partial_t j_i = -\phi\, \partial_i \Big(\frac{\delta F_f}{\delta \phi} + \frac{\delta F_S}{\delta \phi} \Big) + \partial_s \Big(\frac{1}{\phi} j_i j_s \Big) + M_{i\nu} \nabla^2 \frac{\delta F_k}{\delta j_\nu} + \eta_i \ . \tag{10.26}$$

For derivation of this equation the reader is referred to Sect. (9.5.1). We have split the full free energy into three different contributions according to Eq. (9.1). The driving forces can now be represented in various ways, which are all equivalent, of course. First of all, $\delta F_S / \delta \phi = V_S$ so that the term $-\phi \nabla V_S$ is always present when the interaction of the fluid with the solid walls is taken into account. In expressing the first term $-\phi\partial_i(\delta F_f/\delta\phi)$ on the right hand side of Eq. (10.26) we have more freedom.

Analogously to capillary pressure, we can define a capillary chemical potential, which stems from the gradient corrections of the free energy: Eq. (10.10) is replaced with

$$\begin{aligned} \frac{\delta F[\rho]}{\delta\rho(\mathbf{x})} &= \frac{\partial f(\rho(\mathbf{x}),\nabla\rho(\mathbf{x}))}{\partial\rho(\mathbf{x})} - \sum_{i=1}^{3}\frac{\partial}{\partial x_i}\left[\frac{\partial f(\rho(\mathbf{x}),\nabla\rho(\mathbf{x}))}{\partial(\partial_i\rho(\mathbf{x}))}\right] && (10.27) \\ &= \breve{\mu}(\rho(\mathbf{x})) + \breve{\mu}_{cap}(\rho(\mathbf{x})) \equiv \breve{\mu}_{tot}\ . && (10.28) \end{aligned}$$

We remind the reader of the convention that excluding this section, the chemical potential per unit mass is denoted without the breve symbol. Thus, in the rest of this work, we identify

$$\frac{\delta F_p}{\delta\phi} \equiv \mu_p\ . \tag{10.29}$$

where p any acronym for different contributions to total free energy, which may or may not contain gradient corrections: we do not separate the homogeneous and gradient corrections parts anywhere else but in this section. The definition of the chemical potential per mass of the molecule of Eq. (10.10) allows us to write

$$\begin{aligned} -\phi\partial_i(\delta F_f/\delta\phi) = -\phi\partial_i\breve{\mu}_{tot} = -\partial_i(\phi\breve{\mu}_{tot}) + \breve{\mu}_{tot}\,\partial_i\phi &= -\partial_i(\phi\breve{\mu} + \phi\breve{\mu}_{cap}) + \breve{\mu}_{tot}\,\partial_i\phi && (10.30) \\ &= -\partial_i(f + p + \phi\breve{\mu}_{cap}) + \breve{\mu}_{tot}\,\partial_i\phi\ , && (10.31) \end{aligned}$$

where we have used the fact that the thermodynamic part of the chemical potential $\phi\breve{\mu} = \phi(\tilde{f} + \phi\partial\tilde{f}/\partial\phi) = f + p$. For $\kappa = const$, the capillary chemical potential takes a simple form: $\breve{\mu}_{cap} \equiv -\kappa\nabla^2\phi$, which is related to the capillary pressure through $\phi\breve{\mu}_{cap} = p_{cap}$. Thus, we can rewrite Eq. (10.31) as

$$-\phi\,\nabla\frac{\delta F_f}{\delta\phi} = -\nabla p'_{tot} + \breve{\mu}_{tot}\nabla\phi\ , \tag{10.32}$$

where we have defined a modified pressure $p'_{tot} \equiv p_{tot} + f$. It should be noted that p'_{tot} is a known (fixed) function of ϕ just as p_{tot} and p are.

We can now collect the results we have derived above. The driving force term $-\phi\,\delta F_f/\delta\phi$ can be represented in various ways. For example,

$$-\phi\,\frac{\delta F_f}{\delta\phi} = \begin{cases} -\nabla\cdot\sigma^R\ ; \\ -\nabla p'_{tot} + \breve{\mu}_{tot}\nabla\phi\ ; \\ -\phi\nabla\breve{\mu}_{tot}\ . \end{cases} \tag{10.33}$$

When substrate interaction is included, there will be an additional force term $-\phi\,\delta F_S/\delta\phi = -\phi\nabla V_S$ on the right hand side of the momentum balance equation. It is important to notice that if incompressibility condition is not imposed by hand, the gauged pressure term $p'_{tot}(\phi)$ does not have to be solved for: It is a known function of the phase-field ϕ when F_f is used in the variational expression of Eq. (10.33). Was F_t to be used instead, the pressure would become a known function of ϕ and $\mathbf{j}$ ($\mathbf{v}$) just like in some other coarse-grained derivations of hydrodynamics (e.g. lattice-Bolzmann fluids [305]). Similarily to the pressure, $\sigma^R(\phi)$ and $\breve{\mu}_{tot}(\phi)$ are known. Substitution of correct expression on the right hand side of Eq. (10.33) always generates the same driving term when expressed as a function of ϕ. If incompressibility is required in addition to mass and momentum balance equations, then p'_{tot} must modify the fluid's velocity field in such a way that $\nabla\cdot\mathbf{v} = 0$. Consequently, p'_{tot} is not known *a priori*. The problem, of course, have become different then as compared to the compressible case, where the mass balance equation does not reduce to condition $\nabla\cdot\mathbf{v} = 0$. Additional representations can be generated by using thermodynamic identities, but one should be carefull in doing so: the kinematic fields are not necessarily the same as their equilibrium thermodynamic partners.

10.2 Gravity and hydrodynamics

In this section we implement a real gravitational force into the theory with the aid of hydrodynamic description. Specifcally, we derive the form the convective term $\mathbf{v}\cdot\phi$ takes after projecting onto the liquid-gas interface. Our starting point is the following set of equations:

$$\begin{cases} \eta_d\nabla^2\mathbf{v} - \nabla p + \tilde{\mathbf{f}}_b = 0 \ ; \\ \nabla\cdot\mathbf{v} = 0 \ ; \\ \partial_t\phi + \mathbf{v}\cdot\nabla\phi = M\nabla^2\mu_f \ , \end{cases} \tag{10.34}$$

where the dynamic viscosity is denoted by η_d and the pressure field by p. The bulk force term has the form given in Eq. (9.25). Since we will be using as simple form of the free energy as possible, the susbstrate potential V_S does not have to be introduced as will become clear below. Therefore, the bulk force term simplifies to $\tilde{\mathbf{f}}_b = -\phi\nabla\mu_f$. In the topmost equation we have assumed a stationary Stoke's flow. This assumption only makes sense if the fluid has enough time to reach the stationary flow regime which might be difficult to justify in disordered medium but could hold for at least a single capillary tube in which the net driving force (hydrostatic or external pressure gradient and capillary force) is balanced against dissipation. Even though the average traveling velocity of the meniscus is continuously diminished by gravity and mass conservation the inertial effects can be dropped leading to the steady state approximation of Eq. (10.34). The argumentation parallels the derivations of the Washburn's law [306] and meniscus motion in a capillary tube [307]. The incompressibility condition is an extra condition (see App. D.1.2) which cannot be derived from microscopics without using the mass conservation equation and homogeneity of the density, which obviously does not hold for liquid-gas coexistence we consider here. We briefly return to this subject at the end of this section. In the mass conservation equation we have dropped the additional dissipative terms which result from taking the variation of the full free energy F_t with respect to ϕ as specified by Eq. (9.7): $\mu_k \sim v^2$ is dropped as second order effect for slow velocities and $\mu_S \sim V_S$ is left out since we do not use the substrate potential for anything in this section. Since we don't have a separate Stokes equation for the gas and liquid phases, we are rather modeling a situation where one imisicible fluid displaces another. Both fluids are incompressible (as opposed to compressible gas). In addition, the their viscosities are the same. The last condition can be relaxed, though, by introducing a viscosity which depends on the field ϕ: $\eta_d = \eta_d(\phi)$.

The gravitational contribution to the chemical potential is obtained from the gravitational part F_g of the total free energy $F \equiv F_f + F_g$, where

$$F_g \equiv \int dx \int dt\, gz\phi \ ; \tag{10.35}$$

$$F_f = \int dx \int dt \left[\frac{1}{2}|\nabla\phi|^2 + \frac{1}{2}(1+\rho)(\phi^2-1)^2 + \frac{1}{2}(1-\rho)K_w^2(\phi - A)^2\right] \ . \tag{10.36}$$

The form of F_f holds for cases where the fluids do not enter into the third phase (solid phase) whose shifted density field is denoted by ρ. The corresponding chemical potentials are defined below:

$$\mu_g \equiv \frac{\delta F_g}{\delta \phi} = gz \quad ; \quad \mu_f \equiv \frac{\delta F_f}{\delta \phi} \ . \tag{10.37}$$

In order to simplify the projection which we are about to perform, we will introduce a new pressure field p_2 which is related to the old one through: $p_2 \equiv p + \phi\mu_f$. In terms of the new pressure field,

$$-\nabla p + \tilde{\mathbf{f}}_b = -\nabla p_2 + \mu_f \nabla\phi - \phi\nabla\mu_g \tag{10.38}$$

On the right hand side we recognize the capillary force term $\mathbf{f}_{cap} = \mu_f \nabla\phi$ given in Eq. (9.28). Introduction of the new pressure field has made it easier to recognize the origin of capillarity, but the final outcome of the computations to follow does not necessitate the transformation from the old fields $(p,\ \phi\nabla\mu_f)$ to the new ones $(p_2,\ \mu_f\nabla\phi)$ in any way.

Let us isolate the contribution caused by gravitation by throwing away the capillary force term $\mu_f\nabla\phi$, which is active close to the phase boundaries, only. Thus, Eq. (10.34) gets replaced by

$$\begin{cases} \eta_d \nabla^2 \mathbf{v} - \nabla p_2 + \mathbf{f}_g = 0 \ ; \\ \nabla \cdot \mathbf{v} = 0 \ ; \\ \partial_t \phi + \mathbf{v}\cdot\nabla\phi = M\nabla^2\mu_f \end{cases} \tag{10.39}$$

The gravitational force is directed along the z-axis: $\mathbf{f}_g \equiv -\phi\nabla\mu_g = -g\phi\,\mathbf{e}_z$. We will first consider a simpler free energy than the one given in Eq. (10.36). The free energy of the imbibition model is

$$F_f = \int dx \int dt \left[\frac{1}{2}|\nabla\phi|^2 - \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 - \phi A_I\right] \ , \tag{10.40}$$

where typically we fix the coefficients $a = b = 1$. The last term in the free energy is responsible for the dynamics: A_I is a quenched random field just like A is in Eq. (10.36). As discussed before, this free energy does not account for the presence of the solid phase. When plugged into the equation of motion for the phase field, it gives rise to the liquid and gas phases whose capability of entering different regions of space can be controlled by adjusting A_I. In this sense we can take A_I to describe the effect of a random porous substrate through which the liquid propagates displacing the gas (or another fluid). Taking the divergence of the first equation of the set (10.39) and using the incompressibility, $\nabla\cdot\mathbf{v} = 0$, leads to the Poisson equation for the pressure field:

$$\nabla^2 p_2(x,z) = \nabla\cdot\mathbf{f}_g = -g\partial_z\phi(x,z) \ . \tag{10.41}$$

As we now have a Poisson's equation for the pressure field, we have to supplement it with boundary conditions. In the general case these are read off from the conditions on the stress tensor as described in Sect. 11.2. Here we can use a more intuitive reasoning. Clearly, the boundary condition for p_2 is the same as the boundary condition for the original pressure field p because of the boundary condition for the chemical potential: $p_2|_0 = p|_0 + (\phi\mu_f)|_0$, where the substitution is at $z = 0$. Because $\mu_f|_0 = 0$ it follows that $p_2|_0 = p|_0$. If the liquid-gas boundary taken to be straight in the first approximation, the pressure at reservoir level $z = 0$ is the constant hydrostatic pressure which can be gauged equal to zero if we can neglect the effect of the fluid velocity on the pressure as well. Due to the homogeneous boundary conditions the Green's boundary terms vanish when inverting ∇^2-operator in Eq. (10.41). Then, for spatially varying profile of the phase boundary the pressure becomes approximately

$$\begin{aligned} p_2(x,z) &= g\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dz_1\, G_{2D}^I(x,z;x_1,z_1)\partial_{z_1}\phi(x_1,z_1) && (10.42)\\ &= -2g\int_{-\infty}^{\infty} dx_1\, G_{2D}^I(x,z;x_1,\mathrm{H}(x_1,t))\ , && (10.43)\end{aligned}$$

where G_{2D}^I is the familiar Green's function of the imbibition problem. The height of the liquid front measured from the reservoir boundary is denoted by $\mathrm{H}(x,t)$. The phase-field configuration was approximated as $\phi \approx -1 + 2\theta(\mathrm{H} - z)$, which is an approximation to the extremal solution of the free energy functional of Eq. (10.40) with coefficients $a = b = 1$. This choice of the coefficients, which is typical of pure phase-field simulations without hydrodynamics, gives rise to the factor of two in front of the integral in Eq. (10.43).

Since ϕ correponds to the mass density, it would be more physical to choose the values of the coeffients a and b in such a way that ϕ only takes non-negative values: $\phi \approx \Delta\phi\,\theta(\mathrm{H} - z)$, where $\Delta\phi = \Delta\phi(a,b)$ is the miscibility gap which tells the difference of the densities of the liquid and gas phases. The magnitude of $\Delta\phi$ can be changed by redefining the units. To get an idea how this can be done, we can compare the physical dimensions of different terms in Eq. (10.39) to the convective one ($\phi\partial_t\mathbf{v}$), which has been left out: $[\phi\,\partial_t\mathbf{v}] = (kg/m^3)(m/s^2) = (kgm/s^2)/m^3 = N/m^3$, which has correctly the units of force density. The units of the viscosity η_d can be solved from $[\phi\,\partial_t\mathbf{v}] = [\eta_d][\nabla^2\mathbf{v}]$. It follows that $[\eta_d] = (kg/m^3)(m^2/s) = [\phi]m^2/s$. Since pressure is force per area, we consistently have $[\nabla p_2] = (1/m)(N/m^2) = N/m^3$. Finally, the graviational constant has units $[g] = m/s^2$ because $[\mathbf{f}_g] = [\phi g] = (kg/m^3)[g] = N/m^3$. These units hold when density field ϕ has its normal units kg/m^3. Since in the phase-field formalism we prefer to use dimensionless ϕ, $[\phi] = 1$, we have to see how the units of the other fields and parameters change. Comparing the convective term with pressure p_2 defined in new units, we get $[\phi\,\partial_t\mathbf{v}] = [\partial_t\mathbf{v}] = [\nabla p_2]$, or $[p_2] = m^2/s^2$. Comparison of the dissipative term with the convective one gives $[\partial_t\mathbf{v}] = [\eta_d][\nabla^2\mathbf{v}]$ from which we get that $[\eta_d] = m^2/s$. Finally, the units of the gravitational constant can be solved from $[\mathbf{f}_g] = [\phi g] = [g] = [\nabla p_2] = (1/m)(m^2/s^2)$. Therefore, $[g] = m/s^2$ which is the same as in the original system of units.

In the following we shall consider a situation where we are observing a rising liquid front from such a distance that we can take the profile H to be a constant in space: $\mathrm{H}(x,t) \approx \mathrm{H}_0(t)$. Then,

$$G_{2D}^I(x,z;x_1,z_1) = \frac{1}{4\pi}\ln\left[\frac{(x-x_1)^2 + (z+\mathrm{H}_0)^2}{(x-x_1)^2 + (z-\mathrm{H}_0)^2}\right] \tag{10.44}$$

Shifting the integration variable as $(x_1)_{new} = x - x_1$, we see that the pressure p_2 will not be a function of x, but it does depend on z. For general miscibility gap $\Delta\phi$,

$$\begin{aligned} p_2(z) &\approx -\frac{\Delta\phi\, g}{4\pi}\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx_1\, \cos(\epsilon x_1)\ln\left(\frac{x_1^2 + A^2}{x_1^2 + B^2}\right) && (10.45)\\ &= \lim_{c\to 0}\left\{-\frac{\Delta\phi\, g}{2\epsilon}\left(e^{-|B|\epsilon} - e^{-|A|\epsilon}\right)\right\} = -\frac{\Delta\phi\, g}{2}(|A| - |B|)\ , && (10.46)\end{aligned}$$

where we have defined $A \equiv z + \mathrm{H}_0$ and $B \equiv z - \mathrm{H}_0$. Despite the fact that we had to regularize the divergent integral with the aid of constant ϵ in Eq. (10.45), which is a peculiarity of the two-dimensional set-up, we do obtain a sensible answer. When $z < \mathrm{H}_0$, $p_2 = -\Delta\phi\, gz$, which is nothing but the familiar hydrostatic pressure. In the gas phase, $z > \mathrm{H}_0$, the pressure becomes constant: $p_2 = -\Delta\phi\, g\mathrm{H}_0$.

Knowing the pressure, we can now solve for the velocity $\mathbf{v}$. Both of its components satisfy the Poisson equation, as seen from Eq. (10.39). In terms of the density field ϕ we can express the approximate solution of the pressure field through $p_2(z) \approx p_0 - gz\phi$. Therefore,

$$\begin{aligned} v_x &= \frac{1}{\eta_d}\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dz_1\, G_x(x,z;x_1,z_1)\,(\partial_{x_1}p_2 - \mathbf{f}_g\cdot\mathbf{e}_x) + B_x\ ; && (10.47)\\ v_z &= \frac{1}{\eta_d}\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dz_1\, G_z(x,z;x_1,z_1)\,(\partial_{z_1}p_2 - \mathbf{f}_g\cdot\mathbf{e}_z) + B_z\ . && (10.48)\end{aligned}$$

The explicit form of the Green functions will be given below. The boundary terms B_x and B_z will not be zero if we are thinking of modeling a situation where we bring a stochastic porous medium (described by the field A_I) into contact with the fluid reservoir at $z = 0$ *without* modeling the reservoir itself. In this case there will be non-zero velocity gradient at $z = 0$ consistent with the boundary condition $\mu_f(x, z = 0) = 0$. The other option is that we take the reservoir to be part of our system. Denoting its depth by H_{0r} we can perform the calculations presented above by simply setting the lower integration limit to $z = -\mathrm{H}_{0r}$, which correponds to the bottom of the reservoir. This is usefull, because at the bottom of the reservoir the boundary condition for the velocity field is naturally the no-slip condition: $\mathbf{v}(x, z = 0) = 0$. No self-consistent evaluation of μ_f at $z = 0$ is needed. Because of the homogenuity of the boundary condition $B_x = B_z = 0$. Since there is no gravitational force in the x-direction, $\mathbf{f}_g \cdot \mathbf{e}_x = 0$, we get that $v_x = 0$. Replacing $\mathbf{f}_g \cdot \mathbf{e}_z = -g\phi$ in Eq. (10.48) gives

$$\begin{aligned} v_z &= \frac{1}{\eta_d}\int_{-\infty}^{\infty} dx_1 \int_{-\mathrm{H}_{0r}}^{\infty} dz_1\, G_z(x,z;x_1,z_1)\,[-gz_1\partial_{z_1}\phi(x_1,z_1,t)] && (10.49)\\ &\approx -\frac{\Delta\phi\, g}{\eta_d}\int_{-\infty}^{\infty} dx_1\, G_z(x,z;x_1,\mathrm{H}_0)\,\mathrm{H}_0 && (10.50)\end{aligned}$$

With no-slip boundary condition the Green's function of the velocity field becomes the same as that of the pressure field in the chosen geometry: $G_z = G^I_{2D}$. Thus, we can perform a similar calculation as with the pressure field using regularization of the integral:

$$v_z(z) = -\frac{\Delta\phi\, g}{2\pi\eta_d}\mathrm{H}_0 \int_{-\infty}^{\infty} dx_1\, \ln\left[\frac{(x-x_1)^2 + (z+\mathrm{H}_0)^2}{(x-x_1)^2 + (z-\mathrm{H}_0)^2}\right] \approx -\frac{\Delta\phi\, g}{\eta_d}\mathrm{H}_0\, z\ , \tag{10.51}$$

which holds in the liquid phase. One can also readily verify that this result is dimensionally correct in the system of units where $[\phi] = 1$. Since in the equation of motion of the phase-field ϕ the velocity term is multiplied by the gradient of the phase-field, it gets effectively projected onto the plane $z = \mathrm{H}_0$ where $v_z(\mathrm{H}_0) \sim -(\Delta\phi\, g/\eta_d)\mathrm{H}_0^2$ which is the relevant term in the interfacial dynamics. Therefore, the equation of motion for the phase-field can be written in the following form:

$$\partial_t\phi + v_z(t)\,\partial_z\phi = M\nabla^2\mu_f(\phi)\ . \tag{10.52}$$

Thus, we have been able to justify the plausibility of the following simplified model [281], which should be equivalent to the set of equations (10.39):

$$\partial_t\phi + g_{eff}\partial_z\phi = M\nabla^2\mu_f(\phi)\ , \tag{10.53}$$

where g_{eff} is the effective gravitational constant, which is actually proportional to the physical gravitational constant g. It is also pointed out that Eq. (10.52) is the appropriate generalization of the bulk equation of motion (8.2) studied in the previous chapter when v_z is the only nonzero component of the velocity. When all velocity components are non-zero, we should write it in the form to be given in Sect. 10.4, Eq. (10.70), which can be further projected to yield the meniscus and contact line equations as explained in Chap. 8.

Our derivation shows that the convective term with on the left hand side of Eq. (10.53) equation should approximate the Stoke's set when we consider phase boundaries which do not move very fast or have become pinned, in which case H_0 is a constant in time. The correspondence is not exact, though. Not only have we replaced $v_z(z)$ with its value in the vicinity of the phase boundary, but in addition we have decoupled the momentum balance equation (the first equation of the Stokes's set (10.39)) from the mass balance equation (the last equation) by dropping the capillary driving force $-\mu_f \nabla\phi$, whose effects will be discussed in Sect. 10.4. We have also neglected the quenched noise field A_I present in the free energy (Eq. (10.43)) which acts as kind of a stochastic capillary pressure term. Thus, in a sense v_z used in Eq. (10.52) describes the gravitational contribution to the convection velocity only. As a result, relating the interfacial velocity given $v_z(\mathrm{H}_0)$ to the time variation of the mean interface height, we get an underestimate of the true interface velocity relaxation: $d\mathrm{H}_0/dt \sim \mathrm{H}_0^2 \Rightarrow \mathrm{H}_0 \sim t^{-1}$, which is not consistent with the mean field interface evolution equation [281] obtainable from Eq. (10.53):

$$\mathrm{H}_0\, d\mathrm{H}_0/dt = \bar{\alpha}/2 - g_{eff}\mathrm{H}_0 \ , \tag{10.54}$$

where $\bar{\alpha}$ is the mean value of the quenched noise field A_I (which we dropped from our analysis). When H_0 is solved from this equation it actually grows like $t^{1/2}$ for early times and crosses over to exponential relaxation towards the pinning height, where $d\mathrm{H}_0/dt$.

What about the dynamic critical properties? Are they affected by the time dependence $v_z(t)$? As the mean height of the phase boundary H_0 approaches the pinning height, v_z becomes independent of time and we expect to see no effects if the relaxation is sufficiently rapid. Indeed, direct numerical integration of Eq. (10.52), where we have also kept the stochastic contribution to chemical potential due to the quenched noise field A_I and parametrized the velocity as

$$v_z(t) = a_1 - a_2\, \mathrm{H}_0(t)^2 \ , \tag{10.55}$$

with constants a_1 and a_2, indicates that the fluctuations of the phase boundary are not strongly affected by the time dependence of v_z. The values of the critical exponents of the roughening phase boundary are the same as for the 'fake' gravity (Eq. (10.53)), where v_z is independent of time. If we choose to drop the incompressibility, the pressure field does not satisfy a simple Poisson's equation (10.41) as the velocity field cannot be eliminated by taking divergence of both sides of the Stoke's equation. When incompressibility equation, $\nabla \cdot \mathbf{v} = 0$, is left out, we have to express the pressure in terms of the remaining coarse-grained variables of the problem. This can be done by utilizing the coarse-grained free energy functional as explained in Sect. 10.1. Quasi-thermodynamic arguments lead to a relationship $p_2 = p_2(\phi)$.

10.3 Alternative ways to include gravity

In this section we present different approaches to implementation of gravity. We start with a derivation based on Darcy's law goverining the motion of fluid driven by externally imposed pressure gradient through porous matrix. Darcy's law suggests a linear relationship between the (volume averaged) pressure gradient driving the flow and the (volume averaged) velocity of the fluid:

$$\mathbf{v} = \frac{k}{\eta_d}\left(-\nabla p - g\rho\mathbf{e}_z\right) \ . \tag{10.56}$$

The permeability of the porous medium is k; the dynamic viscosity of the fluid is η_d and density of the fluid is ρ. This should not be confused with the density field of the solid, which was also denoted by ρ in Sect. 9.1. Upon substitution of the velocity $\mathbf{v}$, the convective term $(\mathbf{v} \cdot \nabla\phi)$ appearing in the final line of Eq. (10.39) becomes

$$(\mathbf{v} \cdot \nabla\phi) = -\frac{k}{\eta_d}\nabla p \cdot \nabla\phi - \frac{k\rho g}{\eta_d}\partial_z\phi \ . \tag{10.57}$$

The latter term above represents the contribution to the convection flow by gravity. Since the permeability tensor depends on the spatial location the flow field will also be position dependent in general. Only if $k = const$ and the pressure gradient is zero, we can identify the parameter of the imbibition model with gravity. It is pointed out that the pressure field appearing in Eq. (10.56) is a coarse-grained pressure resulting from local volume averaging as will be shown below. The role the phase-field plays in this formalism is not the density of the fluid but rather the concentration, which is a relevant coarse-grained quantity for two-component fluids (see Sect. 9.5.3).

To get some insight into the nontrivial concept of coarse-grained pressure field, let us give a brief derivation of Darcy's law based on Ref. [308]. Start with Stoke's flow

$$\nabla p - \eta_d \nabla^2 \mathbf{v} = 0 \ . \tag{10.58}$$

Taking the divergence on both sides and using the incompressibility of the fluid gives $\nabla^2 p = 0$. Therefore, acting on both sides of Eq. (10.58) with the Laplacian operator ∇^2 yields $\nabla^4\mathbf{v} = 0$. The spatial dependence of the velocity is transferred to a velocity transformation tensor $\mathbf{X}$ via

$$\mathbf{v} = \mathbf{X}(\mathbf{r})\langle v\rangle \ , \tag{10.59}$$

where $\langle v\rangle$ represents an average coarse-grained flow velocity. Obviously, $\mathbf{X}$ depends on the pore structure in a complicated way. Substituting this into Stokes' equation leads to

$$\nabla p = \eta_d[\nabla^2\mathbf{X}]\langle v\rangle \ . \tag{10.60}$$

Averaging of both sides over a local volume of semi-macroscopic size defines the permeability in terms of the average of the velocity transformation tensor: $\nabla\bar{p} = -(\eta_d/k)\langle v\rangle$, where $\bar{p}$ is the coarse-grained pressure. Solving for velocity and taking into account the gravity yields Eq. (10.56). The nontrivial assumptions about connecting the micro and macro scales through k have been improved further in Ref. [309] using lattice gas cellular automata. Without volume averaging the pressure, the linear relationship between the driving pressure gradient and velocity can be derived for a simple capillary tube flow without any porous medium [293]. Similar result holds for Poisell flow in a Hele-Shaw cell [310].

The use of Darcy's law or Stokes' law leads to hydrodynamic models where the phase-field plays the role of density or concentration. Within the pure phase-field formulation alone it is also possible to include the effect of gravity through a phase-field dependent mobility M [311, 312], which should not be confused with the velocity transformation matrix above. The typical order parameter dependence of the mobility is of the form $M(\phi) = 1 - \phi^2$. The equation of motion reads

$$\partial_t\phi = \nabla\Big(M(\phi)\nabla\mu(\phi)\Big) \ . \tag{10.61}$$

As will be shown below, even a simpler form, $M(\phi) = 1 - \phi$, is sufficient to generate a convective term in the the equation of motion of the phase-field reminiscient of Eq. (10.53).

Even though in this case the form of the linear density dependence of the mobility can be justified based on analogy to diffusion constant $D(\phi)$, it remains to be checked that the symmetries of the problem are respected in choosing $M(\phi)$. This obviously applies to more complicated nonlinear density dependent diffusion constants [313], too.

To cast Eq. (10.61) into a form which bears resemblance to our previous formulation with hydrodynamics, we let the gradient operate on the mobility and the chemical potential:

$$\nabla\Big(M(\phi)\nabla\mu(\phi)\Big) = \nabla M \cdot \nabla\mu + M\nabla^2\mu \ . \tag{10.62}$$

Remembering that the hydrodynamic pressure and the chemical potential of a pure phase-field model are analogous (see Ref. [4]), and since the pressure gradient is related to velocity according to Darcy's law, we can roughly write $\nabla M \cdot \nabla\mu \sim \nabla M \cdot \mathbf{v}_{int}$. The velocity at the interface, $\mathbf{v}_{int}$ emerges because $\nabla M = (\partial M(\phi)/\partial\phi)\nabla\phi$ is sharply peaked at the liquid-gas boundary. Therefore, the equation of motion of the phase-field can be represented as

$$\partial_t\phi - M'\,\mathbf{v}_{int}\cdot\nabla\phi = M\nabla^2\phi \ , \tag{10.63}$$

where $M'\,\mathbf{v}_{int} = (\partial M(\phi)/\partial\phi)\nabla\mu$ is analogous to the drift velocity caused by gravity in the mass balance equation (10.39) in the hydrodynamic description. To summarize, all the different ways to include gravity we have introduced, can be made analogous to the hydrodynamic description by suitable redefinition of parameters. In other words, the phase-field evolution equation will contain a convective term of the form $\mathbf{v}\cdot\nabla\phi$ where the drift velocity is either of hydrodynamic origin or comes from phase-field dependent mobility.

10.4 Dimensional estimates of importance of hydrodynamics

Hydrodynamic effects is always important on small enough scales within the boundary layers close to solid walls. It makes sense, though, to ask if they can be neglected on certain time and length scales if the parameters of the theory are replaced with effective, large scale (renormalized) parameters, such as coarse-grained capillary pressure, which is relevant for description of two-phase flow in a porous medium (random disordered network of capillaries). At this level of description, microscopic boundary conditions (boundary layers etc.) do not play a role anymore. In particular, we would like to know if there is a regime where one could neglect the convective $(\nabla\cdot(\mathbf{v}\phi))$ term in comparison to the diffusive mass flux $(M\nabla^2\breve{\mu})$ in the mass balance equation,

$$\partial_t\phi + \nabla\cdot(\mathbf{v}\phi) = M\nabla^2\breve{\mu} \ . \tag{10.64}$$

To solve for the velocity field in terms of the mass density (phase-field), we start with Stokes' flow equation (10.34):

$$\eta_d\nabla^2\mathbf{v} - \nabla p_2 + \mathbf{f}_{cap} = 0 \ , \tag{10.65}$$

where $\mathbf{f}_{cap} \equiv \breve{\mu}\nabla\phi$ is the capillary force. Pressure field is assumed to be fixed through the incompressibility condition $\nabla\cdot\mathbf{v} = 0$, which in the Fourier representation means transversality of the velocity field: $\mathbf{k}\cdot\mathbf{v}(\mathbf{k}) = 0$. Taking the dot product of

$$\mathbf{v}(\mathbf{k}) = [-\imath\mathbf{k}p_2(\mathbf{k}) + \mathbf{f}_{cap}(\mathbf{k})]/(\eta_d k^2) \tag{10.66}$$

with $\mathbf{v}(\mathbf{k})$ allows us to solve the pressure field: $p_2(\mathbf{k}) = -\imath\mathbf{k}\cdot\mathbf{f}_{cap}/k^2$. Substitution of the expression of the pressure back into Eq. (10.66) gives the transversal velocity field,

$$\mathbf{v}_i(\mathbf{k}) = \frac{1}{\eta_d k^2}\Big[-\frac{k_ik_j}{k^2}(f_{cap}(\mathbf{k}))_j + (f_{cap}(\mathbf{k}))_i\Big] = \mathrm{T}_{ij}(\mathbf{k})(f_{cap}(\mathbf{k}))_j \ . \tag{10.67}$$

The tensor appearing on the right is called the Oseen tensor. In Fourier space it looks like

$$\mathrm{T}_{ij}(\mathbf{k}) \equiv \frac{1}{\eta_d k^2}\left(\delta_{ij} - \frac{k_i k_j}{k^2}\right) . \tag{10.68}$$

In real space the Oseen tensor takes a different form depeding on the spatial dimension. In three dimensions

$$\mathrm{T}_{ij}(\mathbf{x}) \equiv \frac{1}{8\pi\eta_d r}\left(\delta_{ij} + \frac{r_i r_j}{r^2}\right) . \tag{10.69}$$

In two dimensions the real space representation of the tensor is $\mathrm{T}_{ij}(\mathbf{x}) = [-\delta_{ij}\ln(r/a) + r_i r_j/r^2]/(4\pi\eta_d)$, where a is a cut-off scale, which nondimensionalizes the argument of the logarithm. Thus, with the aid of Eq. (10.67) the mass balance equation (phase-field equation), $\partial_t\phi + \mathbf{v}\cdot\nabla\phi = M\nabla^2\mu$, can be written in the form

$$\partial_t\phi(\mathbf{x}) = -\int d\mathbf{x}_1 \left[\nabla\phi(\mathbf{x})\cdot\mathrm{T}(\mathbf{x}-\mathbf{x}_1)\cdot\nabla\phi(\mathbf{x}_1)\right]\breve{\mu}(\mathbf{x}_1) + M\nabla^2\breve{\mu}(\mathbf{x}) . \tag{10.70}$$

Basically, we want to find out the physical condition when the first term on the right hand side of Eq. (10.70) dominates over the second. In other words, when is the convective mass flux due to hydrodynamics more important than the diffusive flux due to chemical potential differences?

10.4.1 Units of chemical potential

To be able to match the units of the variables in the mass and momentum balance equations, we now define two systems of units. We denote the variables in the system of units where the generic density symbol $[\rho] = 1$ (equivalently, $[\phi] = 1$) with unprimed symbols and reserve the primed symbols for quantities expressed in the physical unit system with $[\rho'] = kg/m^d$ in d dimensions. This convention does not apply to lengths and time arguments, which have the same units in both systems. Typically, when the mass balance equation is interpreted as the phase-field evolution equation, we set $[\phi] = 1$. In other words the phase-field (mass density) is dimensionless. In App. C.2 we have shown that in the unit system with $[\phi] = 1$, the dimensions of the chemical potential are

$$[\mu(\mathbf{x})] \equiv \left[\frac{\delta F}{\delta\phi(\mathbf{x})}\right] = \left[\frac{F'}{m^d}\right]_1 = \left[\frac{Nm}{m^d}\right]_1 = \left[\frac{kg\, m^2/s^2}{m^d}\right]_1 = [\rho']_1\frac{m^2}{s^2} = \frac{m^2}{s^2} , \tag{10.71}$$

where we have also defined a unital operator $[\cdot]_1$, whose function is to convert all expressions, which have been expressed in physical primed units, into units where $[\phi] = 1$. For example, for any quantity W

$$[W']_1 = [W] . \tag{10.72}$$

The free energy has the units of energy E': $[F'] = [E'] = Nm$. It is important to notice that if we use the (effective) action instead of the equilibrium free energy, the units of the (time dependent) chemical potential do not change:

$$[\mu(\mathbf{x},t)] \equiv \left[\frac{\delta A}{\delta\phi(\mathbf{x},t)}\right] = \left[\frac{A'}{m^d s}\right]_1 = \left[\frac{Nms}{m^d s}\right]_1 = [\rho']_1\frac{m^2}{s^2} = \frac{m^2}{s^2} . \tag{10.73}$$

We have defined the action A' to have units $[A'] = [E']s = Nms$. This must be so because the only difference between the free energy and action is the fact that in the latter there is an extra time integral because the fields depend not only on $\mathbf{x}$ but also time:

$$F = \int d\mathbf{x}\, f(\phi(\mathbf{x})) \quad ; \quad A = \int d\mathbf{x} \int dt\, f(\phi(\mathbf{x},t)) \ . \tag{10.74}$$

In other words, the form of the free energy density f is the same as the action density but the argument fields of A depend additionally on t. Usually we do not use a different symbol for the action but denote it by F. For further details on action, free energy and their interchangeability we refer to App. C.2 and App. D.1.

Using the unprimed unit system together with the definition $\mu = \delta F/\delta\phi$ in Eq. (10.71) is a bit dangerous, since it does not reveal the fact that the chemical defined in such a manner is actually the chemical potential per molecular mass $\breve{\mu}$, which was introduced in Sect. 10.1.1:

$$\breve{\mu} \equiv \frac{\delta F}{\delta \phi} \ . \tag{10.75}$$

As a remainder we note that whenever define the chemical potential through the variational approach, we should used the symbol $\breve{\mu}$. For brevity, we usually just write μ. In the rest of this section, however, we will indicate the normalization of the chemical potential explicitly in order not to confuse the different quantities when converting back to real units. Below we will find the physical units of the chemical potential in the primed unit system and thereby show that it has to be interpreted as the chemical potential per molecular mass m_0:

$$\breve{\mu} = \mu/m_0 \ . \tag{10.76}$$

On the right hand side we have the thermodynamic chemical potential, which has the physical units of energy $[\mu'] = [E'] = Nm = kg(m/s)^2$.

In App. C.2 we have determined the units of various quantities in the unprimed unit system with $[\phi] = 1$. Let us now consider the conserved case with physical units. Leaving out the hydrodynamic convection, the equation of motion for ϕ' reads

$$\partial_t \phi' = M'\nabla^2 \frac{\delta A'}{\delta \phi'} = M'\nabla^2 \breve{\mu}' = M'\nabla^2\Big(-\gamma'\nabla^2\phi' + a'\phi' + b(\phi')^3\Big) \ , \tag{10.77}$$

where we have used the symbol of the action A' instead of the free energy F' to stress the fact that $[A'] = [E']s = Nms$. Explicitly,

$$A'[\phi'] \equiv \int d\mathbf{x} \int dt\, \Big((\gamma'/2)\, |\nabla\phi'(\mathbf{x},t)|^2 + (a'/2)\, (\phi'(\mathbf{x},t))^2 + (b'/4)\, (\phi'(\mathbf{x},t))^2 \Big) \ . \tag{10.78}$$

The units of the coefficients of the action can be fixed from Eq. (10.77) and Eq. (10.78). Using the latter,

$$[A'] = m^d s\, [\gamma'] \frac{1}{m^2} [\phi']^2 \quad \Rightarrow \quad [\gamma'] = \frac{[A']\, m^2}{m^d s\, [\phi']^2} \ . \tag{10.79}$$

Utilizing the last equality of Eq. (10.77) we get an expression for the mobility $[M']$:

$$\frac{[\phi']}{s} = \frac{[M'][\gamma'][\phi']}{m^4} \quad \Rightarrow \quad [M'] = \frac{m^4}{s\,[\gamma']} = \frac{m^{2+d}[\phi']^2}{[A']} \ , \tag{10.80}$$

where the last equality follows from Eq. (10.79). It is easy to see that in the unprimed unit system the units of the mobility reduce to those given in Sect. C.2. On the other hand, using the chemical potential $\breve{\mu}'$ defined in the second equality of Eq. (10.77) gives

$$[\partial_t \phi'] = [M' \nabla^2 \breve{\mu}'] \quad \Rightarrow \quad \frac{[\phi']}{s} = \frac{[M'][\breve{\mu}']}{m^2} \quad \Rightarrow \quad [M'] = \frac{m^2\,[\phi']}{s\,[\breve{\mu}']} \ . \tag{10.81}$$

Equating the two expressions for $[M']$ given in Eq, (10.80) and Eq, (10.81) yields finally the units of the chemical potential:

$$\frac{m^{2+d}\,[\phi']^2}{[A']} = \frac{m^2\,[\phi']}{s\,[\breve{\mu}']} \quad \Rightarrow \quad [\breve{\mu}'] = \frac{[A']}{m^d s\,[\phi']} = \frac{[E']}{m^d\,[\phi']} \tag{10.82}$$

Substitution of the units $[A'] = [E']s = kgm^2/s$ and $[\phi'] = kg/m^d$ gives $[\breve{\mu}'] = (m/s)^2$, which clearly confirms the interpretation that chemical potential defined through the variational derivative of the action with respect to density should be interpreted as the chemical potential per molecular mass:

$$[\breve{\mu}'] = \frac{[\mu']}{[m_0']} = \frac{m^2}{s^2} \ , \tag{10.83}$$

where the physical units of the thermodynamic chemical potential are those of energy: $[\mu'] = [E'] = Nm$. Comparison with Eq. (10.71) and Eq. (10.73) allows us to write

$$[\breve{\mu}(\mathbf{x})] = [\breve{\mu}(\mathbf{x}, t)] = [\breve{\mu}'(\mathbf{x})] = [\breve{\mu}'(\mathbf{x}, t)] = \frac{m^2}{s^2} \tag{10.84}$$

because the physical units of the chemical potential per molecualr mass do not depend on the density. It should also be remembered that the unit change does not change the absolute scale of the variables. That is to say, scale change will take place if we define the potential energy minima of the free energy F to be such that the bulk value of density becomes +1 in the dimensionless units instead of +1000, which would correspond to density of water of $+1000\,kg/m^3$ in the real units.

We close this section by demonstrating the necessity of introducing the new operation denoted by $[\cdot]_1$ in Eq. (10.71). The mobility M may serve as an example. Suppose we in a somewhat carefree manner use the equation of motion $[M\nabla^2\breve{\mu}] = 1/s = [\partial_t \phi]$ to determine the units of M, and write

$$[M] = \frac{m^2}{[\breve{\mu}]s} = \frac{m^2}{\frac{[A]}{m^d s}\,s} = \frac{m^{2+d}}{[A]} \ . \tag{10.85}$$

Even though this relation is consistent with the other relations concerning units of different terms in the equation of motion as shown in Sect. C.2, it has not been fully reduced in the sense that one can still extract density variable out of it if one naivly assumes that since $[A'] = kg(m/s)^2$ does not contain units of density we should have $[A'] = [A]$. If this was true, Eq. (10.85) would give

$$[M] = \frac{m^{2+d}}{[A]} = \frac{m^d}{kg}\,s \ . \tag{10.86}$$

However, since $m^d/kg = 1/[\rho']$ we should really set it equal to one in the unprimed unit system, thus correctly reducing the dimension of $[M] = s$. Despite the fact that we obtained the correct answer finally, it is important to notice that the intermediate steps were incorrect. Instead of Eq. (10.85) we should have written

$$[M] = \left[\frac{m^2}{\breve{\mu}' s}\right]_1 = s \ . \tag{10.87}$$

It is also difficult to try to go back to real units from the unprimed representation, which has been obtained by mixing expressions whose units have not all been converted at the same time as in Eq. (10.85). Trying to obtain the physical units of primed representation from it would give $[M'] = (1/[\rho'])s$, which is clearly not right. The reason is that we do not know the powers of $[\rho']$ multiplying this expression since in the unprimed representation they are equivalent to factor of one. As can be seen from Eq. (10.80) the correct result is $[M'] = (1/[\rho'])\, s[\rho']^2 = [\rho']\, s$.

Alternative unit system

Often in the applications we would like to use variables which are defined per unit volume. It is indeed possible to define such a unit system (variables in these units carry a subscript V) with a little bit of extra work. In other words we would like to have something like $\mu_V = \mu'/V'$, where V is the volume occupied by the system in physical units $[V'] = m^d$. We would also like define μ_V through the variation of the action functional (free energy functional) with respect to density. We will show below that these two requirements cannot be simultaneously satisfied in the physical unit system if we impose also the requirement that the action (free energy) in the new system has its natural units:

$$[A_V] = [A'] = Nms \ . \tag{10.88}$$

Additionally, the time and space variables are also unaffected by the unit transformation, which means that $[V_V] = [V'] = m^d$. Let us first consider the capillary force term, whose expression can be reorganized to give

$$\breve{\mu}'\nabla\phi' \sim \frac{\mu'}{m_0'}\nabla\frac{m_0' N'}{V'} = \frac{\mu'}{V'}\nabla N' = \mu_V \nabla N' \ , \tag{10.89}$$

where N' is the number density of constituent particles (unitless number in any system). Hence, we notice that it is possible to define μ_V to have units of energy density per unit volume if we accept the fact that the density field appearing in the place of the phase-field ϕ is really the number density. This case is different from defining a unit system where the density $[\phi] = 1$ because in such a system $[\mu_V] = (m/s)^2$ as we have shown above.

What happens if we now define $\mu_V = \delta A/\delta\phi$? Let us use a similar techique as above to determine the units of μ_V. Defining the mobility in the new unit system as M_V, the equation of motion reads

$$\partial_t \phi_V = M_V \nabla^2 \ . \tag{10.90}$$

Replacing the primed variables where necessary by the variables carrying subscript V we can proceed in the same manner as above. Analogously to Eq. (10.80) we obtain

$$[M_V] = \frac{m^{2+d}[\phi_V]^2}{[A_V]} \ . \tag{10.91}$$

In the new units Eq. (10.81) becomes

$$[M_V] = \frac{m^2\,[\phi_V]}{s\,[\mu_V]}\ . \tag{10.92}$$

These two equations allow us to solve for the units of the chemical potential per unit volume:

$$[\mu_V] = \frac{[A_V]}{m^d s\,[\phi_V]}\ . \tag{10.93}$$

It is easy to see that indeed $[\mu_V] = [A_V]/(m^d s) = [E]/m^d = Nm^{1-d}$ if we consistently identify ϕ_V as the number density N. Correspondinly, the units of the mobility become $[M_V] = m^{2+d}/[A_V]$.

10.4.2 Relevant time and length scales

To derive Eq. (10.70) we have to solve for the velocity from the Stokes' equation, which in the primed units reads

$$\eta'_d\nabla^2\mathbf{v}' - \nabla p'_2 + \breve{\mu}'\nabla\phi' = 0\ . \tag{10.94}$$

All quantities have their normal units: $[\eta_d] = [\phi]m^2/s$, $[\phi] = kg/m^d$, $[p_2] = [E]/m^{d-1}$, $[\breve{\mu}'] = [\breve{\mu}] = [\mu]/[\phi] = [E]/(m^d[\phi])$ and $[E] = Nm = kg(m/s)^2$. In the unprimed unit system, where $[\phi] = 1$, Eq. (10.94) reads

$$\eta_d\nabla^2\mathbf{v} - \nabla p_2 + \breve{\mu}\nabla\phi = 0\ . \tag{10.95}$$

Because the dimensions of length and time do not change in the unit transformation, we have $[\mathbf{v}] = [\mathbf{v}']$. The unit of the viscosity is $[\eta_d] = m^2/s$ in the unit system with $[\phi] = 1$. Thus, the kinematic and dynamic viscosities have the same units when mass density is dimensionless. Velocity has units $[\mathbf{v}] = m/s$. Thus, $[\eta_d\nabla^2\mathbf{v}] = m/s^2$. As we have shown in Sect. 10.2, in the representation, where $[\phi] = 1$, the units of the pressure field become $[p_2] = m^2/s^2$ and thus, the dimensionality of the second term in Stoke's equation is consistent with the first one. Finally, we have (as we should), $[\breve{\mu}\nabla\phi] = [\breve{\mu}](1/m) = m/s^2$.

Since the boundary condition of the stress tensor in the normal direction is due to the capillary force, we can estimate $\mathbf{f}_{cap} \sim \nabla p_2 \sim (1/L)\Delta p_2 \sim (1/L)\,\sigma\mathcal{K} \sim \sigma/L^2$, where L is the observational length scale on which the all spatial derivatives are evaluated. The value of the surface tension in the units where $[\phi] = 1$ is σ. To get a relation between the physical surface tension σ' and σ, we first note that $\nabla p_2 \sim \breve{\mu}\nabla\phi \Rightarrow [\breve{\mu}] = [p_2] = [\sigma/L]$, where

$$[\sigma] = m^3/s^2\ . \tag{10.96}$$

On the other hand, since $\mathbf{f}_{cap} = \breve{\mu}\nabla\phi \sim \breve{\mu}/L$, we obtain the following relation between the chemical potential and the surface tension: $\breve{\mu} \sim \sigma/L$. In the physical units we have correspondinlgy $\breve{\mu}' \sim \sigma'/L$. Therefore, owing to the simple linear relationship between the units of the surface tension and the chemical potential, we can write,

$$\frac{[\mu']}{[\breve{\mu}']} = \frac{[\mu']}{[\breve{\mu}]} = \frac{[\sigma']}{[\sigma]} = [\rho'] = \frac{kg}{m^d}\ . \tag{10.97}$$

The mobility parameter M appearing in the equation of motion of the phase-field ϕ can be related to its partner M' in the same way. This can be seen by comparing the equations of motion in the two different unit systems: $[\partial_t\phi'] = [M'\nabla^2\breve{\mu}']$ and $[\partial_t\phi] = [M\nabla^2\breve{\mu}]$. Comparing $[\partial_t\phi']$ with $[\partial_t\phi]$ we see immediately that the former contains an extra factor of units of density as compared with the latter. To compensate for that the right hand side $[M'\nabla\breve{\mu}']$ must also contain the same factor as compared with $[M\nabla\breve{\mu}]$. Because $[\breve{\mu}] = [\breve{\mu}']$, the extra factor has to reside in M' and therefore,

$$\frac{[M']}{[M]} = [\rho'] = \frac{kg}{m^d} \ . \tag{10.98}$$

Plugging in the units we obtain,

$$[M'] = [\rho']\, s \ . \tag{10.99}$$

This equation should be compared with the results presented at the end of Sect. 10.4.1, where it is shown that one should be carefull in trying to reconstruct the units of the physical primed representation from the units of the unprimed one.

Unlike the chemical potential, the physical dimension of the Oseen tensor depends on spatial dimension: in 3D $\mathrm{T} \sim 1/(\eta_d L)$ whereas in 2D $\mathrm{T} \sim 1/\eta_d$. Evaluation of the the second term on the right hand side of Eq. (10.70) in two and three dimensions gives $M\nabla^2\breve{\mu} \sim M(1/L^2)(\sigma/L) = M\sigma/L^3$. The first term gives

$$\int d\mathbf{x}_1 \left[\nabla\phi(\mathbf{x}) \cdot \mathrm{T}(\mathbf{x}-\mathbf{x}_1) \cdot \nabla\phi(\mathbf{x}_1)\right] \breve{\mu}(\mathbf{x}_1) \sim L^3 \frac{1}{L}\left(\frac{1}{\eta_d L}\right)\frac{1}{L}\,\frac{\sigma}{L} = \frac{\sigma}{\eta_d L} \ . \tag{10.100}$$

In 2D the same result holds because $\int d\mathbf{x}_1 \left[\nabla\phi \cdot \mathrm{T} \cdot \nabla\phi\right] \breve{\mu} \sim L^2(1/L)(1/\eta_d)(1/L)(\sigma/L) = \sigma/(\eta_d L)$. Thus, the condition for the dominance of the diffusive term is

$$\sigma/(\eta_d L) \ll M\sigma/L^3 \quad \Rightarrow \quad L \ll (M\eta_d)^{1/2} \ . \tag{10.101}$$

Thus, the hydrodynamic description is relevant for large length scales $L \gg \sqrt{M\eta_d}$ in 3D. This condition has been derived in Ref. [314] in the three dimensional case and it is easy to show that it also holds in 2D (rather trivially, since $\partial_t\phi$ on the right of Eq. (10.70) has no dependence on dimensionality on space). The condition for the time scale where diffusive description makes sense can be obtained through relation $\partial_t\phi = M\nabla^2\breve{\mu}$, or $1/t \sim M\sigma/L^3$. Solving for the length scale we get that $L \sim (M\sigma t)^{1/3}$. Plugging this into the inequality (10.101) yields

$$t \ll M^{1/2}\eta_d^{3/2}\sigma^{-1} \ . \tag{10.102}$$

Dimensions of the parameters are: $[M] = s$, $[\eta_d] = m^2/s$ and $[\sigma] = m^3/s^2$. Of course, the time scale given in Eq. (10.102) should be compared with the other time (length) scales obtained from comparing the magnitude of the inertial terms to the convective ones.

10.4.3 Relevance of turbulence for capillary flow

We conclude this section by estimating the scales where turbulence becomes important. This is to be expected for capillaries where there are large gradients in the velocity field. Generally speaking, large Reynolds number Re ($\mathcal{O}(1000)$) characterizes turbulent flow. Reynold's number $Re \equiv Lv/\nu$ is the dimensionless combination of the typical velocity and length scales and the kinematic viscosity. When Re is small ($Re \ll 1$) it gives a rough estimate on the scales where the viscous term ($\nu\nabla^2\mathbf{v}$) in the Navier-Stokes equation dominates over the nonlinear convective term ($\mathbf{v}\cdot\nabla\mathbf{v}$). Therefore, turbulence is expected if $L\bar{v}/\nu > 10^3$, where $\bar{v}$ is the average velocity of the fluid in capillary tube. The characteristic velocity is obtained from the hydrodynamic result for the averaged meniscus speed of fluid column under gravity [281]:

$$\bar{v} = dh/dt = \frac{R^2}{8\eta_d}(p_c/h(t) - g\phi) \ , \tag{10.103}$$

where $h(t)$ is the height of the liquid in the tube. R is the radius of the tube and $p_c \equiv 2\sigma/R$ is the capillary pressure in the units where $[\phi] = 1$. This formula holds for spontaneously rising front with no external pressure gradient driving, which would alter Eq. (10.103) substantially. It is clear that the liquid rises higher the narrower the tube is. However, it also rises faster the wider the tube radius is. Of course, this behaviour seazes to hold when the radius becomes so large that the conditions under which Eq. (10.103) has been derived break down. In the Washburn regime the condition for the onset of turbulence becomes

$$h < 10^{-3}\,\frac{R^2\sigma}{\nu\eta_d} \equiv h_{cr} \ . \tag{10.104}$$

Notice that $\nu \equiv \eta_d/\phi$ and $[\phi] = 1$. The upper limit of the tube radius can be determined from the condition that gravitational effects must not dominate the meniscus shape: the derivation presumes a spherical cap.

Eq. (10.104) is easier to evaluate if we use the physical units for all variables. Substituting the values of water [293] we set $\nu' \approx 10^{-6} m^2/s$, $\eta_d' \approx 10^{-3} Ns/m^2$ and $\sigma' \approx 10^{-1} N/m$ we estimate that for a capillary whose radius is of the order of $1mm$ the critical height h_{cr} below which Reynolds number is in the turbulent regime, is of the same order ($\mathcal{O}(1cm)$) as the capillary length. For capillaries with radius smaller than $0.1mm$ the critical height is about hundred times smaller as it scales like R^2. Analogous scaling relation holds also in the case of driven flow between two plates separated by distance x [315]: The average flow velocity v goes like $v \propto x^2$. Thus, if Eq. (10.104) is to be believed, for capillaries of this size turbulence should not be a problem except for a small fraction of the capillary height. Of course, it should be remembered the Washburn equation (10.104) does not hold for small enough heights: when $h \to 0$, the velocity becomes infinite, which is of course unphysical. Also, in the derivation of the mean velocity of the meniscus one has assumed quasi-stationary Stokes' flow, which does not hold for small altitudes where the velocity field experiences rapid changes [279]. The distance X_P at which the parabolic velocity profile typical of Poiseuille flow assumed in the derivation has been reached, depends on the capillary radius and Reynolds number. A simple formula, which gives a rouhg estimate [316] is $X_P/R = Re/15$.

Chapter 11

Emergence of boundary conditions

In standard sharp-interface hydrodynamics one needs to supplement the partial differential equations of mass, momentum and energy densities (and other fields relevant for large scale description) with proper boundary conditions. This section demonstrates that the Poisson bracket formulation of hydrodynamics, in which the boundaries are diffuse and no boundary conditions are needed, is capable of mimicking the sharp-interface hydrodynamics governed by standard Navier-Stokes equations. In other words, the new non-linear coupling terms in the equations of motion arising from the Poisson bracket formalism give effectively rise to the boundary conditions of the sharp-interface model (standard Navier-Stokes), whose evolution equations contain a smaller number of driving force terms. Boundary conditions can be modeled with the aid of *bulk* fields, which is a great advantage especially when flows take place in a geometrically complicated (disordered) medium.

11.1 Classical boundary conditions

According to the standard hydrodynamics of simple liquids the boundary conditions that a single component viscous two-phase flow has to satisfy are the following.

- Fluid-fluid boundary. Normal stress is continuous across a straight boundary. If the boundary is curved there is a discontinuity in normal stress components given by Laplace's formula. Tangential stress is continuos if the surface tension is constant and the fluids can be considered immiscible. Otherwise discontinuity appears also in tangential direction (p. 234 of Ref. [293], p.11 of Ref. [317]). Both normal and tangential velocities are continuous (the same on both sides of the boundary), See [318] p.56 derivation for irrotational fluid.

- Fluid-solid boundary. In the frame moving with the boundary the normal velocities of the fluid must be zero. For viscous fluid the also the tangential velocities are the same on both sides (p. 95, Ref. [299]). These requirements give rise to the no-slip condition $\mathbf{v} = 0$ at solid boundaries in the frame where the solid stays fixed.

Unless elastic properties of the solid are accounted for, one cannot say anything about the behaviour of the stress tensor at solid-fluid boundaries (p. 8 of Ref. [292]). The only thing which can be said on general grounds is that the both tangential and normal forces (stress vector) across the interface are continuous (p. 45 Ref. [299]) (except when shock waves are present), according to the action-reaction principle of Newton's. In a more refined treatment it is possible to derive equilibrium conditions for the stresses across the fluid-solid boundary analogous to Laplace's formula for fluid-fluid interfaces (p. 18 Ref. [292]), whose presence is not taken into account in our list above. As the solid is considered completely inert spectator phase in our description, we will not consider these refinements at this point but settle for studying only the standard conditions mentioned in the list above. We will also assume that the interfaces are charge neutral. For charged interfaces one should also include electric stresses (p. 10 Ref. [317], Ref. [319]).

The boundary conditions can be formulated in many ways dependening on the choice of the variables and method of solution. For example, in the case of single phase flow, we can cast out the pressure field altogether by projecting onto the longitudinal momentum component that satisfies the ideal fluid boundary condition $\mathbf{v} \cdot \mathbf{n} = 0$, where $\mathbf{n}$ is the normal vector of the solid. Therefore, we do not need to set boundary condition for pressure using this description. It can always be expressend in terms of the velocity as shown in (p. 39 Ref. [304], see also boundary conditions of the pressure field in Helmholtz-Hodge decomposition). Sometimes vorticity representation is preferred over velocity, boundary conditions for this type of formulation can be found in (p. 635 Ref. [320]). The standard boundary conditions for our purposes are most conviniently formulated in terms of the velocity field and stress tensor:

$$\begin{cases} \mathbf{v}(\mathbf{x}) = 0 \ , \quad \mathbf{x} \in \partial\Omega_S \ . \\ (p_1 - p_2 - \sigma\mathcal{K})n_i = \Big((\tau_{ik})_1 - (\tau_{ik})_2\Big)n_k + \partial\sigma/\partial x_i \ , \end{cases} \tag{11.1}$$

where the subscripts $(1, 2)$ refer to the two sides of the boundary. The first condition is the no-slip condition at fluid-solid boundary $\partial\Omega_S$. The second condition is the stress tensor condition at fluid-fluid boundaries. For incompressible fluid the viscous part of the stress tensor is defined as

$$(\tau_{ik})_\alpha \equiv (\eta_d)_\alpha \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right)_\alpha , \tag{11.2}$$

and $\alpha = 1, 2$. When surface tension gradients are not present, the latter condition in Eq. (11.1) reduces at equilibrium to Laplace's formula $\Delta p = \sigma\mathcal{K}$, where $\mathcal{K} \equiv 1/R_1 + 1/R_2$ is the local curvature with principal radii of curvature R_1 and R_2 in 3D. The components of the unit normal vector of the fluid-fluid interface are denoted with n_k in Eq. (11.1).

The sign of the $\partial\sigma/\partial x_i$ term reveals that it should be interpreted as contractive surface pressure gradient analogous to the bulk force ∇p. Moreover, in Eq. (11.1) the surface tension is strictly defined on the boundary only. In other words, $\sigma = \sigma'(\xi_2(\mathbf{x}), \xi_3(\mathbf{x}))$, where ξ_2 and ξ_3 are the curvlinear coordinates spanning the interface and ξ_1 is defined to be the normal coordinate of the interface, whose position in the Cartesian frame can be obtained from the relation $\xi_1(\mathbf{x}) = 0$. We will prove now that the cartesian gradient $\nabla\sigma$ is a tangential vector, which is physically clear from the action of this term (contraction of the interface). First, we define an auxiliary surface tension $\tilde{\sigma}'(\xi_1, \xi_2, \xi_3) \equiv \sigma'(\xi_2, \xi_3)\delta_S$, where $\delta_S \equiv |\nabla\xi_1|\delta(\xi_1)$ is the surface delta function. Taking the Cartesian gradient $\nabla \equiv \mathbf{e}_1\partial_1 + \mathbf{e}_2\partial_2 + \mathbf{e}_3\partial_z$ $(\partial_i \equiv \partial/\partial x_i)$ on both sides of the defining equation we get

$$\nabla\tilde{\sigma}'(\xi_1, \xi_2, \xi_3) = \left(\frac{\partial\sigma'}{\partial\xi_2}\nabla\xi_2 + \frac{\partial\sigma'}{\partial\xi_3}\nabla\xi_3\right)\delta_S + \sigma'\nabla\delta_S \ . \tag{11.3}$$

Since the orthonormal basis vectors of the curvlinear system [321] are given by $\mathbf{a}_i \equiv \nabla\xi_i/|\nabla\xi_i|$ $(i = 1, 2, 3)$, we see that the last term on the right hand side of Eq. (11.3) points in the direction of the normal $\mathbf{n} \equiv \mathbf{a}_1$: $\nabla\delta_S = \mathbf{nn}\cdot\nabla\delta_S$. Clearly, the expression in parenthesis, $\nabla\sigma'$ is orthogonal to $\mathbf{n}$. Therefore, we can say that the Cartesian derivative of σ' is tangential, which also applies to $\sigma(\mathbf{x})$

$$\sigma'(\xi_2(\mathbf{x}), \xi_3(\mathbf{x})) \equiv \sigma(\mathbf{x}) \ , \tag{11.4}$$

which lives only at the boundary. To make the tangentiality of the term $\nabla\sigma$ apparent, we should replace $\partial\sigma/\partial x_i$ in Eq. (11.1) with $(\delta_{ik} - n_i n_k)\partial\sigma/\partial x_k = (\nabla - \nabla_n)\sigma$, where $\nabla_n \equiv \mathbf{nn}\cdot\nabla$. With this modification, it is straightforward to split the condition on stress tensor into its normal and tangential parts. Let n_i be the components of the unit normal and s_i the components of the tangent vector (in some preferred direction on the tangential plane). The normal and tangential derivatives are given by $\partial_n \equiv \mathbf{n}\cdot\nabla = n_i\partial/\partial x_i$ and $\partial_s \equiv \mathbf{s}\cdot\nabla = s_i\partial/\partial x_i$, respectively. Contraction of the pressure tensor gives

$$\begin{aligned}
n_i\,(\tau_{ik})_\alpha n_k &= (\eta_d)_\alpha\, n_i \left(\frac{\partial v_i}{\partial x_k}\right)_\alpha n_k + (\eta_d)_\alpha\, n_i \left(\frac{\partial v_k}{\partial x_i}\right)_\alpha n_k && (11.5)\\
&= 2(\eta_d)_\alpha\, n_k \left(\frac{\partial v_k}{\partial n}\right)_\alpha \ ; && (11.6)\\
s_i\,(\tau_{ik})_\alpha n_k &= (\eta_d)_\alpha\, s_i \left(\frac{\partial v_i}{\partial x_k}\right)_\alpha n_k + (\eta_d)_\alpha\, s_i \left(\frac{\partial v_k}{\partial x_i}\right)_\alpha n_k && (11.7)\\
&= (\eta_d)_\alpha\, s_i \left(\frac{\partial v_i}{\partial n}\right)_\alpha + (\eta_d)_\alpha \left(\frac{\partial v_k}{\partial s}\right)_\alpha n_k \ . && (11.8)
\end{aligned}$$

Using the results above, we can resolve the stress tensor condition (11.1) into to scalar equations for the normal and tangential directions:

$$\begin{aligned}
p_1 - p_2 - \sigma\mathcal{K} &= 2(\eta_d)_1\, n_k \left(\frac{\partial v_k}{\partial n}\right)_1 - 2(\eta_d)_2\, n_k \left(\frac{\partial v_k}{\partial n}\right)_2 \ ; && (11.9)\\
(\eta_d)_2 \left(s_i\frac{\partial v_i}{\partial n} + n_k\frac{\partial v_k}{\partial s}\right)_2 - (\eta_d)_1 \left(s_i\frac{\partial v_i}{\partial n} + n_k\frac{\partial v_k}{\partial s}\right)_1 &= \frac{\partial\sigma}{\partial s} \ . && (11.10)
\end{aligned}$$

We have thus reproduced the results of Refs. [322, 323]. We will return to these equations in Sect. 11.2 where we show how they arise from the Poisson bracket formalism, and indicate how corrections to them can be generated.

11.2 Derivation of boundary condition for stress tensor

Sect. 11.1 reviewed the classical boundary conditions of fluid mechanics for sharp-interface models. The jump condition of the stress tensor can also be *derived using the sharp interface model* assuming a singular stress distribution on the phase boundary (cf. $\tilde{\sigma}'$ above):

$$\mathbf{P} \equiv \mathbf{P}^+\theta^+ + \mathbf{P}^-\theta^- - \sigma(\mathbf{I} - \mathbf{nn})\,\delta_S \ , \tag{11.11}$$

where $\mathbf{P}^\pm \equiv p^\pm\mathbf{I} - \boldsymbol{\tau}^\pm$ and $\theta^\pm \equiv \theta(\pm\xi_1(\mathbf{x}, t))$. The bulk fields can be divided into two parts indicating medium 1 with + and medium 2 with −:

$$\phi = \phi^+\theta^+ + \phi^-\theta^- \ \ ; \ \ \mathbf{v} = \mathbf{v}^+\theta^+ + \mathbf{v}^-\theta^- \ \ ; \ \ \boldsymbol{\tau} = \boldsymbol{\tau}^+\theta^+ + \boldsymbol{\tau}^-\theta^- \ . \tag{11.12}$$

The bulk values of the density on both sides are denoted by $\phi^\pm$. Substitution of these definitions into the momentum balance equation, $\partial_t(\phi\mathbf{v}) + \nabla\cdot(\phi\mathbf{vv}) = -\nabla\cdot\mathbf{P}$ gives a regular and singular contribution. The latter is given by

$$(p^+ - p^-)\mathbf{n} = (\boldsymbol{\tau}^+ - \boldsymbol{\tau}^-)\cdot\mathbf{n} + \mathcal{K}\sigma\mathbf{n} + \nabla\sigma \ , \tag{11.13}$$

which is precisely the same as Eq. (11.1). This result with viscous effects added has been derived in Refs. [262, 324]

11.2.1 Limiting value of capillary stress in diffuse boundary formulation

We now turn to derivation of the boundary condition for the stress tensor using *diffuse interface* description where the evolution equations are obtained from Poisson bracket formalism. In this case no boundary conditions are needed (because there are no sharp boundaries in the first place). Instead, the nonlinear couplings among the coarse-grained fields (order parameter fields) give rise to effective boundary conditions, which in the sharp interface limit approach the classical ones. In equilibrium the momentum balance equation (9.26) yields the Laplace's pressure drop condition. For zero velocity the surviving terms fulfil the force balance

$$-\nabla p_2 + \mu_f \nabla\phi = 0 \ . \tag{11.14}$$

On scales large compared with the bulk correlation length the capillary force $\mu_f\nabla\phi$ is a sharply peaked function at phase boundaries because $\nabla\phi$ changes rapidly there. Approximating $\nabla\phi \approx \delta(\mathbf{x}-\mathbf{x}_b)$, where $\mathbf{x}_b$ denotes the spatial position of the phase boundary we see that capillary force becomes proportional to the chemical potential evaluated at the interface: $(\mu_f)_{int} \equiv \mu_f(x_b)$. At curved fluid-fluid interfaces $(\mu_f)_{int} \approx -\sigma\mathcal{K}/\Delta\phi$, where $\Delta\phi$ is the miscibility gap. Integrating Eq. (11.14) over the phase boundary yields the boundary condition for the normal component of the stress tensor:

$$\Delta p_2 = \sigma\mathcal{K}/\Delta\phi \ . \tag{11.15}$$

In the unit system where $[\phi]=1$, we usually scale the magnitude of the bulk density in such away that $\Delta\phi = 2$. By defining a new pressure field $\tilde{p}_2 \equiv p_2/\Delta\phi$ we can cast Eq. (11.15) into the standard form.

In the tangential direction the term $\mu_f\nabla\phi$ gives rise to another force if the surface tension is not a spatial constant. This possibility rises if there are for instance surfactants present in the solution. The tangential force is balanced against the viscous stresses as will be shown later. Below we show how it arises from the diffuse boundary description. Projection of the tangential force mediated by the capillary stress term $\mu_f\nabla\phi$ in the direction $\mathbf{s}$ is given by $\mu_f\mathbf{s}(\mathbf{s}\cdot\nabla\phi) = \mu_f\partial_s\phi\,\mathbf{s}$. Integrating this force across the phase boundary yields

$$\int du\, \mu_f \frac{\partial\phi}{\partial s}\mathbf{s} = \int du\, \frac{\delta F_f}{\delta\phi}\frac{\partial\phi}{\partial s}\mathbf{s} \approx \int du\, \frac{\partial f}{\partial s}\mathbf{s} \ . \tag{11.16}$$

To obtain the last approximate equality, we have made use of the free energy density f ($F_f = \int dV\, f$). It has also been assumed that the gradients of $\phi(u,s)$ in the direction s are negligible in comparison to the gradients in the normal direction u. Specifically,

$$\frac{\partial}{\partial s}\int du\, f(\phi) \approx \frac{\partial}{\partial s}\int du \left[\tfrac{1}{2}|\partial_u\phi|^2 + V(\phi)\right] \tag{11.17}$$

$$= \int du \left[-\partial_u^2\phi(u,s) + V'(\phi(u,s))\right]\partial_s\phi(u,s) \approx \int du \frac{\delta F_f}{\delta\phi}\partial_s\phi \ . \tag{11.18}$$

Finally, at the level of accuracy where the tangential derivative terms can be left out, we show that

$$\int du\, \frac{\partial f}{\partial s}\mathbf{s} \approx \frac{\partial\sigma}{\partial s}\mathbf{s} \ . \tag{11.19}$$

Owing to the specific form of the free energy F_f, which we are using, the bulk free energy is normalized to zero. This means that the free energy F_{++} of single phase composition with no phase boundaries is zero: $F_{++} = 0$. The surface tension σ is defined to be the free energy difference between a system with a single phase boundary between phases + and − (free energy $F_{+-} = F_f$), and the free energy of a pure system divided by the boundary area A. Thus,

$$\sigma \equiv \frac{1}{A}(F_{+-} - F_{++}) = \frac{1}{A}F_{+-} = \frac{1}{A}\int dV\, f = \frac{1}{A}\int dA \int du\, f \approx \int du\, f \ , \tag{11.20}$$

where we have assumed that $\int du\, f(u,s)$ depends very weakly on the tangential variable s. Since $\partial\sigma/\partial s \approx \int du\, \partial f/\partial s$ according to Eq. (11.20), we have been able to show that the extra force term

$$\mu_f \nabla\phi \approx \left(\sigma\mathcal{K}\mathbf{n} + \frac{\partial\sigma}{\partial s}\mathbf{s}\right)\delta_S + \mathcal{O}(\xi) \ . \tag{11.21}$$

When the width of the phase boundary ξ goes to zero we expect the correction terms to vanish (like some power of ξ in general) and we are left with a distribution of force which is concentrated at the boundary regime indicated by the surface delta function δ_S. Based on the effective form of the force term $\mu_f\nabla$ derived in Eq. (11.21) we show now how it contributes to boundary condition of the stress tensor in the limit $\xi \to 0$.

11.2.2 Boundary condition of stress tensor through electromagnetic analogue

To derive the boundary condition for the stress across the interface between two fluids, we make use of an electromagnetic analog. Jump conditions for electric displacement $\mathbf{D}$ and magnetic field vector $\mathbf{H}$, which are the macroscopic averaged counterparts of the microscopic electric field $\mathbf{E}$ and magnetic induction $\mathbf{B}$ inside macrosopic medium, can be derived directly from Maxwell's equations. This can be done by enclosing a small volume dV around the boundary layer, where the permeabilities change, into (for instance) a cylinderical pill box, whose height is let to approach zero. In this way one obtains conditions [259] regarding either normal or tangential (or both) components of the fields, which they have to satisfy when crossing the boundary region. Analogously, we try to find out what are the conditions on the stress tensor (velocity field) when we cross a boundary between two fluids with possibly different macroscopic (averaged) properties such as viscosities. It should be noted that the conditions are enforced by the structure (nonlinear coupling terms) of the equations of motion themselves, they are not put in by hand. Our starting point is the momentum balance equation without stochastic terms:

$$\phi d\mathbf{v}/dt = -\nabla \cdot \mathbf{P} + \mu_f \nabla\phi \ , \tag{11.22}$$

where $\mathbf{P} \equiv p\mathbf{I} + \boldsymbol{\tau}$ is the full stress tensor with viscous stresses included. We enclose a small boundary region ΔV in a cyliderical pillbox whose bottom and top are on different sides of the boundary. When the height of the cylinder approaches zero, the volume integral over the left hand side of the equation of motion, $\int_{\Delta V} dV\, \phi\, d\mathbf{v}/dt \to 0$ because the integrand is assumed to be bounded. This statement may not hold if the there are strong anomalies such as shock waves present.

Let us take the volume integrals of the right hand side of the equation of motion. Transformation of the divergence of the tensor field $\mathbf{P}$ into a surface integral gives

$$-\int_{\partial V} \mathbf{P} \cdot d\mathbf{S} + \int_V dV\, \mu_f \nabla \phi = 0 \ , \tag{11.23}$$

where ∂V is the surface area of the pillbox. We take the bottom and top areas of the pillbox to be the same: $\Delta S_{top} = \Delta S_{bottom} \equiv \Delta S$. The normal vector of the top is denoted by $\mathbf{n}$ and the normal vector of the bottom is opposite to it. As the height of the pillbox goes to zero, the surface integral of Eq. (11.23) yields in the limit

$$-\int_{\partial V} \mathbf{P} \cdot d\mathbf{S} \rightarrow (\mathbf{P}^{+} - \mathbf{P}^{-}) \cdot \mathbf{n} \Delta S \ . \tag{11.24}$$

The remaining volume integral over the capillary force density can be calculated with the aid of Eq. (11.21):

$$\int_{\Delta V} dV\, \mu_f \nabla \phi \approx \int dS \int du \left(\sigma \mathcal{K} \mathbf{n} + \frac{\partial \sigma}{\partial s} \mathbf{s} \right) \delta_S = \Delta S \left(\sigma \mathcal{K} \mathbf{n} + \frac{\partial \sigma}{\partial s} \mathbf{s} \right) \ . \tag{11.25}$$

Combining Eqs. (11.25) and (11.24) and canceling out the common factor ΔS gives us the final answer:

$$(p^{+} - p^{-}) \mathbf{n} = (\boldsymbol{\tau}^{+} - \boldsymbol{\tau}^{-}) \cdot \mathbf{n} + \sigma \mathcal{K} \mathbf{n} + \frac{\partial \sigma}{\partial s} \mathbf{s} \ . \tag{11.26}$$

This is consistent with the standard stress tensor jump condition and with the result based on the singular distribution method leading to Eq. (11.13), where $\nabla \sigma$ must be understood as tangential derivative.

11.2.3 Dimensional estimation of strength of viscous stress

Even though viscous stresses are always important close to phase boundaries, we can ask how strong is the effect of viscous stresses on the stress tensor boundary condition. If the viscous pressure drop across fluid-fluid boundary is negligible as compared to the surface tension contribution, we can simplify the analysis of a situation where the two fluids have different viscosities: If we can set the terms on the right hand side of Eq. (11.9) to zero in comparison to the $\sigma \mathcal{K}$ on the left, we could neglect the fact that $\eta_d = \eta_d(\phi)$ as far as the normal component of the stress tensor boundary condition is concerned. Besides giving some idea of the magnitude of the viscous pressure drop across the divinding surface, this could be useful for a numerical simulation in case the spatially varying viscosity caused any problems: Inside the transition zone (thickness of the phase boundary) it would be possible to use a constant effective viscosity, which would be the same for both fluids. The assumption about constant effective viscosity in the vicinity of the phase boundary would also simplify the tangential stress tensor condition to mere identity. If the surface tension is a spatial constant the tangential stresses obviously cancel each other as can be seen from Eq. (11.10) by setting $(\eta_d)_1 = (\eta_d)_2$. Of course, we would also have to assume that the derivatives of the velocity are continuous across the phase boundary which seems reasonable as no sudden jumps should appear when the width of the boundary is finite (a few lattice units in simulation).

From the expression of the viscous stress tensor we have $\boldsymbol{\tau} \sim \eta_d \partial v / \partial x \sim \eta_d \Delta v / \Delta x \equiv S_1$. The Laplace pressure drop S_2 is given by $S_2 \sim \sigma / R$, where R is the characteristic size of the radius of curvature. Hence, the size of the transition region where the surface tension effects dominate over viscous effects can vary spatially with the spatial variation of the curvature $\mathcal{K}$. Situation simplifies considerably in cases where the curvature is the same constant along the whole phase boundary. A narrow capillary tube with spherical meniscus ($R \sim$ radius of the tube) has a constant curvature and serves as a test bench below. The condition for the dominance of surface tension effects is thus $S_1 \ll S_2$, or

$$\eta_d \Delta v/\Delta x \ll \sigma/R \quad \Rightarrow \quad \eta_d \Delta v/\sigma \ll \Delta x/R \ . \tag{11.27}$$

Let us see what the condition for the ratio $\Delta x/R$ in case of a capillary tube. The length scale Δx corresponds to the meniscus width Δx within which the pressure drop Δp takes place, and R is the radius of the tube. The surface tension of water-air interface is $\sigma \approx 10^2 erg/cm^2 = 10^{-1} N/m$, and the viscosity of water is $\eta_d \approx 10^{-3} Ns/m^2$. We will also assume that the velocity jumps from zero to average advancing velocity of the front, which is take to be $\Delta v = v_{ave} \approx 10^{-3} m/s$. Plugging these numbers into Eq. (11.27) yields $\Delta x/R \gg 10^{-5}$ which should be an experimentally realizable figure.

11.3 Solid-fluid interaction

We will show now that the substrate potential V_S is not a redundant parameter when we are considering the velocity field $\mathbf{v}$ of the fluid in addition to its density ϕ. As argued in Sect. 9.1 for equilibrium situations when the momentum density of the fluid can be left out of description, we can replace $V_S(z)$ (which is small but non-zero in the fluid domain close to the solid boundaries) with the wall potential A, which vanishes in the fluid domain D. Equivalently, based on the density functional results, we can say that keeping the integrated value of $\int_{d_w}^{\infty} dz_n \, V_S(z_n)$ constant, where d_w is the depth of the microscopic depletion zone just above the solid surface, is equivalent to fixing a certain value to wall potential A as far non-zero contact angles are considered. Also complete wetting can be achieved through a wall potential, which vanishes in the fluid domain. However, it is not possible to vary the depth of the wetting layer unless one extends the support of A into the fluid domain D: $A = A(x, y, z)$, where A is non-zero close to solid boundaries even if $z \in D$. Alternatively, one can use $V_S(z)$ instead of $A(z)$ as we have noted before.

Below we will first show how the force term $\nabla V_S(z)$, where z is the coordinate normal to the solid surface, naturally explains the boundary condition $\mathbf{v}_n = 0$ which holds for both viscous and non-viscous fluids. In other words, the substrate potential turns out to be responsible for bringing the moving fluid elements into contact with the solid walls and for preventing them from entering the solid domain D'. In Sect. 11.3.2 we discuss the possible mechanicms of the tangential velocity condition, $\mathbf{v}_t = 0$, along solid wall in a viscous fluid.

11.3.1 Vanishing normal velocity at solid wall

We drop everything else from the equation of motion and concentrate on the effect of f_{wall} term in Eq. (9.24):

$$\phi \partial_t \mathbf{v} = -\phi \nabla V_S \ . \tag{11.28}$$

The term $-\phi \nabla V_S$ on the right hand side of the previous equation is active only in the vicinity of the solid-fluid boundaries. Let us give a hand waving proof that Eq. (11.28) plays a role in the emergence of the boundary condition typical of a viscous fluid or nonviscous fluid. First, consider separately components of the velocity field normal (v_n) and tangential (v_t) to the solid boundary:

$$\begin{aligned} \partial_t v_n &= -\partial_n V_S \ ; \qquad (11.29) \\ \partial_t v_t &= -\partial_t V_S \ . \qquad (11.30) \end{aligned}$$

Since the potential changes much more rapidly in the normal than in the tangential direction, we can effectively set $\partial_t V_S \approx 0$. Then, the second equation only posesses the trivial solution $v_t \neq v_t(t)$ and thus the wall potential is not seen to affect the dynamics parallel to the wall in this approximation. Thus, we are only left with Eq. (11.29) to describe the dynamics with the boundary layer close to the wall. The term on the right is clearly a force term which pulls the fluid elements into the potential well located at the minimum of V_S. Simultaneously, it prevents the fluid from entering the interior of the solid phase because V_S becomes (infinitely) repulsive right at the location of the solid boundary.

11.3.2 No-slip condition

The action of the force ∇V_S is sufficient to explain the emergence of the macroscopic condition $\mathbf{v}_n = 0$ which prevents the fluid particles entering the interior of the solid because their momentum perpendicular to the solid wall will be zero at the solid-fluid boundary. Macroscopically, we know that this condition is satisfied by a non-viscous fluid satisfying Euler's equation of motion. However, there are no terms in the present equation of motion which would naturally explain the vanishing of the momentum parallel to the wall leading to macroscopic no-slip condition $\mathbf{v} = 0$ typical of simple viscous fluids.

Since the no-slip condition cannot be generated by ∇V_S in the manner described above, we have to search for other mechanisms. One possibility is to resort to a concept of effective dynamic viscosity η_d^*, which in a way becomes infinitely large close to solid boundaries and thus enables the normal dissipative force term $\eta_d^* \nabla^2 \mathbf{v}$ to take care of removal of fluid elements kinetic energy close to solid walls. Inside the fluid $\eta_d^* = \eta_d$ is the same as the normal dynamic viscosity of the fluid. This approach can be shown to be consistent with zero slipping length of the fluid elements at the wall [325]. The momentum equation of motion has the form

$$\phi \left(\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla)\, \mathbf{v}\right) = -\nabla p_2 - \eta_d \nabla^2 \mathbf{v} + \mathbf{f}_b \ , \qquad (11.31)$$

where the boundary force term $\mathbf{f}_b$ contains the capillary contribution and the potential barrier generated by V_S: $\mathbf{f}_b \equiv \mathbf{f}_{cap} - \phi \nabla V_S = \mu_f \nabla \phi - \phi \nabla V_S$. It is worth pointing out that in Ref. [325] it is shown that the normal Navier-Stokes equation (Eq. (11.31) without the boundary force $\mathbf{f}_b$) supplemented with boundary conditions

$$\mathbf{j}_{\|}|_b = \delta_{wall}\, \partial_n \mathbf{j}_{\|}|_b \quad , \quad \mathbf{j}_{\perp}|_b = 0 \ , \qquad (11.32)$$

is a sufficient large scale description of the microscopic NEMD (Non-Equilibrium Molecular Dynamics) simulation of molecular fluid. There are new phenomenological parameters introduced in Eq. (11.32): $\mathbf{j}_{\|}$ is the momentum flux in the direction of the wall and $\mathbf{j}_{\perp}$ is the flux perpendicular to it. The slipping length is δ_{wall} and the fluxes are evaluated at the boundary $|_b = |_{z_0}$, where z_0 is the height at which the diffuse solid-fluid boundary is taken to be. In terms of the velocity field we can equivalently write $\partial_z v_s|_b = v_s|_b / \delta_{wall}$ for $s = x, y$ with z as the perpendicular direction. In other words it is possible to find out the values of the new parameters z_0 and δ_{wall} from the simulation data by using a linear response argument relating the force on the fluid elements at the wall to autocorrelation function of the parallel momentum fluctuations via a generalized Green-Kubo relation. If the microscopic interaction potential of the fluid and wall particles satisfies certain conditions, it follows that $\delta_{wall} = 0$ and consequently the no-slip condition holds.

Even though the previous method can be called an *ab initio* derivation of the boundary condition, it still relies on the traditional form of the Navier-Stokes equation which holds for bulk fluids. Consequently, it does not really reveal where the dissipation comes from on the level of the forces. We can even cast it in the usual form by trading the boundary conditions of Eq. (11.32) to an effective viscosity η_d^* which dependes on the fluid and solid density fields ϕ and ρ:

$$\phi\left(\partial_t \mathbf{v} + (\mathbf{v}\cdot\nabla)\,\mathbf{v}\right) = -\nabla p_2 - \eta_d^*(\phi,\rho)\nabla^2\mathbf{v} + \mathbf{f}_b \ , \tag{11.33}$$

It is supposed that η_d^* becomes infinitely large close to solid boundaries such that the sharp interface boundary condition $\mathbf{v} = 0$ is satisfied. The possibility of having a density (order parameter) dependent viscosity has been suggested in Ref. [25] not to model the effect of solid walls but to allow the components of the binary fluid have different viscosities.

Anther possibility for obtaining the no-slip condition is to add a new force term (to be derived from free energy, of course) which acts on a faster time scale than the other terms since $\mathbf{v} = 0$ is an instantaneous condition. In this way we could avoid introduction of $\eta_d^*(\phi,\rho)$ which obviously complicates both some aspects of analytic and numerical work, though it does save us from the pain of imposing the no-slip at every solid-fluid boundary, something which might prevent the simulation attempt of fluid flow in complicated porous medium using traditional tools. If we choose to implement the no-slip condition by introduction of a new force term instead of using effective viscosity η_d^*, we should repeat the Green-Kubo analysis of Ref. [325] to see how the extra force term exactly appears in the linear response argument. As it is, it only contains contribution from the dissipative force $\eta_d\nabla^2\mathbf{v}$.

11.3.3 Remarks on effective viscosity

So far we have considered two possibilities which give rise to viscosity coefficient that acquires spatial dependence. In Sect. 11.3.2 we introduced the concept of effective dynamic viscosity $\eta_d^*(\phi,\rho)$, whose dependence on the fluid and solid density fields lead to no-slip boundary condition at solid boundaries. In Sect. 9.5.3 the description of two-component flow in terms of total momentum led to a density dependent viscosity $\eta_d(\phi)$, which becomes equal to the viscosity of each fluid component within the components domain. In this section we demonstrate that at least on the level of Stoke's flow, where the inertial terms of the Navier-Stokes equation can be left out, the use of effective dynamic viscosity η_d^* still allows us to obtain the formal analytic solution of the velocity and pressure fields. This can be usefull for analysis of flow and liquid-gas boundary properties in complex solid matrix. Instead of Eq. (10.39) we have

$$\left\{\begin{array}{l} \eta_d^*(x,y)\nabla^2\mathbf{v} - \nabla p_2 + \mathbf{f}_g = 0 \ ; \\ \nabla\cdot\mathbf{v} = 0 \ ; \\ \partial_t\phi + \mathbf{v}\cdot\nabla\phi = M\nabla^2\mu_f \ . \end{array}\right. \tag{11.34}$$

In 2D the effective viscosity is $\eta_d^*(x,y) \equiv \eta_d^*(\phi(x,y),\rho(x,y))$. Dividing both sides of the first equation with η_d^* and taking the divergence, we get

$$-\nabla\cdot\left(\frac{1}{\eta_d^*}\nabla p_2\right) + \tilde{\mathbf{f}}_g = 0 \ , \tag{11.35}$$

where we have defined $\tilde{\mathbf{f}}_g \equiv \nabla\cdot(\mathbf{f}_g/\eta_d^*)$. This type of equation is difficult to solve in the general case but in 2D one can resort to complex function techniques. Supposing it is possible to find a conformal mapping between the $z = x + \imath y$ plane and the w-plane where $w = g(z)$, the gradient transforms as

$$\nabla_z = \bar{g}'\nabla_w \ , \tag{11.36}$$

where $\bar{g}$ denotes the comples conjugate of g. If we could identify g' with $1/\eta_d^*$ it is straightforward to proceed solving Eq. (11.35). In general, there is no guarantee, that such a conformal g-function exists. However, the Riemann mapping theorem guarantees [326] that almost arbitrarily complicated region can be conformally mapped onto a regular one in the w-plane. Therefore it should be possible to at least get rid of the complicated spatial dependence of the prefactor function $1/\eta_d^*$ by making a transformation which straightens the phase boundary into a straight line. Then one can proceed solving Eq. (11.35) by other standard methods.

11.4 Dissipative effects close to solid boundaries

As molecular processes close to solid boundaries are not modeled at the current level of sophisitication, it cannot be expected that the Poisson bracket formalism with the free energy given in Eq. (9.1) would produce the no-slip boundary condition without addition of any extra terms to F_t. However, it is interesting to see *if* there are any mechanisms built-in in the current formalism which enable dissipation of kinetic energy of the fluid elements close to solid walls. Indeed, in App. D.2.2 it has been shown that when the momentum density is treated as the fundamental coarse-grained quantity, and its equation of motion is used to generate the evolution equation of the velocity field through substitution $\mathbf{j}(\mathbf{x}) = \phi(\mathbf{x})\mathbf{v}(\mathbf{x})$, we generate extra terms on the right hand side of the Navier-Stokes equation. The derivation of of the full evolution equation of the velocity field is presented in App. D.2.2. Here it suffices to study the following reduced form of the Eq. (D.80):

$$\phi\, dv_i/dt = -\Gamma_{00}\Big[\nabla^2\Big(-\frac{1}{2\phi^2}j^2 + \mu_2\Big)\Big]v_i = \Gamma_{00}(\nabla^2\mu_k)\,v_i - \Gamma_{00}(\nabla^2\mu_2)\,v_i \ . \tag{11.37}$$

For free energy of Eq. (9.1), $\delta F/\delta\phi = -j^2/(2\phi^2) + \mu_2$, where $\mu_2 \equiv \mu_f + V_S$. The chemical potential of the fluid is μ_f and V_S is the averaged substrate potential of the solid, which couples linearly to ϕ. Whether or not this simple interaction is sufficient and how it is to be modified to create dissipation of kinetic energy of fluid elements depends crucially on the magnitude and form of the constituents of μ_2.

The first term in the square brackets in Eq. (11.37) tries to even out kinetic energy differences. This can be seen in the following way. First, drop the second term and multiply both sides by velocity v (1D). Equation of motion becomes $\partial_t E \propto (\partial_x^2 E)\,E$, where $E = v^2$ is proportional to kinetic energy for constant mass density. If the initial profile is sinusoidally varying in space, we see that in the regions where $\partial_x^2 E < 0$ (hill tops) the energy is lowered, whereas the energy of those regions with $\partial_x^2 E > 0$ (valleys) increases.

To be able to say that the second term in the square brackets corresponds to a viscous dissipative force we need to show that the prefactor $\Gamma_{00}(\nabla^2\mu_2) > 0$. If this is so, then in principle $\Gamma_{00}(\nabla^2\mu_2)v_i$ can be generated by taking variation with respect to v_i of a positive-definite functional, Rayleigh dissipation functional, which is quadratic in velocity. Obviously, the prefactor does not have to be positive everywhere in space. To be able to say that the prefactor has something to do with no-slip boundary condition, however, it suffices to prove that the curvature of μ_2 is positive close to solid boundaries. Of course, even this is not sufficient for effective generation of no-slip boundary condition: for that to be true, one would have to show that the magnitude of the prefactor is so large that on macroscopic scales the kinetic energy of the fluid element is dissipated almost instantaneously. In addition, a further requirement that a force term responsible for producing the no-slip effect should satisfy, is that its support is concentrated in the vicinity of the solid boundaries. Clearly, there is no guarantee that $\Gamma_{00}(\nabla^2\mu_2)$ will actually behave so in every situation.

Let us see how far we can get by using the current form of the free energy. In equilibrium (without thermal fluctuations) the velocities of the fluid elements are zero and the momentum balance equation reduces to condition $\nabla\mu_2 = 0$. In order for the fluid to equilibriate in a capillary tube set-up, for example, one must add the gravitational chemical potential to expression of μ_2. Only when the fluid elements are moving can there be nonzero curvature for the potential μ_2, which complicates analysis considerably. Although static arguments are insufficient we may gain some insight by considering the form of $\mu_2 = \mu_f + V_S$. The solid potential V_S is unaffected by motion of the fluid whereas μ_f changes as a function of $\mathbf{v}$. The static wall potential is strongly repulsive at short distances, rising very deeply on approaching the outermost atomic layer of the wall. Therefore, it does not sound unreasonable to assume that $V_S \gg \mu_f$ close to the walls. If the fluid is not driven too fast, we can roughly take μ_f to be the same constant in both liquid and gas phases. Thus, if the overall potential μ_2 close to the wall is dominated by V_S and further away from walls it is given by μ_f, there must be a region of positive curvature in-between. This can be made more quantitative as follows: Normalizing $V_S - \mu_f = 1$ in suitable units, we can write $\mu_2 \approx -\theta(x) + \theta(x - L)$, where L is the separation between two walls (consider system with two vertical walls at $x = 0$ and $x = L$ for simplicity). This approximation means that we have calibrated the bulk value of $\mu_f = 0$ between the walls and taken the phase boundaries to be infinitely sharp. Then, the derivative $\partial_x\mu_2 \approx -\delta(x) + \delta(x - L)$. Taking into account the fact that in nature no boundary is absolutely sharp we can approximate the delta function with $\delta(x) \approx Ae^{-A^2x^2/2}$, where the (large) value of A is fixed by the molecular length scale determining the finite physical width of the solid-fluid phase boundary. The second derivative is given by $\partial_x^2\mu_2 \approx -A^3x\,e^{-A^2x^2/2} + A^3(x-L)\,e^{-A^2(x-L)^2/2}$. Plotting curvature of the chemical potential μ_2 versus the spatial location ensures that within the fluids domain $\partial_x^2\mu_2$ takes positive values only in the immediate vicinity of the solid boundaries and consequantly $-\Gamma_{00}(\nabla^2\mu_2)\,v_i$ dissipates kinetic energy fast due to the largeness of the prefactor A.

The biggest shortcoming of our argumentation is that the assumption of V_S dominating over μ_f and having the step function profile mentioned above close to the boundaries seems to be contradicting our earlier requirement that $\mu_2 = V_S + \mu_f = const$ when approaching equilibrium. One should be careful, though, since we have also assumed that the total chemical potential does not experience any discontinuities when crossing the solid-fluid boundary whereas the pressure field is confined inside the fluid phase only. To be more faithfull to the phase-field philosophy we should also study the extensions of the pressure field inside the solid phase and see if there are any anomalous contributions close to the phase boundary. Finally, we conclude that if it is possible to study the dissipation at solid boundaries by adding new terms to the free energy (coarse-grainable from microscopics) it might also be possible to cast some light into the ab initio derivation of the dissipative effects at contact line and in thin precursor films (dissipation channels) discussed in Sect. 8.9.

Chapter 12

Stochastic properties of interfaces and lines

Having produced the dynamics of the relevant bulk variables of classical fluids (Sect. 3.1.2, Chap. 9) and having shown how the dynamics of lower dimensional structures such as liquid-gas boundaries and triple lines can be projected out of the bulk equations of motion (Chap. 8), we will now consider the stochastic aspects of the equations of motion of the projected collective coordinates. Stochasticity of the bulk equations of motion can result at least from three different sources. Part of it is due to the coarse-graining process itself as explained in Sect. 1.1 and Sect. 2.3.5. Static frozen impurites (or partial information of the embedding environment) can have a strong effect on the dynamics of collective coordinates. Also, non-linear deterministic (or stochastic) terms in the equation of motion of relevant variables can sometimes be approximated by a special type of noise fields in the equations of motion of the collective coordinates. It is mainly the last two types of stochasticty that we will concentrate on in this chapter.

In Sect. 12.1 we discuss the relevance of lines and interfaces as defects of order parameter fields as seen from a perspective of defect dynamics, which is a natural continuation of the coarse-graining chain which can be achieved by 'integrating out' the bulk degrees of freedom. Sect. 12.2 gives several examples of stochastic phenomena, which can be attacked by means to be developed in the last section 12.3, where we develope a new method for constructing an effective noise correlator for the moving interface, which is very different from the static bulk disorder correlator giving rise to it.

12.1 General coarse-graining aspects

The use of collective coordinates such as interfaces and lines is by no means separate issue but falls naturally into the theme of the coarse-graining. Lower dimensional collective coordinates such as triple lines and interfaces are important as many physically important processes take place at boundary region separating different media. For example, catalytic reactions typically take place on surfaces, impurites in many cases migrate to grain boundary region, surfactants residing in the interfacial region between different fluids may alter the local surface tensions, and so on. Defect structures can typically be considered as quasi-particle types of observables described by some collective coordinates. Defects are abundant in the area of the condensed matter physics: For instance, vortices in superconductors and dislocations in crystals play an important role in explaining both equilibrium properties and dynamics of phase transitions. Since defects can be seen as singularites of the order parameter fields, they can also be seen as relevant 'macro' variables, which can allow a further reduction of total number of degrees of freedom, if we can somehow integrate out the bulk dynamics of the order parameter fields.

Defects are formed when symmetry breaking takes place. On the other hand, when continuous symmetries are broken, Goldstone modes emerge. These two concepts can be seen to be connected via the the order parameter, which in the Madelung parametrization ($\psi = \chi(\mathbf{x})e^{\imath\theta(\mathbf{x})}$) contains both amplitude and phase fluctuations (considering scalar order parameters for simplicity). The Goldstone modes are associated with the long wave length spatial phase fluctuations of the order parameter, whose energy goes to zero for $k \to 0$, and which are continuously related to the ground state. Defects have to do with the very short scale spatial amplitude fluctuations of the order parameter, which are not continuously connected to the ground state [327]. The traditional Landau free energy is an expansion in the amplitude of the order parameter, which is assumed to be small. At sufficiently high temperatures the amplitude fluctuations cannot be neglected unlike for low-energy (low temperature) part of the spectrum, where the phase-fluctuations dominate in the form of Goldstone modes [328]. However, defects can be long lived (e.g. topological defects), so in this sense they behave like Goldstone modes. Even though the amplitude fluctuations of the order parameter are energetically more expensive than phase fluctuations, they nevertheless need to be taken into account in modeling various types of phenomena. For example, topological defects called vortices determine most of the fundamental properties of superconductors and their responses to external static and oscillating electromagnetic fields [204]. Domain wall types of defects play an important role in phase-ordering kinetics [314] in fluids (liquid-gas phase boundary) and solids (e.g. ferromagnetic domain walls). In Sect. 12.3 we mainly concentrate on domain wall types of defects and consider the effect of frozen bulk impurities on the dynamics of defects.

Finally, we point out a natural group theoretical continuation of the coarse-graining scheme, which is suitable for analysis of defect structures. Just like we utilized the dynamic symmetry group to find out the relevant order parameters, one can use homotopy (group) theory to study the em topology of the vacuum manifold [20]. The group theoretic approach may not be the most efficient to find the defects in a specific application but it helps us to see the analogs more clearly. Thus, the situation is analogous to extracting the relevant variables which can be done group theoretically by constructing the dynamic symmetry group or by using other means, which can be much more efficient for specific applications. All in all, it is important to realize that at least in principle, very complicated problems can be cast into a standard representation (group theory e.g.), which provides the answers. This fact can be used as a starting point of developing systematic approximative classification schemes.

12.2 Examples of quenched processes

Several examples of quenched noise processes will be presented below. We want to demonstrate that in all cases the equation of motion for the relevant macro variable takes a form of a nonlinear Langevin equation with driving force and noise field *deriveable* from the underlying microscopic physics.

12.2.1 Dendritic growth

Dendrites are commonly observed microstrucure in metals, where the heat diffusion from liquid to bulk phases controls the morphology of the solidfication front. To model these types of problems one has typically utilized two techniques in the materials science: One has either studied a so-called sharp-interface models (e.g. Stefan or Hele-Shaw models [268]) or the phase-field approach [329]. In the traditional setting the phase-field is seen as an *auxiliary* field which only imposes the correct boundary condition at solid-liquid boundary. It is lacking the physical meaning which is associated with it in Sect. 7. As an auxiliary field it cannot be interpreted as a defect structure, contrary to the case where it is seen to represent the domain wall separating two phases.

In this section we present the sharp interface analog of the equations of motion for dendritic growth and compare it with the contact line motion in three dimensions and liquid-gas boundary motion in two dimensions (imbibition). As we have pointed in Sect. 8.3 It is possible to derive the sharp interfaced model parameters by projecting out the bulk dynamics of the phase-field models, whose parameters themselves can be obtained from more microscopic theories via density functional methods. In Ref. [270] the sharp-interface parameters have been derived by performing an asymptotic inner-outer expansion and matching the solutions at the phase boundary. In other words, the experimentally important parameters appearing in the projected equation of motion of the phase boundary such as the kinetic coefficient β, capillary length d_0 and surface tension σ are expressible in terms of molecular properties of the solidifying material.

Interestingly, it turns out the in the one sided dendritic growth model (no heat diffusion in the solid phase) and in a quasistationary situation, where diffusion lenght is large, we obtain and equation of motion which is almost exactly like the imbibition equation [4]

$$\int ds'\, G(x(s), h(x(s)); x(s'), h(x(s')))v_n(x(s'), t) = \mu\sigma K(s) + B + \alpha_D(x(s), t) \ , \qquad (12.1)$$

where $\alpha_D(x(s), t)$ is the projected noise (stochastic undercooling) expressed in the curvlinear coordinate system following the phase boundary,

$$\alpha_D(x(s), t) \equiv \int ds'\, G(x(s), h(x(s)); x(s'), h(x(s')))\, \eta(x(s'), t) \ . \qquad (12.2)$$

The normal velocity of the interface is denoted by v_n in Eq. (12.1), G is the Green function and B is the boundary condition term. Jacobian is included in measure ds'. Eq. 12.1 should be compared with the results derived in Refs. [330, 269]. Thus, the equation of motion of the phase boundary is similar to the equation of motion of the 2D liquid-gas phase boundary in imbibition [4], or the equation of the motion of the triple line to discussed below. To make the analogy complete one should assume that undercooling field is not constant but stochastic, which could result from impurities of the solidifying substance.

12.2.2 Contact line

We have seen in Chap. 8 that the equation of motion for the fluctuating Fourier modes of the contact line coordinate $c(k, t)$ becomes very similar to Eq. 12.1 corresponding to a different physical system. Namely,

$$\partial_t c(k, t) = F_{CL}(k, t)\, c(k, t) + \alpha_{CL}([c], t) \ , \qquad (12.3)$$

where the F_{CL} is the driving force and α_{CL} is the quenched noise field. Notation $[c]$ means that α_{CL} is actually a functional of the contact line position c. The origin of α_{CL} can be traced back to the chemical impurities on the walls confining the liquid. If there are two vertical walls present, quite generally we can write the following coupled set of equations of motions for the contact lines c^a and c^b on the two walls:

$$\begin{cases} a\partial_t c^a + b\partial_t c^b + cc^a + dc^b = \alpha_{CL}([c^a]) \; ; \\ a\partial_t c^b + b\partial_t c^a + cc^b + dc^a = \alpha_{CL}([c^b]) \; . \end{cases} \tag{12.4}$$

The coeffiecients a, b, c and d are linear operators defined in App. C.14.6. When the separation of the two walls goes to infinity we recover Eq. (12.3). These type of coupled equations appear when we project out the defect structure from inhomgeneous bulk macrovariable fields. A similar equation of motion can be obtained at the mean field level of phenomenological models for the interacting step edges to be discussed in Sect. 12.2.3. It should also be noted that memory effects will always be present due to the coupling of the collective coordinates even if the retarded effects are left out when expressing the higher dimensional field (meniscus in this case) in terms of the lower dimensional one (contact line). Thus, even if the quasi-stationary limit (App. C.11.1) is applied, solving contact line profile c^b in terms of c^a from the latter of Eq. (12.4) and substituting it into the former, we see that c^a will depende on past times. Dynamic hysteresis effects can in general be seen to arise in this way. As for the dendritic growth, the complicated noise correlations of α_{CL} field can be worked out in detail by knowing the distribution and statistics of the chemical impurities on solid walls, which hinder the motion of the triple lines. This will be demonstrated via a simplified example in Sect. 12.3.

12.2.3 Charge density waves and step-flow growth of crystals

Charge density waves (CDW) which are periodical modulations of the electron density resulting from the electron-phonon interaction. As we have mentioned at the beginning of Chap. 12, the order parameter of CDW can be written as [331]

$$\psi(\mathbf{x}, t) = \rho_c(\mathbf{x}, t) \cos(\mathbf{Q} \cdot \mathbf{x} + \theta(\mathbf{x}, t)) \; , \tag{12.5}$$

which can be seen as the real part of the exponential Madelung representation. The constant wave number of the periodic modulation is given by $\mathbf{Q} = 2k_F$, where k_F is the Fermi momentum, ρ_c is the amplitude of the CDW and θ is the phase modulation. Goldstone modes of the problem are phasons [162] and the defects are dislocations of the CDW lattice, where one part of the density wave moves relative to the rest. The dynamics of a driven charge density wave can be phenomenologically modeled via a modified Swift-Hohenberg equation as shown in Ref. [332]. Thus, the problem appears as a phase-field model with a free energy functional having a stochastic pinning potential describing the presence of frozen impurites, which can distort the moving CDW. If one was only interested in the dynamics of the hill-tops or valley-bottoms of the waves, it would be possible to develop an effective field theory of these one dimensional 'lines', which would appear very much like the model of interacting contact lines described in the previous section. This can be done by continuing the series of effective descriptions by approximating the Swift-Hohenberg model with a simple ϕ^4-type of phase-field model (Model A), which can sustain multi-kink configurations [333]. Imagining that we are interested in the dynamics of the hill-tops, we can associate them with the position of the kinks in the Model A, and derive equations of motion for them by projection as usual.

At this point further analogs appear. Phase-field model of type A with giving rise to a multi-kink configuration can also be generated using a periodic, say sinusoidally varying potential in the free energy. In this case, all the multiple minima of the potential can be imagined to characterize of phase of their own, which could also be interpreted to describe different steps on the vicinal surface of a growing crystal. By projection one ends up producing a set of coupled equations of motion for the interacting step edges, which are similar to equations of motion of the coupled contact lines. In particular, the stochastic structure is the same. Fixing the one of the edges to be the reference plane and measuring distance of the adjacent step edge from it by $h(\mathbf{x}, t)$, it can be shown to satisfy [334]

$$\partial_t h(k,t) = F_{SE}(k,t)\, h(k,t) + \alpha_{SE}([h]) \ , \tag{12.6}$$

where the subscript SE refers to Step Edge. In the step flow problem the physical origin of the stochastic term comes from the presence of impurities contaminating the surface. The action of the force kernel $F_{SE}(k,t)$ is exponentially damped meaning that the the step edges only see each other when they come closer than the distance of the bulk correlation length. The reason for lacking a long-range repulsive entropic forces is that in deriving Eq. (12.6) thermal fluctuations have been neglected. Thermal fluctuations have been included in different types of non-equilibrium phase-field descriptions of vicinal growth. For example, Karma and Misbah [335] have considered an extension of the Burton-Cabrera-Frank model, which again bears a close resemblance to the dendritic growth model described in Sect. 12.2.1 with temperature field of the melt-solid system replaced by adatom concentration on terraces.

The long range entropic effects are not relevant for the charge density problem but they do play an important role in the kinetics of step edges. In many cases, the potential energy of neighboring steps with average distance L can be written as $V(L) = A/L^2$ [336]. To arrive at such a potential by integrating out the bulk (terrace) degrees of freedom is quite nontrivial and has not been performed under time-dependent close-to-equilibrium conditions. In principle the derivation could be doable along the same lines as the drumhead model derivation of Kawasaki's [337]: In the path integral formalism one can see the effect of multi-kink configurations and thermal fluctuations on interactions between kinks without having to restrict oneself to zero temperature conditions. If the long range forces can be derived in this way, it means that the zero temperature fixed point cannot dominate unlike in some related problems with quenched disorder discussed Sect. 8.2.3.

12.2.4 Polymere in a solvent and vortices in superconductors

Polymers do not represent defects of the order parameter field but their dynamics in solution can be mapped into a form, which resembles the equations of motion of the line-like collective coordinates of precious examples. Similar conclusion holds for vortices, which are genuine defects. Starting with polymers, we follow Ref. [338] and write the following equation of motion for the monomers of the polymer chain:

$$M\frac{d\mathbf{v}_n(t)}{dt} = \mathbf{f}_n(t) + \xi[\mathbf{u}(\mathbf{r}_n(t) - \mathbf{v}_n(t))] \ , \tag{12.7}$$

where M is the mass of the monomer, $\mathbf{f}_n$ is the force on the string force on the nth monomer and $\mathbf{v}_n$ is the velocity field of the nth monomer. Finally, $\mathbf{u}_n(\mathbf{r}_n(t,t))$ is the velocity field of the solvent at $\mathbf{r}_n$ at time t and coefficient ξ accounts for viscous effects. Neglecting the inertial effects we ignore the left hand side of Eq. (12.7) and solve for $\mathbf{v}_n$:

$$\mathbf{v}_n(t) = \frac{1}{\xi}\mathbf{f}_n(t) + \mathbf{u}(\mathbf{r}_n(t), t) \ . \tag{12.8}$$

It is easy to derive an explicit expression for the solvent velocity using linearized hydrodynamics [339]. Knowing its form we can replace the discrete index n by a continuous parameter s, which gives the arc length of the chain. In this representation the string force becomes $\mathbf{f}_n \approx K\partial_s^2\mathbf{R}(s,t) \equiv \xi F_{PS}(\partial_s)$, where $\mathbf{R}$ is the spatial position vector pointing from the origin to point s in the chain. Eq. (12.8) becomes

$$\partial_t\mathbf{R}(s,t) = F_{PS}(\partial_s)\mathbf{R}(s,t) + \alpha_{PS}([\mathbf{R}]) + \mathbf{f}_d \ , \tag{12.9}$$

where the 'quenched' noise field is related to the velocity field of the solvent: $\alpha_{PS} = \mathbf{u}(\mathbf{r}_n(t),t) = \mathbf{u}(\mathbf{R}(s,t),t)$. Stochasticity arises from the thermal fluctuations of the momentum density (velocity $\mathbf{u}$). We have also replaced the monomer velocity with a term $\partial_t\mathbf{R}(s,t)$ on the right hand side of Eq. (12.9) and added an external driving force $\mathbf{f}_d$ on the right.

Large scale properties of magnetic vortices (flux lines) in type II superconductors can be described by an equation of motion very similar to the one above [340]:

$$\frac{1}{\mu}\partial_t\mathbf{R}(x,t) = -\frac{\delta H}{\delta\mathbf{R}} = \partial_x^2\mathbf{R} + \alpha_{FL}(x,\mathbf{R}(x,t)) + \mathbf{f}_d \ , \tag{12.10}$$

where x corresponds to s in Eq. (12.9) for small curvatures. The bulk Lorentz force is denoted by $\mathbf{f}_d$ and the stochastic force α_{FL} is defined to the gradient of the pinning potential $\alpha_{FL}(x,\mathbf{R}(x,t)) \equiv -\nabla V(x,\mathbf{R})$. Since the origin of α_{PS} in the polymer example is in the thermal fluctuations, the polymer does not become pinned unlike the flux line, which experiences the force α_{FL} stemming from the frozen impurities. Nevertheless, similar tools can be applied to the analysis of both types of quenched (= field dependent) forces as will be demonstrated in Sect. 12.3.

12.2.5 Domain boundaries in random magnets

Many physical problems can be mapped onto the Random Field Ising model (RFI) or some of its variants. The discrete version is defined by the Hamiltonian $H = J\sum_{ij} S_iS_j + \sum S_i\alpha_i$, where the summation is over the nearest neighbors and α_i is the random field at site i. In the continuum limit

$$H = \int d\mathbf{x}\left(\tilde{J}|\nabla S(\mathbf{x})|^2 + V(S(\mathbf{x})) + \alpha(\mathbf{x})S(\mathbf{x})\right) \ , \tag{12.11}$$

where $V = aS^2 + bS^4$ is the double well potential. Projection of the order parameter (spin) field onto the domain boundary between up and down spins with $S(x,y) \approx 2\theta(y-h(x)) - 1$, where h is the distance from a reference plane, gives

$$H_{1D} = \sigma\int dx\,\sqrt{1+(\partial_x h)^2} + \int dx\int_0^{h(x)} dy\ \alpha(x,y) \ . \tag{12.12}$$

Here we have considered a two-dimensional set-up: $\mathbf{x} = (x,y)$. Forming the dissipative dynamics of model A type by setting $\partial_t h = -\delta H_{1D}/\delta h$ yields

$$\partial_t h(x,t) = F_{RFI}(\nabla)\,h(x,t) + \alpha_{RFI}([h]) \ . \tag{12.13}$$

As in the case of the polymer, there is a surface tension term $F_{RFI}(\partial_x) \equiv \sigma\nabla^2$. The quenched random term $\alpha_{RFI}([h])$ arises from the projection of the bulk field α: $\alpha_{RFI}([h])(x,t) \equiv \alpha_{RFI}(x,h(x,t))$. The purpose of the next section 12.3 is to show how we can calculate the correlations of the projected noise α_{RFI} from the known correlations of the frozen randome field $\alpha(x,y)$.

12.3 Reduction of bulk noise to effective interfacial noise

This section provides new functional means to obtain the effective noise correlator seen by a moving interface or line. The continuum formulation of the Random field Ising model, which is also known as the Quenched Edwards-Wilkinson equation will serve as a test bench. The basic idea is the following: Given the stochastic properties of the frozen background field, say $\langle \alpha(x,y)\rangle = \bar{\alpha} = const$ and $\langle \alpha(x,y)\alpha(x',y')\rangle = D\delta(x-x')\delta(y-y')$, we have to find out what is $\langle \alpha_{RFI}(x,t)\rangle \equiv \langle \alpha(x,h(x,t))\rangle$ as a function of x and t. We should also be able to express the correlation function $\langle \alpha_{RFI}(x,t)\alpha_{RFI}(x',t')\rangle \equiv \langle \alpha(x,h(x,t))\alpha(x',h(x',t'))\rangle$ as a function of x, x' t and t'.

The background field correlations do not have to be Gaussian white noise but more general forms can be used. In literature the effective noise correlator concept has been used in the context of Functional Renormalization Group (FRG) from a slightly different perspective (see e.g. Ref. [341] and Ref. [342]). The method developed in this section offers an alternative to it. The main findings of the present section are the following. Even if the background noise has simple short-range static correlations, the effective noise correlations $\langle \alpha_{RFI}(x,t)\alpha_{RFI}(x',t')\rangle$ can be long ranged with nontrivial power law kernels both in space and time variables. Also, the projection of thermal noise does not have to be thermal as nontrivial time kernel can emerge. Knowing the correlations of α_{RFI} we can replace it in Eq. (12.13) by en *effective* noise α_{eff}, which has the same correlations:

$$\partial_t h(x,t) = F_{RFI}(\nabla)\, h(x,t) + \alpha_{eff}(x,t) \ . \tag{12.14}$$

The advantage is that it is easier to compute various statistical averages in terms of $\alpha_{eff}(x,t)$ because it does not depend on the height field h anymore. We can also see Eq. (12.14) as an equivalent stochastic process, which produces the same two-point functions as the original process of Eq. (12.13) at a given level of approximation (e.g. two-point correlation functions will be correctly reproduced when we truncate the effective noise correlations at Gaussian level). It is also possible, though we do not directly utilize this feature below, to include some nonlinear deterministic terms in the definition of $\alpha_{eff}(x,t)$ and take their influence into account stochastically. In this sense we come close to Eyink's method [343] of approximating the non-linear deterministic dynamics in terms of a linearized stochastic model. The equivalent stochastic process reaches a steady-state for finite size systems in the manner familiar from various surface growth models even if fluctuation-dissipation theorem would not hold in the traditional sense.

12.3.1 Equations of motion

The full equation of motion for the 'height' field H (just a generic stochastic field obeying equations of motion of the type to be discussed in Chap. 12) is assumed to be given by

$$\partial_t H(x,t) = \sigma\nabla^2 H(x,t) + F + \alpha(x,H(x,t)) \ . \tag{12.15}$$

We have added a constant driving force F on the right hand side. Field α is the quenched random field, the subscript RFI is dropped for convenience. Let us consider different strategies for solving Eq. (12.15). Construction of the solution can be done by splitting the equation of motion into mean-field part ($\tilde{h}_0$) and fluctuations ($\tilde{h}$) around it. This partitioning is not unique, of course. For example, we can define a new noise field $\tilde{\alpha}(x,H) \equiv \alpha(x,H) - \langle \alpha(x,H)\rangle$

from which it follows that $\langle\tilde{\alpha}(x,H)\rangle = 0$. This gives the following equations of motion:

$$\begin{aligned}\partial_t \tilde{h}_0(t) &= F + \langle \alpha(x, \tilde{h}_0 + \tilde{h})\rangle = F + \langle\alpha\rangle(t) \ , &(12.16)\\ \partial_t \tilde{h}(x,t) &= \sigma\nabla^2 h(x,t) + \tilde{\alpha}(x, \tilde{h}_0(t) + \tilde{h}(x,t)) \ . &(12.17)\end{aligned}$$

In other words, we can write $h_0(t) \equiv Ft + v(t)$, where $v(t) \equiv \langle\alpha(x,\tilde{h}_0 + \tilde{h})\rangle$ is the velocity of the mean interface height. In this approach h_0 will have to be solved self-consistently as it is unknown from the outset.

Another type of splitting, which will be employed in the rest of the text is achieved by setting h_0 equal to a *known* value: Define H as follows to be $H(x,t) \equiv h_0(t) + h(x,t)$ with $h_0(t) \equiv Ft$. The equation of motion Eq. (12.15) takes the following form

$$\begin{aligned}\partial_t h_0 &= F \ , &(12.18)\\ \partial_t h(x,t) &= \sigma\nabla^2 h(x,t) + \alpha(x, h_0(t) + h(x,t)) \ . &(12.19)\end{aligned}$$

We note that h_0 is *not* the mean field solution and h is not a correction to it. Function h contains the full information of the original problem and is easier to work with in the current formalism than H. Moreover, Fourier transforming this equation one does not have to worry about zero modes as the driving term F is missing from both sides of the equation of motion for h. The price that we have to be comes about through nonzero noise average $\langle h\rangle$, contrary to the method used in Eq. (12.17)

Solving Eq. (12.19) formally gives us the following representations of h which shall be used later on. In Fourier space

$$h(k,t) = \int_0^t ds\, e^{-\sigma k^2 (t-s)} \int dx_1\, e^{-\imath k x_1} \alpha(x_1, h_0(s) + h(x_1,s)) \ . \qquad (12.20)$$

In real space,

$$\begin{aligned}h(x,t) &= \int dk \int dx_1\, e^{\imath k(x-x_1)} \int_0^t ds\, e^{-\sigma k^2 (t-s)}\, \alpha(x_1, h_0(s) + h(x_1,s)) &(12.21)\\ &= \int_0^t ds \int dx'\, K(x-x', t-s)\alpha(x', h_0(s) + h(x',s)) \ , &(12.22)\end{aligned}$$

where $K(x,t) \equiv (4\pi\sigma t)^{-d/2} \exp(-x^2/(4\sigma t))$ is the heat kernel and d is the dimensionality of the space.

The formal solution of Eq. (12.19) can be presented in the form of functional fixed point problem $h = T[h]$ which one can try to solve by successive iterations:

$$h_{i+1} = T[h_i] \ . \qquad (12.23)$$

For amplitude limited white noise in a system which has a finite extent in the direction of propagation of the height field h (y-direction) it is possible to show that T is a contraction operator. Thus, higher and higher order iterations will converge to a fixed point and no small expansion parameter is needed as usually in perturbative calculations. The noise has also been assumed to be Fourier transformable, which does not hold for genuine white noise. To simplify the actual calculations below, we drop the amplitude limitation and assume that the background noise field has a delta function correlator. Starting the iterations from h_0 and applying the nonlinear operator T once generates first order iterative approximation to full h:

$$\begin{aligned} h_1(x,t) &= T[h_0] = \int dk_1 \int dx_1\, e^{\imath k_1(x-x_1)} e^{-\sigma k_1^2 t} \int_0^t ds\, e^{\sigma k_1^2 s} \alpha(x_1, h_0(s)) && (12.24)\\ &= \int dk_1 \int dx_1\, e^{\imath k_1(x-x_1)} e^{-\sigma k_1^2 t} \int_0^t ds\, e^{\sigma k_1^2 s} \int dq e^{\imath q h_0(s)} \alpha_q(x_1)\ . && (12.25) \end{aligned}$$

we will be utilizing this result when computing the explicit forms of the effective noise correlators and structure factors. More details are presented in App. B.

12.3.2 Scaling of effective noise correlator

In the next sections we will perform a quick and dirty derivation of the most important scaling properties which will suffice to produce the correct results. A much more detailed account is given in App. B. It is mainly reserved for those readers who want to get an idea of the math involved. More intuitive physical arguments are presented below.

The effective noise correlator has the following representation

$$\langle \alpha(x_1, H(x_1,t_1))\alpha(x_2, H(x_2,t_2))\rangle = C_0(x_1,t_1;x_2,t_2) + C_{\alpha\alpha'}(x_1,t_1;x_2,t_2) \qquad (12.26)$$

Term C_0 can be computed exactly (its scaling is studied in Sect. 12.3.2) whereas the term $C_{\alpha\alpha'}$ we have constructed iteratively in the App. B. Even though it is possible to determine the non-Gaussian features of the effective correlator (this is shown in the appendices) we ease our job below by trying to find the *best Gaussian* process which accurately reproduces the same expectation values for certain observables as the original quenched stochastic process. Term C_0 corresponds to noise contribution which can be thought of arising from decoupling the degrees of freedom perpendicular to the mean interface direction from those parallel to it. It should be noted that this is also the starting point of the functional RG calculations, but we will see that it is not the whole story. Part $C_{\alpha\alpha'}$ contains the mixed contribution. In the second order iterative approximation it further subdivided into four pieces

$$C_{\alpha\alpha'} = C_A + C_B + C_C + C_D \qquad (12.27)$$

The scaling of the first one of these C_A is computed below. First, however, we concentrate on the scaling of C_0, which represents the most straightforward contractions of the noise fields.

Scaling of C_0, $Ft/W_t \gg 1$, $L \to \infty$

Below we shall check that annealed noise correlator of the Edwards-Wilkinson problem is recovered when the dimensionless parameters of the problem approach certain limits. Correlator C_0 gives rise, in this limit to the annealed noise correlator whereas the contribution from terms $C_{\alpha\alpha'}$ vanishes. The important scale in the problem is the ratio $Ft/W_t \to \infty$ which can be seen by nondimensionalizing the correlation function G_c appearing in the expression of C_0 (see App. B.1 and App. B.3):

$$\tilde{C}_0(k, ts_1; k', ts_2) = D[G_c^{(1)}(0, ts_1, ts_2)]^{-1/2} \exp\left(\frac{(Ft)^2(s_1-s_2)^2}{G_c^{(1)}(0, ts_1, ts_2)}\right) \qquad (12.28)$$

The correlation function scales as

$$G_c^{(1)}(0, ts_1, ts_2) = W_t^2 \left[s_1^{2\beta_1} f_w(0) + s_2^{2\beta_1} f_w(0) - 2g(0, s_1, s_2, 0) \right] \ , \tag{12.29}$$

where

$$g(0, s_1, s_2, 0) = \int dk_1 \, e^{-k_1^2 |s_1 - s_2|} \left(1 - e^{-2k_1^2 \min\{s_1, s_2\}} \right) / (2k_1^2) \ . \tag{12.30}$$

Define new variables that will make the limit more obvious:

$$s_i' \equiv s_i / \sqrt{G_c^{(1)}(0, ts_1, ts_2)} \ , \ s = 1, 2 \ . \tag{12.31}$$

Multiplying and dividing by (Ft) gives

$$\begin{aligned} \tilde{C}_0(k, ts_1; k', ts_2) &= \frac{D}{Ft} [G_c^{(1)}]^{-\frac{1}{2}} \lim_{M_w \to \infty} M_w \exp\left(M_w^2 (s_1' - s_2')^2 \right) && (12.32) \\ &\to \frac{D}{Ft} [G_c^{(1)}]^{-\frac{1}{2}} \, \delta(s_1' - s_2') = \frac{D}{Ft} [G_c^{(1)}]^{-\frac{1}{2}} [G_c^{(1)}]^{\frac{1}{2}} \, \delta(s_1 - s_2) && (12.33) \\ &= \frac{D}{F} \, \delta(t_1 - t_2) \ , && (12.34) \end{aligned}$$

where we have used the definition $M_w \equiv Ft/W_t$. This is the correct annealed noise limit for $H = h_0(t) = Ft$. Note that the limit $\sigma k^2 t \gg 1$ needed to make C_i $(i = A, B, C, D)$ vanish plays no role here because C_0 is independent of that. The equality in Eq. (12.33) strictly speaking only holds if $G_c^{(1)}$ is constant, independent of s_i, which is not true. How to get around this obstacle more rigorously is explained in App. B.8.

Scaling of $C_A^{(1)}$, $Ft/W_t \ll 1$

Next, we determine the scaling behaviour of $C_A^{(1)}$ with the aid of some shaky mathematical arguments which lead more directly to the correct result derived in App. B.4. There are, of course, many ways to arrive at the correct scaling result. In the regime $M \equiv Ft/W_t \ll 1$ the exponential term $\exp(-M_w^2 m_2) \approx 1$ in the full expression of the noise correlator (Eq. (B.69), App. B.4) $C_A^{(1)}$. Similarly, the expression in square brackets $[-1 - 2M_w^2 m_1] \approx -1$.

$$\begin{aligned} \tilde{C}_A^{(1)}(k, t_1; k', t_2) \approx -\frac{D^2 \pi \sqrt{2}}{2w_2} \int^L dx \, e^{-\imath kx} \int_{\frac{1}{L}} dk_3 \, e^{-\sigma k_3^2 t_1} \int_0^{t_1} ds_1 \, e^{\sigma k_3^2 s_1} \\ \int_{\frac{1}{L}} dk_4 \, e^{\imath k_4 (x_1 - x_2)} \, e^{-\sigma k_4^2 t_1} \int_0^{t_1} ds_2 \, e^{\sigma k_4^2 s_2} \, a_1(x, t_1, t_2)^{-\frac{3}{2}} \ . \end{aligned} \tag{12.35}$$

First noting that $a_1 \sim w_1$, we can neglect its x-dependence and pull it out. Also, integration over s_1 is easy:

$$\begin{aligned} \tilde{C}_A^{(1)} &\approx -\frac{D^2 \pi}{w_2 w_1^3} \int_{\frac{1}{L}} dk_3 \, \frac{1 - e^{-2\sigma k_3^2 t_1}}{\sigma k_3^2} \int^L dx \, e^{-\imath kx} \int_{\frac{1}{L}} dk_4 \, e^{\imath k_4 x} \, \frac{1 - e^{-2\sigma k_4^2 t_1}}{\sigma k_4^2} && (12.36) \\ &\approx -\frac{D^2 \pi}{w_2 w_1^3} \left(\int_{\frac{1}{L}} dk_3 \, \frac{1 - e^{-2\sigma k_3^2 t_1}}{\sigma k_3^2} \right) \frac{1 - e^{-2\sigma k^2 t_1}}{\sigma k^2} && (12.37) \\ &\propto -\frac{D^2}{w_2 w_1^3} \frac{(\sigma t_1)^{2\beta_1}}{\sigma} \frac{1 - e^{-2\sigma k^2 t_1}}{\sigma k^2} = -\frac{D^2}{w_2 w_1^3} \frac{F w_1^2}{D} \frac{1 - e^{-2\sigma k^2 t_1}}{\sigma k^2} && (12.38) \\ &= DF \frac{1}{w_1 w_2} \frac{1 - e^{-2\sigma k^2 t_1}}{\sigma k^2} \ . && (12.39) \end{aligned}$$

The early and late time scaling regimes are:

$$\tilde{C}_A \approx F^2(\sigma t)^{1/2}\ ,\ \sigma k^2 t \ll 1\ ; \tag{12.40}$$

$$\tilde{C}_A \approx F^2 L\ ,\ \sigma k^2 t \gg 1\ . \tag{12.41}$$

All other correlators scale essentially in the same way in the corresponding limits.

12.3.3 Results for scaling

We can either compare the structure factors S_A and S_0, or the noise correlators $C_A^{(1)}$ and $C_0^{(1)}$ directly because

$$S_i = e^{-2\sigma k^2 t} \int_0^t ds_1 \int_0^t ds_2\, e^{\sigma k^2 (s_1+s_2)}\, \tilde{C}_i(k.s_1.s_2)\ , \tag{12.42}$$

which means that when we make the two time integrals dimensionless, we just get a prefactor t^2. Since $\tilde{C}_0^{(1)} \sim D/G_c^{(1)} \sim D/W_t$ we obtain immediately a condition for the dominance of $C_0^{(1)}$:

$$C_0^{(1)} \gg C_A^{(1)} \Rightarrow \frac{D}{W_t} \gg F^2 L\ , \tag{12.43}$$

This is consistent only if the requirement $Ft/W_t \ll 1$ holds, and for late enough times: $\sigma k^2 t \gg 1 \forall k \Rightarrow \sigma t/L^2 \gg 1$. This is proven below by showing that the two requirements (dominance of $\tilde{C}_0^{(1)}$ and late time requirement) lead to the same consistency condition $D\sigma \gg (FL)^3$:

$$\frac{D}{W_t} \gg F^2 L \Rightarrow \frac{D^2}{W_t^2} \gg F^4 L^2 \Rightarrow D^2 \gg \left(\frac{D}{F\sigma} L\right) F^4 L^2 \Rightarrow D\sigma \gg (FL)^3\ ; \tag{12.44}$$

$$W_t \gg Ft \Rightarrow W_t^2 \gg F^2 t^2 \gg F^2 \frac{L^4}{\sigma^2} \Rightarrow D\sigma \gg (FL)^3\ . \tag{12.45}$$

(In the infinite system size limit this can only be satisfied if the driving $F \to 0$ which is a somewhat singular limit in this formulation.) This means that for late times the exponent χ is determined by the scaling of $C_0^{(1)}$ ($S_0^{(1)}$). Since $S_0^{(1)}(L) \sim L^{4-\chi_1} = L^{7/2} \sim L^{2\chi_2+1}$, i.e $\chi_2 = 5/4$.

Condition for dominance of $C_i^{(1)}$ over $C_0^{(1)}$ is shown to be consistent with the requirement that $Ft \gg W_t$:

$$F^2(\sigma t)^{1/2} \gg \frac{D}{W_t} \Rightarrow F^2(\sigma t)^{1/2} W_t^2 \gg \frac{D}{W_t} W_t^2 \Rightarrow F^2(\sigma t)^{1/2} \frac{D}{F\sigma}(\sigma t)^{1/2} \gg DW_t \tag{12.46}$$

$$\Rightarrow F^2(\sigma t)^{1/2} \frac{D}{F\sigma}(\sigma t)^{1/2} \gg DW_t \Rightarrow FDt \gg DW_t \Rightarrow Ft \gg W_t\ . \tag{12.47}$$

This means that when $Ft/W_t \gg 1$ and for small enough times $\sigma k^2 t \ll 1$ the dynamic roughness exponent β is given by the scaling of $C_i^{(1)}$ ($S_i^{(1)}$). This scales as (cf. Eq. (B.83))

$$C_A^{(1)} \sim t^{2-d/2-4\beta_1} \sim t^{2\beta_2 + d/z_2} = t^{(2+d/\chi_2)\beta_2}\ , \tag{12.48}$$

from which it follows, $\beta_2 = 25/28$. Finally determining the remaining exponent from the definition $z_2 = \chi_2/\beta_2 = 7/5$. The velocity exponent can be obtained from the exponent identity. Since the upper critical dimension is $d = 2$ in this perturbative approach, only the $d = 1$ result, i.e. $\beta_1 = 1/4$ can safely be taken as the starting point of the iterative construction of the scaling exponents. With the aid of self-consistent methods higher dimensional estimates can be achieved. Let us now compare our findings to the other results from literature in the form a the following table:

Method	χ	β	z
E N C	$5/4 \approx 1.25$	$25/28 \approx 0.89$	$7/5 \approx 1.40$
N U M	1.25	0.88	1.42
F R G-1	1	$3/4 \approx 0.75$	$4/3 \approx 1.33$
F R G-2	1.43	0.85	1.68

Acronym ENC (Effective Noise Correlator) stands for our analytic results, NUM refers to numerical results obtained in Ref. [344]. The first order ϵ-expansion results of Functional Renormalization Group (FRG-1) are also taken from Ref. [344] whereas the second order (ϵ^2) results (FRG-2) are taken from Ref. [345]. As we can see, the effective noise correlator method seems to offer a competitive alternative for the functional renormalization group. It must be remembered, though, that estimated values of the FRG results (for results including higher order corrections) deviate less from the numerical values than the ϵ^2 results. For the ENC-method this conclusion cannot be drawn as no tests have been made. It should also be remembered that the exponents presented above are specific to certain scaling regimes whose limits have been provided above. Depending on which one of the competing terms in the correlator wins, there are other scaling regimes associated with different exponents.

12.3.4 Approach to pinning limit

For sufficiently large pinning force strength and small enough velocity the interfaces and lines can become pinned by the frozen impurities. Mathematically, this can be expressed by expressing the dependence of the propagation velocity v as a function of the driving force F:

$$v \to \begin{cases} F & , \text{ for } F \gg F_c \\ (F - F_c)^\theta & , \text{ for } F \to F_c \text{ from above} . \end{cases}$$

The critical driving force is F_c (for smaller driving the average interface stops) and the velocity exponent is θ. Typically θ is less than one. We should be able to write the mean velocity of the interface in the form which reproduces the limit in Eq. (12.3.4) correctly. The simplest guess is that for $\theta < 1$ we can write

$$v \approx (F - F_c) + |F - F_c|^\theta + \ldots \tag{12.49}$$

Can we cast the perturbative result for $v = F + \langle \partial_t h \rangle$ into this form? We first note that

$$\langle \partial_t h \rangle = \langle \sigma \nabla^2 h \rangle + \langle \alpha(x, h_0 + h) \rangle = \langle \alpha(x, h_0 + h) \rangle \ , \tag{12.50}$$

because $\langle \nabla^2 h \rangle$ vanishes for any noise when we have periodic boundary conditions. From physical point of view we should remember that the average of the quenched noise represents the random energy content of the wandering phase boundary. When one approaches pinning the system has had enough time such that the boundary has found the minimum energy configuration, i.e. $|\langle \alpha(x, h_0 + h) \rangle\|$ has taken its maximum value. In other words, the interface is not necessarily moving when $\langle \alpha(x, h_0 + h) \rangle \neq 0$. Only when $\langle \alpha(x, h_0 + h) \rangle \geq -F_c$ the phase boundary has a nonzero velocity. To the second order accuracy with which the exponents have been determined the velocity does not reveal any pinning behaviour. There is just an initial transient regime as the phase boundary accelerates towards its steady state velocity F around we have expanded.

$$\langle \partial_t h_2 \rangle = F + v(t) \ , \tag{12.51}$$

with $v(t) \to 0$ for $t \to \infty$. This is a rather peculiar result given that the functional RG calculations (which should be consistent with the results here after transforming to the comoving frame), which only contain few of the lowest order diagrams resulting from the expansion of the exponential factors $\exp(vt + H)$ in powers of H, predict pinning and nontrivial velocity exponent. However, here we have summed over infinitely many more diagrams and end up with some smooth behaviour.

Our aim is now try to see if there is any nonanalytic behaviour in the expression $\langle \alpha(x, h_0 + h_2) \rangle$ which appears in the third order iterative approximation to velocity $\langle \partial_t h_3 \rangle$. The nonanalyticity should manifest itself via making some integrals divergent for $F < const = c$. Then we can identify $c = F_c$. Going to higher order iterations (3rd) turns out not to solve the problem despite the fact that in principle one should find out the possible pinning behaviour simply by studying the exact equation

$$\langle \partial_t h \rangle = \int dq \, \imath q \langle \frac{\delta h(x,t)}{\alpha_q(x)} \exp(\imath q h(x,t)) \rangle \tag{12.52}$$

To get the functional derivative of h we 'only' need to solve the following *linear* integral equation

$$\frac{\delta h(x,t)}{\alpha_q(x)} = f_1(x,t,q) + \int dx_1 \int dt_1 \, K(x - x_1, t - t_1) f_2(x_1, t_1) \frac{\delta h(x_1, t_1)}{\alpha_q(x)} \ , \tag{12.53}$$

where

$$f_1(x,t,q) \equiv \int dk_1 \int dx_1 \int dt_1 \, e^{-\sigma k_1^2 (t-s)} e^{-\imath q (v t_1 + h(x, t_1))} \tag{12.54}$$

$$f_2(x_1, t_1) \equiv \int dq \, \imath q \, e^{\imath q (v t_1 + h(x_1, t_1))} \alpha_q(x_1) \ . \tag{12.55}$$

Similarity to Schrödinger's equation for electron in the random potential is obvious. In a system, where the underlying lattice of frozen impurity field has been discretized leading to finite noise correlation lengths of the order of the lattice constant Δx in the x-direction we have used dimensional arguments to derive an expression for the critical force [346],

$$F_c = \left(\frac{D^2}{\sigma a} \right)^{1/3} g \left(\frac{D L^3}{\sigma^2 a^2}, \frac{\Delta x}{L} \right) \ , \tag{12.56}$$

where the physical length of the domain satisfies $L = N \Delta x$, N being the number of lattice sites in the x-direction. The precise form of the scaling function g is unknown but its limiting behaviour can be worked out. The lattice spacing in the growth direction is denoted by a (which naturally translates into the background noise correlation length in the y-direction). Hence, this result suggests that it can make a difference whether we assume perfect delta function correlations (zero correlation length) for the frozen noise field or not. Interestingly, in the functional RG treatment on considers the random force correlations of the growth direction to decoupled from the other directions even if the background noise field does not support this asymmetry [278].

Chapter 13

Conclusions

We summarize below the main results derived in the thesis. They are categorized into general and specific ones the former having a broader applicability not restricted to any specific example we have discussed.

General results:

We have discussed and compared several methods devoted to description of non-equilibrium thermodynamics. The non-equilibrium generating functional formalism, which is the method of choice in this work, has been shown to combine many of the features one would wish a general theory of non-equilibrium thermodynamics to have. The generating functional naturally combines the known quantum many-body density functional theories with the phase transition dynamics familiar from the models of critical dynamics. It is also possible to relate it to the phase-field models, which are very popular in the materials science modelling. The generating functional formalism produces the equations of motion for the relevant variables and performs averaging over the non-equilibrium density matrix naturally, without having to worry about whether one has been able to find a complete set of macro variables or not. Any subset will do. Moreover, the functional is naturally suited for renormalization group studies. We have also shown how to apply the quantum field theoretic formalism to classical many-body systems and lattice-gas type of more coarse-grained starting points.

We have also tried to shed some light on the very difficult open question on finding the relevant macro variables. We proposed to study the symmetries of the effective action of the generating functional. Alternatively, one can study the symmetries of the dynamic density matrix of the system. Density matrix based approach provides explicit operator representations of the relevant variables given that its dynamic group can be found. This is close to impossible for any realistic system but approximatively the task can be carried out in the vicinity of suitable chosen reference states. Therefore, physical intuition (as expected) cannot be replaced by a mechanical machinery but the intuition may be guided by having a machinery to aid in the process of isolating the relevant physics.

All in all, the generating functional can be used in many different ways. Sometimes it is better to use more conventional approaches, which have been designed for a more specific purpose. Yet, the strength of the generating functional concept lies in the fact that it brings together many apparently different fields of physics (variational principles, thermodynamics, quantum mechanics, particle physics concepts, dynamical system's theory, stochastic analysis, density functional theory, RG, etc.). It also offers a whole lot of theoretical challenges, which should be put on a more firm ground mathematically. There are at least two immediate application fields for the generating functional formalism, which are worth putting some effort into. One is the derivation of coarse-grained density functional models of complex liquids and colloidal suspensions. Dynamic mean-field theories are immediately obtained. The real challenge comes when trying to take into account the higher order non-perturbative density corrections. If we can find rather general and robust ways of doing this, we can give the coarse-grained dynamic density functional description corresponding to any Molecular Dynamics simulation, say. On the quantum mechanical side we have already demonstrated the strength of the symmetry analysis in order parameter extraction, which can be readily applied to systems as complicated as He^3. This gives some hope that it might be possible (though difficult) to obtain some new information about the high temperature superconductors, too, using the techniques presented here. Also, some of the methods (such as partial symmetry analysis) will play a major role at this stage. Of course, being able to extract the order parameter and the effective Lagrangian of a high-temperature superconductor from microscopics sounds like a far fetched speculation but it should be kept in mind that a fair amount of information has already been gathered on the symmetries of cuprate compounds and experimental information has been used to construct the static dynamic symmetry group of the effective Hamiltonian. These pieces of information can be utilized in filtering out the unwanted parts of the complicated microscopic Hamiltonian.

Specific results:

We showed how to find the order parameters and relevant conserved variables of superconductors, superfluids and classical (simple) liquids based on the symmetries of the density matrix (or Hamiltonian describing the steady-state). Time-retarded effective interaction was shown to result from the non-renormalized action of the phonons on the electrons in the ordinary superconductor. We did not make use of the full power of the formalism but settled for rederiving the standard time-dependent Ginzburg-Landau equation. Similarly, we derive the Gross-Pitaevskii equation for the order parameter of a weakly interacting Bose fluid having first found it using the symmetry analysis. In these cases it was easy to find the associated symmetry operator but in more complicated cases where there are hidden symmetries the story gets more interesting and challenging.

We displayed the analogs between quantum and classical density functional theories and showed how they are connected thorough the concept of generalized Legendre transformation. The effective action of the solid-fluid-gas system obtained from classical density functional theory was shown to correspond to the free energy of the phase-field model, which had been previously used by us in simulating fluid flow in complex geometries. We showed how the macroscopic parameters of the phase-field model can be expressed in terms of the microscopic simulation parameters by computing surface tensions in both ways (from MD and from phase-field model). We explained how randomness present in real experiments (surface roughness of solid walls or chemical impurities) can be modelled mathematically, and what its connection to the theoretical parameters is.

Equations of motion were derived for triple lines and liquid-gas boundaries confined by solid walls. To start with, we only considered mass balance equation and then later on took into account the momentum balance equation of the fluid, as well. This results in extra driving terms in the evolution equations of the meniscus and contact line. It was shown, how the physically important time and length scales can be extracted from the partially linearized equations of motion. The stochastic properties arising from the presence of chemically impure walls were analyzed in the Appendices. We also showed that a whole plethora of seemingly unrelated models can be cast into an analogous form by choosing correctly the collective coordinate (step edges of growing crystals, dendritic side branches, contact line, flux line, polymer chain, domain wall of random magnet etc.) To extract the dynamics of the collective coordinates (domain walls and lines) a new projection technique was developed based on a variational method. The analysis of the ensuing stochastic equations required the development of computational tools for quenched noise processes, which surprisingly yielded better results for the simple test case of random ferromagnet (QEW) than the functional renormalization group method (Sect. 12.3.3).

Finally, we demonstrated how the boundary conditions, which in the conventional sharp-interface hydrodynamics are imposed as extra constraints, can be effectively taken into account as extra driving terms in the balance equations of the conserved quantities. Since the explicit form of these extra terms can be derived using the generating functional technique, it means that there exist a systematic way of *deriving* the sharp interface boundary conditions from microscopics. In addition, it is possible to derive corrections to the boundary conditions due to finite interface width, which is more physical than the idealized assumption about the infinitesimally thin boundary layer.

Part III

Appendices

Appendix A

Convexity of action functional

This set of notes tries to shed some light on the different properties of the free energy (action) and its density both in finite and infinite systems. Infinite system in the case of lattice models of magnets means that the total number of spins $N \to \infty$. In the case of particles in continuum medium the number of particles N and the volume of the system V go to infinity in such a way that the density $\rho = N/V$ stays finite. In continuum order parameter description (see the Ginzburg-Landau-Wilson free energy functional below) the previous statement is equivalent to having a finite pointwise density $\phi(x)$ and letting $V \to \infty$.

There are many ways of deriving the thermodynamic Helmholtz free energy $F(M, T, N)$ (we are considering a model of a magnet system for simplicity). Total magnetization is denoted by M and temperature is T (below $\beta = 1/T$ where the temperature is expressed in units J/k_B where J is the spin-spin interaction coupling constant). The first way is to start from the probability weights fixed by the microscopic Hamiltonian $H = \sum_{<i,j>} s_i s_j$ and trace over all spin degrees of freedom $\{s_i\}$ for which it holds that the local magnetization in a cell (i.e. group of spins) located at x_m is $\phi(x_m)$. This leads to so-called Ginzburg-Landau-Wilson free energy density functional $F_l[\phi]$:

$$Z' = \sum_{\{s_i\}} \prod_{m=1}^{N_b} \delta\left(\phi(x_m) - (1/N_c)\textstyle\sum_{n=1}^{N_c} s_n\right) e^{-\beta \sum_{<i,j>} s_i s_j} \propto e^{-\beta F_l[\phi]} \ , \tag{A.1}$$

where Z' denotes the restricted partition function, and $F_l[\phi] = \int_V dx\, f_l(\phi(x))$. The number of spins in any cell N_c and the number of cells (number of block spins) N_b satisfy $N_c N_b = N$. The pointwise free energy *density* comes out to be

$$f_l(\phi(x)) \approx (1/2)|\nabla\phi(x)|^2 + a\phi^2(x) + b\phi^4(x) + \mathcal{O}(\phi^6) \ . \tag{A.2}$$

The attribute pointwise is used just to stress the fact that f_l depends on the spatial location x and thus characterizes spatial inhomogeneity present e.g. in locally equilibrated systems.

The series expansion holds actually for small values of the order parameter (ϕ) only, so the higher order terms have been dropped. Summing over the remaining degrees of freedom, i.e. letting the local magnetization (order parameter ϕ) take *any* value in each cell with the constraint that the *global* magnetization has a fixed value M, results in

$$Z = \int D\phi(x)\, \delta\left(M - V^{-1}\int_V dx\, \phi(x)\right) e^{-\beta F_l[\phi]} \equiv e^{-\beta F(M,T,N)} \ . \tag{A.3}$$

(The particle number N is a bit ambiguous since the continuum approximation, that is, the replacement of block spins by smooth field $\phi(x)$, assumes that $N_b = N/N_c \to \infty$. In other words the number of block spins N_b should also approach infinity. Thus we have to 'rediscretize' to make some sense out of the last equality in Eq. (A.3).) The simplest working interpretation of the functional integration measure is to take it to be a product of pointwise measures:

$$\int D\phi(x) \equiv \prod_{i=1}^{N_b} \int_{-\infty}^{\infty} d\phi_i \ , \tag{A.4}$$

where the index i runs from one to the total number of cells (block spins) in the system.

The second way of arriving at the same result is to simply leave out the intermediate block spin summation:

$$Z = \sum_{\{s_i\}} \delta\left(M - N^{-1}\textstyle\sum_{j=1}^{N} s_j\right) e^{-\beta \sum_{<i,j>} s_i s_j} = e^{-\beta F(M,T,N)} \ . \tag{A.5}$$

Notice that the summation in the delta function is over all spins N, not over the spins in a single cell as above. It should also be noted that M appearing in the argument of F is the spatially averaged magnetization. The third way of obtaining F is to first use the Gibbs free energy G and then make a Legendre transformation

$$e^{-\beta G(H,T,N)} = \sum_{\{s_i\}} e^{-\beta \sum_{<i,j>} s_i s_j + \beta H \sum_i s_i} \ . \tag{A.6}$$

The external magnetic field H has here taken to be constant globally. Then we can relate F and G through $G(M,T) = F - HM$, where the external field is related to the global magnetization through the equation of state:

$$\frac{1}{\beta}\frac{\partial g(H,T)}{\partial H} = -M(H,T) \ , \tag{A.7}$$

where g is the Gibbs free energy density. In Eq. (A.7) the magnetization M is the ensemble averaged quantity in contrast to the spatial average appearing in Eq. (A.5). For self-averaging systems these should be the same but not necessarily in general. Being a bit more careful we should write $\lim_{N\to\infty} 1/(\beta N)\, \partial G(H,T,N)/\partial H = -M(H,T)$. Although M didn't appear explicitly in the partition function in Eq. (A.6), it is defined through Eq. (A.7.) It should also be remembered that Eq. (A.7) does not result from minimization of free energy G but is a thermodynamic identity which holds for *equilibrium* free energy $G(H,T,N)$. Similar argument holds for the Helmholtz free energy density: $\lim_{N\to\infty} 1/(\beta N)\, \partial f(M,T,N)/\partial M = H(M,T)$.

Minimization is needed for the *phenomenological Landau* free energy, the generalization of which to spatially inhomogeneous cases we have called the Ginzburg-Landau-Wilson free energy (see Eq. (A.2)). Magnetization (order parameter in general) can be thought of as a (macroscopic) state variable which takes on values others than those characteristic of thermodynamic equilibrium, too. In this sense expressing free energy as a function of order parameter means that we have generalized the concept of free energy to nonequilibrium situations. All of the generalized thermodynamics potentials can be thought of depending on this extra parameter whose equilibrium value is fixed by the condition that the corresponding potential will be minimized [347].

Specifically, in the Landau theory the order parameter (magnetization) is a free parameter, which does not depend on T and H to begin with. Only in equilibrium (which corresponds to minimum of F_l) M becomes a function of the the temperature T and the external field H. In Ref. [249] the starting point is the free energy density Γ which for a magnetic system looks like

$$\Gamma(\eta, T, H) = \Gamma_0(T, H) - \frac{\eta H}{k_B T} + \frac{t\eta^2}{2} + \frac{1}{4}\eta^4 \ , \tag{A.8}$$

where M corresponds to η in the notation of Ref. [249]. Minimizing Γ with respect to η results in the equation of state

$$\frac{H}{k_B T} = \eta t + \eta^3 + \dots \ , \tag{A.9}$$

which is an approximation to Eq. (A.7). Notice that Eq. (A.9) holds only in equilibrium where η (or M) becomes a function of T and H.

How can we derive 'non-equilibrium' free energies like Γ in Eq. (A.8)? Again, the form can be justified in a couple of different ways. Starting from microscopics, we can require that on the average each spin feels the same average magnetization which justifies the nomenclature 'mean-field' approach. Naively, we are trying to perform a summation over spin configurations with the constraint that *each* individual spin takes the same value M:

$$Z'' = \sum_{\{s_i\}} \prod_{n=1}^{N} \delta\left(M - s_n\right) e^{\beta \sum_{<i,j>} s_i s_j} \ . \tag{A.10}$$

This is, however, ill-defined mathematically since fixing $-1 < M < 1$ would always give zero weight for all spin configurations since individual spins can only have values ± 1. To get around this obstacle we require less restrictively that each *block-spin* must take the same average value M. Using the coarse-grained free energy F_l and performing the functional integral over spatially homogeneous configurations $\phi(x) = M$ defines the mean-field free energy F_{mf}:

$$Z'' = \int D\phi(x) \delta(M - \phi(x)) e^{-\beta F_l[\phi]} \equiv e^{-\beta F_{mf}(M,H,T,N)} \approx e^{-\beta(aM^2 + bM^4 - HM)N} \ , \tag{A.11}$$

where we have changed the microscopic Hamiltonian from $H = \sum_{ij} S_i S_j$ to $H = \sum_{ij} S_i S_j + H \sum_i S_i$, since otherwise F_l would not contain H, which is needed in the expression of the mean-field free energy F_{mf} in Eq. (A.11). So, the crucial difference between the previous equation and Eq. (A.3) is that in the latter case one has a less restrictive constraint the integral in the delta function being over the whole volume of the system leaving for the individual block spins considerable freedom to fluctuate. In Eq. (A.11) we have defined the mean-field approximation for the (non-equilibrium) free energy density f_{mf} as

$$f_{mf} \equiv F_{mf}/N \approx a(T)M^2 + bM^4 + \mathcal{O}(M^6) - HM \ . \tag{A.12}$$

Hence, we see that f_{mf} is Γ, essentially.

To get an approximation for the thermodynamic free energy from this mean field expression one should still minimize the argument of the exponential function which yields the condition of Eq. (A.9) tying together the equilibrium value of M with T and H. For simplicity we can set $H = 0$. Substituting the equilibrium solution $M(T, H = 0)$ into the free energy density f_{mf} in Eq. (A.12) one can see that the result $f_{mf}(M(0,T),0,T)$ is convex in T even though $f_{mf}(M,H,T)$ is not convex in M below the critical temperature $T < T_c$.

Doing all this simply means that we are approximating the value of the functional integral $\int D\phi(x)\, \exp(-\beta F_l[\phi])$ with its value at the extremal of the integrand F_l because for the homogeneous configuration $\phi(x) = M = const$ minimizes the gradient term $|\nabla\phi|^2$ (pp. 25-26 [81]) after which we find the minimum of the remaining expression by solving Eq. (A.9). In other words,

$$\int D\phi(x)\, e^{-\beta F_l[\phi]} \approx e^{-\beta F_{mf}(M(H,T),H,T,N)} \ . \tag{A.13}$$

This result is analogous to the saddle point approximation of integrals, see for example the computation of the partition function for the infinite range Ising model, where the saddle point approximation becomes exact in the thermodynamic limit $N \to \infty$.

Some additional points:

- The true thermodynamic free energy $F(M,T,V,N)$ can be non-convex (below T_c) since the domain walls cost energy. In other words the free energy goes like

$$F(M,T,V) = V f_b(M,T) + A f_s(M,T) + \dots \ , \tag{A.14}$$

where the bulk free energy density is denoted by f_b and the free energy density cost of domain boundaries is f_s (cf. p. 25 [249]). Similarly, the homogeneous free energy density (remember, the pointwise f_l is a different thing) f_b can be non-convex for finite system size V (or N). Only in the thermodynamic limit the homogeneous free energy *density* f_b becomes strictly convex (even for $T < T_c$):

$$\lim_{V\to\infty} \frac{F(M,T,V)}{V} \to f_b(M,T) \ , \tag{A.15}$$

where the surface term (and other correction terms) vanishes because $A/V \to 0$.

- The mean-field results given above can be interpreted as much more restricted trace operation than summing over all spins having just the *global* magnetization M fixed (Eq. (A.3)). In the former case one does not allow any spatial fluctuations between the cells and therefore there are much fewer configurations that one sums over. In this sense the outcome corresponds to a 'non-equilibrium' situation resulting in further need to minimize the free energy F_{mf} (or Γ) with respect to the value of the order parameter M. The value of of $M = M_{eq}$ minimizing the generalized free energy should then be substituted back into Γ to produce an approximation to the true thermodynamic free energy defined in Eq. (A.3).

- What are the extra degrees of freedom whose presence is manifested in the presence of order parameter having a non-equilibrium value in the expression of the generalized free energy? It must be the fact that all the block spins were forced to have the same value. The bigger blocks we are using the more configurations can be included in the configurational sum of the partition function and more closely we are approximating the equilibrium situation which corresponds to just one big block of the size of the system. Since the partition function grows the more configurations are included in the configurational sum, the free energy will become more and more negative being defined as $F = -1/\beta \ln Z$. The need to minimize the mean-field theories comes about through the same mechanism: averages of products of spin operators (order parameter products, in general) are assumed to be equal to products of averages of individual spin operators, which is equivalent to assuming a constant 'block-spin' value in each cell. Using the infinite range Ising model as familiar example, we can write the magnetization in the following way

$$\sum_{\{s_k\}}(N^{-1}{\textstyle\sum_i} s_i)\, e^{-\beta\sum_{j,k}s_js_k+\beta H\sum_j s_j} \equiv \langle N^{-1}{\textstyle\sum_i} s_i\rangle = \langle \tanh\Big(\beta(H+N^{-1}{\textstyle\sum_i} s_i)\Big)\rangle \ , \quad (A.16)$$

where we have first defined the ensemble averaging $<\cdot>$. Mean field approximation (which becomes exact in the thermodynamic limit in this simple case) means that we write

$$\langle \tanh(\beta(H+N^{-1}{\textstyle\sum_i} s_i))\rangle \ \approx \tanh(\beta(H+\langle N^{-1}{\textstyle\sum_i} s_i\rangle)) = \tanh(\beta(H+\langle s_i\rangle)) = \langle s_i\rangle \ , \quad (A.17)$$

where we have used the fact that $\langle N^{-1}\sum_i s_i\rangle = \langle s_i\rangle$. In other words, more generally we are first expanding in powers of the order parameter and then neglecting cross-correlations:

$$\begin{aligned} \langle \tanh(\beta(H+s_i))\rangle &= \langle (H+s_i+\frac{1}{3}s_i^3+\ldots)\rangle = H+\langle s_i\rangle+\frac{1}{3}\langle s_i^3\rangle+\ldots & (A.18)\\ &\approx H+\langle s_i\rangle+\frac{1}{3}\langle s_i\rangle^3+\ldots\ . & (A.19)\end{aligned}$$

It should be remembered that for some simple systems mean-field approximation is exact but usually this is not the case. Since the mean-field approximation can be carried out technically in many ways, it should be pointed out that using it to evaluate the lower or upper bounds for the entropic contribution to the free energy can lead to overestimation or *underestimation* of the actual free energy. (In other words,

$$Z=\sum_i g_i e^{-\beta E_i}\ , \quad (A.20)$$

where the multiplicities g_i of configurations having an energy E_i may be evaluated using the mean-field approximation.) So, the term 'mean-field' does not necessarily imply higher free energy than the thermodynamic free energy.

- These questions are related to the previous point where we concluded that the need for further minimization of the mean-field free energy arose from the fact that the degrees of freedom we had excluded by making all block-spins take the same value resulted in an extra parameter, the order parameter not having its equilibrium value in the expression of the generalized free energy. So, how do we know weather we should minimize further just by looking at the summation in the partition function? Is it always certain that a global constraint (like global magnetization) will result in convex density f_b without any need for further minimization? What about more local constraints?

- The exact free energy of a model having sufficiently long range interactions does not necessarily have to be convex (cf. the infinite range Ising model) Furthermore, it is possible to have a phase transition even in $d=1$ for long range interactions which vanish slowly enough at infinity [348, 349]. The non-convexity can also result from the mean-field approximation as shown above (e.g. Bragg-Williams approximation see for example the book by Guggenheim and Fowler [350]).

- Is the bump in the free energy important for physics at all? Since its height grows proportionally to the area A of the domain boundaries in the system we have that $A\sim L^2$ in

$d = 3$ (assuming non-fractal boundaries). In terms of volume $A \sim V^{2/3}$ because $V \sim L^3$. The Lee-Yang theorem guarantees the existence of the free energy density which is independent of the shape of V if the surface area increases no faster than $V^{2/3}$ (p. 208 [220]). Taking the thermodynamic limit means that we let $V \to \infty$. Therefore also the height of the bump in the free energy for $T < T_c$ will grow to infinity. This observation explains the ergodicity breaking mentioned in the first chapter of Ref. [249]: imagine performing a Monte-Carlo simulation of kinetic Ising model (or some variant of it). Start the simulation at some high temperature and then quench it below the critical temperature T_c. The dynamics of the system can be chosen in various ways, for further references on Monte Carlo methods consult for example Ref. [351]. For example, one can choose a spin at random and make an attempt to flip it. If the the total energy of the system is lowered after the flip, the trial will be accepted with probability one, otherwise the acceptance probability will have some fixed value $p \propto e^{-\beta\Delta E} < 1$ where ΔE is the energy difference between the final (after spin flip attempt) and initial (before attempt) spin configurations. More refined algorithms can swap complete spin clusters guaranteeing a faster approach to equilibrium. Below T_c reversing the magnetization of the system (that is, hopping from the potential well with $m = -1$ to the well $m = +1$ or vice versa) requires an amount of energy $\Delta E \sim A \sim V^{2/3}$ which diverges to infinity in the thermodynamic limit $V \to \infty$. So, the bigger the system is, the probability of being able to switch magnetization approaches zero. In the thermodynamic limit the system becomes stuck in one of the wells. Ergodicity is broken because the 'mirror' spin states have become unreachable. The lesson to be drawn from this story is that if one only concentrates on the properties of the the free energy *density* one misses the kinetic effect which derives from the fact that the free energy can be non-convex for $T < T_c$ (even for $N \to \infty$) but the density of it (total free energy over total volume) will be convex in the limit.

Appendix B

Formalism for quenched processes

B.1 Effective noise correlator: construction

The noise correlator seen by the moving interface is computed perturbatively although certain contributions will be nonperturbative as seen below. Unless specifically stated, in what follows the noise average $\langle\cdot\rangle$ is always over the field α whose properties will be determined shortly. We suppose that the noise field is Fourier transformable with respect to the coordinate perpendicular to the interface (y-coordinate in this case) in which case we write

$$\alpha(x, H(x,t)) = \int dq_1\, e^{\imath q_1 H(x,t)} \alpha_{q_1}(x)\ . \tag{B.1}$$

Note that the integrals over variables q (e.g. q_1, q_2, q' etc.) are always one dimensional, whereas integrals over k and x can have any dimensionality, in which case dot products are understood.

Using the Fourier transform with respect to the second argument we can cast the noise correlator into the following form:

$$\langle \alpha(x_1, H(x_1,t_1))\alpha(x_2, H(x_2,t_2))\rangle \tag{B.2}$$

$$= \int dq_1 \int dq_2\, \langle \alpha_{q_1}(x_1)\alpha_{q_2}(x_2) e^{\imath q_1 H(x_1,t_1)} e^{\imath q_2 H(x_2,t_2)}\rangle \tag{B.3}$$

$$\begin{aligned} &= \int dq_1 \int dq_2\, \langle \alpha_{q_1}(x_1)\alpha_{q_2}(x_2)\rangle \langle e^{\imath q_1 H(x_1,t_1)} e^{\imath q_2 H(x_2,t_2)}\rangle \\ &+ \int dq_1 \int dq_2\, \langle\, [\alpha_{q_1}(x_1) \sqcap [\alpha_{q_2}(x_2) \sqcap e^{\imath q_1 H(x_1,t_1)} e^{\imath q_2 H(x_2,t_2)}]]\,\rangle \end{aligned} \tag{B.4}$$

$$\equiv C_0(x_1,t_1;x_2,t_2) + C_{\alpha\alpha'}(x_1,t_1;x_2,t_2)\ , \tag{B.5}$$

where

$$C_0 \equiv \langle \alpha_{q_1}(x_1)\alpha_{q_2}(x_2)\rangle \langle e^{\imath q_1 H(x_1,t_1)} e^{\imath q_2 H(x_2,t_2)}\rangle\ ; \tag{B.6}$$

$$C_{\alpha\alpha'} \equiv \int dq_1 \int dq_2\, \langle\, [\alpha_{q_1}(x_1) \sqcap [\alpha_{q_2}(x_2) \sqcap e^{\imath q_1 H(x_1,t_1)} e^{\imath q_2 H(x_2,t_2)}]]\,\rangle\ . \tag{B.7}$$

Notation $\langle\, [\alpha_{q_1} \sqcap [\alpha_{q_2} \sqcap f(\alpha)]]\,\rangle$ means that first α_{q_2} is contracted with some α field in $f(\alpha)$, then α_{q_1} is contracted with another noise field in the remaining expression $[\alpha_{q_2} \sqcap f(\alpha)]$. The noise average $\langle\cdot\rangle$ takes care of contracting the remaining α's. In other words, the second term on the right hand side of Eq. (B.4) performs all other contractions except those where α_{q_1} is contracted with α_{q_2} and the exponentials among themselves (first term on the right). To illustrate the method in practice, consider

$$[\alpha_1 \sqcap \alpha_2^3] = [\alpha_1 \sqcap \alpha_2]\alpha_2^2 + \alpha_2[\alpha_1 \sqcap \alpha_2]\alpha_2 + \alpha_2^2[\alpha_1 \sqcap \alpha_2] = 3[\alpha_1 \sqcap \alpha_2]\alpha_2^2 \ . \tag{B.8}$$

Performing the averaging gives

$$\langle[\alpha_1 \sqcap \alpha_2^3]\rangle = 3[\alpha_1 \sqcap \alpha_2]\langle\alpha_2^2\rangle = 3\langle\alpha_1\alpha_2\rangle\langle\alpha_2^2\rangle \ , \tag{B.9}$$

because for two fields only $[\alpha_1 \sqcap \alpha_2]$ reduces to $[\alpha_1 \sqcap \alpha_2] = \langle\alpha_1\alpha_2\rangle$.

After simplifying the notation by defining $H(1) \equiv H(x_1, t_1)$; $H(2) \equiv H(x_2, t_2)$ we get

$$C_0(x_1, t_1; x_2, t_2) = \int dq_1 \int dq_2 \, \langle\alpha_{q_1}(x_1)\alpha_{q_2}(x_2)\rangle\langle e^{\imath q_1 H(1)} e^{\imath q_2 H(2)}\rangle \tag{B.10}$$

$$= \int dq_1 \int dq_2 \, D\varphi_{\|}(x_1 - x_2)\varphi_{\perp}(q_1, q_2)\langle e^{\imath(q_1 H(1) + q_2 H(2))}\rangle \tag{B.11}$$

Here we have defined the correlations of the noise field α to have correlations $\varphi_{\|}(x_1 - x_2)$ in the direction parallel to the interface and $\varphi_{\perp}(q_1, q_2)$ in the perpendicular direction. In many of our applications we are assuming that the noise is Gaussian white noise (short-ranged, in general) in which case $\langle\alpha_{q_1}(x_1)\alpha_{q_2}(x_2)\rangle = D\,\delta(x_1 - x_2)\,\delta(q_1 + q_2)$. In this case

$$C_0(x_1, t_1; x_2, t_2) = D\,\delta(x_1 - x_2) \int dq_1 \, \langle e^{\imath q_1 (H(1) - H(2))}\rangle \ . \tag{B.12}$$

Expanding the exponential to second order in h and averaging gives

$$\langle e^{\Delta_H}\rangle = 1 + \langle\Delta_H\rangle + \frac{1}{2}\langle(\Delta_H)^2\rangle + \mathcal{O}(\Delta_H^3) \tag{B.13}$$

where we have defined $\Delta_H \equiv (\imath q_1)(H(1) - H(2))$ Taking logarithms on both sides of previous equation and using again the Taylor expansion: $\ln(1 + x) = x - x^2/2 + \ldots$ we notice that

$$\ln\left(e^{\Delta_H}\right) = \langle\Delta_H\rangle + \frac{1}{2}(\langle\Delta_H^2\rangle - \langle\Delta_H\rangle^2) + \ldots + \mathcal{O}(\delta_H^3) \tag{B.14}$$

Re-exponentiating and keeping only second order terms yields

$$\langle e^{\Delta_H}\rangle \approx e^{(\imath q_1)\kappa_1(\Delta_H) + (\imath q_1)^2\kappa_2(\Delta_H)} \ , \tag{B.15}$$

where $\kappa_1(\Delta_H) \equiv \langle\Delta_H\rangle$ and $\kappa_2(\Delta_H) \equiv \langle\Delta_H^2\rangle - \langle\Delta_H\rangle^2$. More information how to use the cumulant expansion to include non-Gaussian aspects are discussed in App. B.6. Gaussian approximation in Eq. (B.12) leads to

$$C_0(x_1, t_1; x_2, t_2) \equiv D\,\delta(x_1 - x_2) \int dq_1 \, \langle e^{\imath q_1 (H(1) - H(2))}\rangle \tag{B.16}$$

$$\approx D\,\delta(x_1 - x_2) \int dq_1 \, e^{(\imath q_1)\kappa_1(\Delta_H) + (\imath q_1)^2\kappa_2(\Delta_H)} \tag{B.17}$$

$$= D\,\delta(x_1 - x_2)[G_c(x_1, t_1; x_2, t_2)]^{-1/2} \exp\left(-\frac{\Delta^2(t_1, t_2)}{G_c(x_1, t_1; x_2, t_2)}\right) \ . \tag{B.18}$$

The following short-hand notation has been used above:

$$\begin{aligned}\Delta(t_1,t_2) &\equiv \kappa_1(\Delta_H) && \text{(B.19)}\\ &\equiv h_0(t_1)-h_0(t_2)+\langle h(x_1,t_1)\rangle-\langle h(x_2,t_2)\rangle && \text{(B.20)}\\ &= h_0(t_1)-h_0(t_2)+\langle h\rangle(t_1)-\langle h\rangle(t_2)\ ; && \text{(B.21)}\end{aligned}$$

$$\begin{aligned}G_c(x_1,t_1;x_2,t_2) &\equiv \kappa_2(\Delta_H) && \text{(B.22)}\\ &\equiv \langle (H(1)-H(2))^2\rangle-\langle (H(1)-H(2))\rangle^2 && \text{(B.23)}\\ &= \langle (h(1)-h(2))^2\rangle-\langle (h(1)-h(2))\rangle^2\ , && \text{(B.24)}\end{aligned}$$

where $h(1)\equiv h(x_1,t_1)$ and $h(2)\equiv h(x_2,t_2)$ are the spatially varying parts of $H(1)$ and $H(2)$. The second cumulant κ_2 has been renamed as G_c which is the familiar two-point correlation function used in kinetic growth theory.

B.2 Effective noise correlator: contractions

The difficulty of forming all possible contractions can be circumvented by using functional differentiation instead of explicit noise averaging. We introduce the following definition

$$\frac{\delta}{\delta\alpha_1}\,\alpha_2 \equiv D\,\delta(x_1-x_2)\delta(q_1+q_2)=\langle \alpha_{q_1}(x_1)\alpha_{q_2}(x_2)\rangle\ , \tag{B.25}$$

where $\alpha_i\equiv\alpha_{q_i}(x_i)$, $i=1,2$. Had we long range noise correlations, we could define

$$\frac{\delta}{\delta\alpha_1}\,\alpha_2 \equiv D\varphi_{\|}(x_1-x_2)\varphi_{\perp}(q_1,q_2)\ . \tag{B.26}$$

Eq. (B.25) is sufficient for white noise, which we shall be mainly using. Let us first compute the action of a single contraction.

$$\begin{aligned}&[\alpha_1\sqcap\exp(\imath q_1 h(1))\ \exp(\imath q_2 h(2))]=[\alpha_1\sqcap\exp(\imath q_1 h(1)+\imath q_2 h(2))] && \text{(B.27)}\\ &=\frac{\delta}{\delta\alpha_1}\ \exp(\imath q_1 h(1)+\imath q_2 h(2))=\frac{\delta}{\delta\alpha_1}\sum_{n=0}^{\infty}\frac{1}{n!}(\imath q_1 h(1)+\imath q_2 h(2))^n && \text{(B.28)}\\ &=\left(\imath q_1\frac{\delta h(1)}{\delta\alpha_1}+\imath q_2\frac{\delta h(2)}{\delta\alpha_1}\right)\sum_{n=1}^{\infty}\frac{1}{(n-1)!}(\imath q_1 h(1)+\imath q_2 h(2))^{n-1} && \text{(B.29)}\\ &=\left(\imath q_1\frac{\delta h(1)}{\delta\alpha_1}+\imath q_2\frac{\delta h(2)}{\delta\alpha_1}\right)\exp(\imath q_1 h(1)+\imath q_2 h(2)) && \text{(B.30)}\end{aligned}$$

Two contractions is equally simple to produce (note that it doesn't matter whether we contract α_2 prior to α_1 or vice versa):

$$\begin{aligned}&[\alpha_1\sqcap[\alpha_2\sqcap\exp(\imath q_1 h(1)+\imath q_2 h(2))]] && \text{(B.31)}\\ &=\frac{\delta}{\delta\alpha_1}\left\{\left(\imath q_1\frac{\delta h(1)}{\delta\alpha_2}+\imath q_2\frac{\delta h(2)}{\delta\alpha_2}\right)\exp(\imath q_1 h(1)+\imath q_2 h(2))\right\} && \text{(B.32)}\\ &=\left\{\left(\imath q_1\frac{\delta h(1)}{\delta\alpha_1}+\imath q_2\frac{\delta h(2)}{\delta\alpha_1}\right)\left(\imath q_1\frac{\delta h(1)}{\delta\alpha_2}+\imath q_2\frac{\delta h(2)}{\delta\alpha_2}\right)\right. && \text{(B.33)}\\ &\left.+\left(\imath q_1\frac{\delta^2 h(1)}{\delta\alpha_1\delta\alpha_2}+\imath q_2\frac{\delta^2 h(2)}{\delta\alpha_1\delta\alpha_2}\right)\right\}\exp(\imath q_1 h(1)+\imath q_2 h(2))\ . && \text{(B.34)}\end{aligned}$$

Supposing that h is known for a particular realization of the noise α, well-posed *linear* integral equations will be generated for the functional derivatives of h ($(\delta h)/(\delta\alpha)$, $(\delta^2 h)/(\delta\alpha\delta\alpha')$). These formal solutions can be substituted back into Eq. (B.34) to fix the form of the contraction. Next, compute the functional derivate of h_1 defined in Eq. (12.25) with respect to noise,

$$\begin{aligned}\frac{\delta h_1(x,t)}{\delta\alpha_{k_1}(x_1)} &= \int dk' \int dx'\, e^{\imath k'(x-x')} e^{-\imath k'^2 t} \int_0^t ds\, e^{\imath k'^2 s} \int dq\, e^{\imath q h_0(s)} D\,\delta(x_1-x')\,\delta(q+k_1) \\ &= D \int dk'\, e^{\imath k'(x-x_1)} e^{-\sigma k'^2 t} \int_0^t ds\, e^{\imath\sigma k'^2 s} e^{-\imath k_1 h_0(s)} \;. \qquad \text{(B.35)}\end{aligned}$$

In the first order approximation the second functional derivative is zero:

$$\frac{\delta^2 h_1(x,t)}{\delta\alpha_{k_1}(x_1)\delta\alpha_{k_2}(x_2)} = 0 \;, \qquad \text{(B.36)}$$

because there is now α-dependence left in Eq. (B.35). For higher order approximations this is not true and some genuinely new structure will emerge out of Eq. (B.36)

B.3 Effective noise correlator: constituents

The full effective noise correlator consists of two main pieces:

$$\langle \alpha(x_1, h(1))\alpha(x_2, h(2))\rangle \approx C_0(x_1,t_1;x_2,t_2) + C^{(1)}_{\alpha\alpha'}(x_1,t_1;x_2,t_2) \qquad \text{(B.37)}$$

The superscript '1' of $C^{(1)}_{\alpha\alpha'}$ means that we use the first iterative correction h_1, i.e $H(x,t) \approx h_0(t) + h_1(x,t)$. After performing the noise contractions in $C_{\alpha\alpha'}$ yields

$$\begin{aligned} C^{(1)}_{\alpha\alpha'} &= \int dq_1\, e^{\imath q_1 h_0(t_1)} \int dq_2\, e^{\imath q_2 h_0(t_2)} \Big\langle e^{\imath q_1 h_1(1) + \imath q_2 h_1(2)} \\ &\quad \left(\imath q_1 \frac{\delta h_1(1)}{\delta\alpha_1} + \imath q_2 \frac{\delta h_1(2)}{\delta\alpha_1}\right) \left(\imath q_1 \frac{\delta h_1(1)}{\delta\alpha_2} + \imath q_2 \frac{\delta h_1(2)}{\delta\alpha_2}\right) \Big\rangle \qquad \text{(B.38)} \\ &= \int dq_1\, e^{\imath q_1 h_0(t_1)} \int dq_2\, e^{\imath q_2 h_0(t_2)} \left(\imath q_1 \frac{\delta h_1(1)}{\delta\alpha_1} + \imath q_2 \frac{\delta h_1(2)}{\delta\alpha_1}\right) \\ &\quad \left(\imath q_1 \frac{\delta h_1(1)}{\delta\alpha_2} + \imath q_2 \frac{\delta h_1(2)}{\delta\alpha_2}\right) \left\langle e^{\imath q_1 h_1(1) + \imath q_2 h_1(2)} \right\rangle \;, \qquad \text{(B.39)} \end{aligned}$$

Using again the cumulant expansion to take care of the noise average of the exponentials at Gaussian order we get

$$\begin{aligned} &\langle \exp\left(\imath q_1 h_1(1) + \imath q_2 h_1(2)\right)\rangle = \exp\Big(\kappa_1(\imath q_1 h_1(1) - \imath q_2 h_1(2)) \\ &+\frac{1}{2!}\kappa_2(\imath q_1 h_1(1) - \imath q_2 h_1(2)) + \ldots\Big) \approx \exp\Big(\imath q_1 \langle h_1(1)\rangle + \imath q_2 \langle h_1(2)\rangle \\ &-\frac{1}{2}[\langle (q_1 h_1(1) + q_2 h_1(2))^2\rangle - \langle (q_1 h_1(1) + q_2 h_1(2))\rangle^2]\Big) \qquad \text{(B.40)} \\ &= \exp\left(-\frac{1}{2}q_1^2 \langle h_1^2(1)\rangle - \frac{1}{2}q_2^2\langle h_1^2(2)\rangle - q_1 q_2 \langle h_1(1) h_1(2)\rangle\right) \qquad \text{(B.41)} \\ &= \exp\left(-\frac{1}{2}q_1^2 w_1^2 - \frac{1}{2}q_2^2 w_2^2 - q_1 q_2 S\right) \;. \qquad \text{(B.42)} \end{aligned}$$

In simplifying the previous result we have made use of the fact that $\langle h_1 \rangle = 0$ (but $\langle h \rangle \neq 0h$). In the last line we have introduced a short-hand notation: $w_1^2 \equiv \langle h_1^2(1) \rangle$; $w_2^2 \equiv \langle h_1^2(2) \rangle$; $S \equiv \langle h_1(1) h_1(2) \rangle$. Explicitly,

$$\begin{aligned} w_1^2(t, L) &= \frac{D}{F} \int_{1/L} dk \, \frac{1 - e^{-2\sigma k^2 t}}{2\sigma k^2} = \frac{D}{F\sigma} (\sigma t)^{2\beta_1} f_w(\sqrt{\sigma t}/L) \ ; & \text{(B.43)} \\ S(x_1, t_1; x_2, t_2, L) &= \frac{D}{F} \int_{1/L} dk \, e^{\imath k(x_1 - x_2)} e^{-\sigma k^2 |t_1 - t_2|} \, \frac{1 - e^{-2\sigma k^2 \min\{t_1, t_2\}}}{2\sigma k^2} \ , & \text{(B.44)} \end{aligned}$$

where we have defined the growth exponent $\beta_1 \equiv (2 - d)/4$, d being the dimensionality of the space. The universal scaling function

$$f_w(\sqrt{\sigma t}/L) \equiv \int_{\sqrt{\sigma t}/L} dk \, \frac{1 - e^{-2k^2}}{2k^2} \ . \tag{B.45}$$

In the limit $x \to 0$ the scaling function f_w approaches a constant. For $x \to \infty$ it scales as $f_w \to x^{-2\chi_1}$. Here $\chi_1 = (2 - d)/2$ is the roughness exponent. Where the system size dependence is not important, we drop out the system size L from the list of arguments.

Expanding the products in Eq. (B.39) and using the Gaussian approximation for the noise averaged exponential (Eq. (B.42)) we can split the different contributions to four parts:

$$C^{(1)}_{\alpha\alpha'} = C^{(1)}_A + C^{(1)}_B + C^{(1)}_C + C^{(1)}_D \tag{B.46}$$

Specifically,

$$\begin{aligned} C^{(1)}_A(x_1, t_1; x_2, t_2) &\equiv \int dq_1 \, (\imath q_1)^2 e^{\imath q_1 h_0(t_1)} \int dq_2 \, e^{\imath q_2 h_0(t_2)} \\ &\quad \frac{\delta h_1(x_1, t_1)}{\delta \alpha_{q_1}(x_1)} \frac{\delta h_1(x_1, t_1)}{\delta \alpha_{q_2}(x_2)} \exp\left(-\frac{1}{2} q_1^2 w_1^2 - \frac{1}{2} q_2^2 w_2^2 - q_1 q_2 S \right) \ ; & \text{(B.47)} \\ C^{(1)}_B(x_1, t_1; x_2, t_2) &\equiv \int dq_1 \, (\imath q_1) e^{\imath q_1 h_0(t_1)} \int dq_2 \, (\imath q_2) e^{\imath q_2 h_0(t_2)} \\ &\quad \frac{\delta h_1(x_1, t_1)}{\delta \alpha_{q_1}(x_1)} \frac{\delta h_1(x_2, t_2)}{\delta \alpha_{q_2}(x_2)} \exp\left(-\frac{1}{2} q_1^2 w_1^2 - \frac{1}{2} q_2^2 w_2^2 - q_1 q_2 S \right) \ ; & \text{(B.48)} \\ C^{(1)}_C(x_1, t_1; x_2, t_2) &\equiv \int dq_1 \, (\imath q_1) e^{\imath q_1 h_0(t_1)} \int dq_2 \, (\imath q_2) e^{\imath q_2 h_0(t_2)} \\ &\quad \frac{\delta h_1(x_2, t_2)}{\delta \alpha_{q_1}(x_1)} \frac{\delta h_1(x_1, t_1)}{\delta \alpha_{q_2}(x_2)} \exp\left(-\frac{1}{2} q_1^2 w_1^2 - \frac{1}{2} q_2^2 w_2^2 - q_1 q_2 S \right) \ ; & \text{(B.49)} \\ C^{(1)}_D(x_1, t_1; x_2, t_2) &\equiv \int dq_1 \, e^{\imath q_1 h_0(t_1)} \int dq_2 \, (\imath q_2)^2 e^{\imath q_2 h_0(t_2)} \\ &\quad \frac{\delta h_1(x_2, t_2)}{\delta \alpha_{q_1}(x_1)} \frac{\delta h_1(x_2, t_2)}{\delta \alpha_{q_2}(x_2)} \exp\left(-\frac{1}{2} q_1^2 w_1^2 - \frac{1}{2} q_2^2 w_2^2 - q_1 q_2 S \right) \ . & \text{(B.50)} \end{aligned}$$

The partial noise correlators C_B and C_C are symmetric functions of their arguments:

$$\begin{aligned} C^{(1)}_B(x_1, t_1; x_2, t_2) &= C^{(1)}_B(x_2, t_2; x_1, t_1) \ ; & \text{(B.51)} \\ C^{(1)}_C(x_1, t_1; x_2, t_2) &= C^{(1)}_C(x_2, t_2; x_1, t_1) \ . & \text{(B.52)} \end{aligned}$$

Owing to the symmetry $C^{(1)}_A(x_1, t_1; x_2, t_2) = C^{(1)}_D(x_2, t_2; x_1, t_1)$ we only have to calculate C_A, say. Defining

$$U(q_1, q_2) \equiv \exp\left(-\frac{1}{2} q_1^2 w_1^2 - \frac{1}{2} q_2^2 w_2^2 - q_1 q_2 S \right) \tag{B.53}$$

and suppressing the arguments x_i and t_i, which are redundant at this stage, we note that the powers of $(\imath q_i)$ appearing in the integrals above can be generated by differentiating U with respect to 'variables' w_i^2 and S:

$$2\partial_{w_1^2} U = (\imath q_1)^2 U \; ; \; 2\partial_{w_2^2} U = (\imath q_2)^2 U \; ; \; \partial_S U = (\imath q_1)(\imath q_2) U \; . \tag{B.54}$$

Utilizing this and substituting the functional derivatives $\delta h/\delta\alpha$ given by Eq. (B.35) decorated with proper arguments we are left with computation of the following expressions:

$$C_A^{(1)}(x_1,t_1;x_2,t_2) = 2D^2 \partial_{w_1^2} \int dq_1 \, e^{\imath q_1 h_0(t_1)} \int dq_2 \, e^{\imath q_2 h_0(t_2)} \, U(q_1,q_2) \tag{B.55}$$

$$\int dk \, e^{\imath k(x_1-x_1)} e^{-\sigma k^2 t_1} \int_0^{t_1} ds \, e^{\sigma k^2 s} e^{-\imath q_1 h_0(s)} \int dk \, e^{\imath k(x_1-x_2)} e^{-\sigma k^2 t_1} \int_0^{t_1} ds \, e^{\sigma k^2 s} e^{-\imath q_2 h_0(s)} .$$

$$C_B^{(1)}(x_1,t_1;x_2,t_2) = D^2 \partial_S \int dq_1 \, e^{\imath q_1 h_0(t_1)} \int dq_2 \, e^{\imath q_2 h_0(t_2)} \, U(q_1,q_2) \tag{B.56}$$

$$\int dk \, e^{\imath k(x_1-x_1)} e^{-\sigma k^2 t_1} \int_0^{t_1} ds \, e^{\sigma k^2 s} e^{-\imath q_1 h_0(s)} \int dk \, e^{\imath k(x_2-x_2)} e^{-\sigma k^2 t_2} \int_0^{t_2} ds \, e^{\sigma k^2 s} e^{-\imath q_2 h_0(s)} .$$

$$C_C^{(1)}(x_1,t_1;x_2,t_2) = D^2 \partial_S \int dq_1 \, e^{\imath q_1 h_0(t_1)} \int dq_2 \, e^{\imath q_2 h_0(t_2)} \, U(q_1,q_2) \tag{B.57}$$

$$\int dk \, e^{\imath k(x_2-x_1)} e^{-\sigma k^2 t_2} \int_0^{t_2} ds \, e^{\sigma k^2 s} e^{-\imath q_1 h_0(s)} \int dk \, e^{\imath k(x_1-x_2)} e^{-\sigma k^2 t_1} \int_0^{t_1} ds \, e^{\sigma k^2 s} e^{-\imath q_2 h_0(s)} .$$

$$C_D^{(1)}(x_1,t_1;x_2,t_2) = 2D^2 \partial_{w_2^2} \int dq_1 \, e^{\imath q_1 h_0(t_1)} \int dq_2 \, e^{\imath q_2 h_0(t_2)} \, U(q_1,q_2) \tag{B.58}$$

$$\int dk \, e^{\imath k(x_2-x_1)} e^{-\sigma k^2 t_2} \int_0^{t_2} ds \, e^{\sigma k^2 s} e^{-\imath q_1 h_0(s)} \int dk \, e^{\imath k(x_2-x_2)} e^{-\sigma k^2 t_2} \int_0^{t_2} ds \, e^{\sigma k^2 s} e^{-\imath q_2 h_0(s)} .$$

Factors of D arising from functional differentiation have been placed in front of the expressions. The temporal scaling features of the noise correlators are scrutinized in App. B.4.

B.4 Special scaling features of noise correlators

In this section we will derive the scaling behaviour and functional form of the different noise correlators. To illustrate the general methods we use $C_A^{(1)}$ as a working example. We have derived the following form for it in Eq. (B.55):

$$C_A^{(1)}(x_1,t_1;x_2,t_2) = 2D^2 \partial_{w_1^2} \int dq_1 \, e^{\imath q_1 h_0(t_1)} \int dq_2 \, e^{\imath q_2 h_0(t_2)} \, U(q_1,q_2) \tag{B.59}$$

$$\int dk_3 \, e^{-\sigma k_3^2 t_1} \int_0^{t_1} ds_1 \, e^{\sigma k_3^2 s_1} e^{-\imath q_1 h_0(s_1)} \int dk_4 \, e^{\imath k_4(x_1-x_2)} e^{-\sigma k_4^2 t_1} \int_0^{t_1} ds_2 \, e^{\sigma k_4^2 s_2} e^{-\imath q_2 h_0(s_2)}$$

Next, regroup all integrals containing integration over q_i $(i = 1, 2)$ and define a new symbol I (substitute $h_0(t) = Ft$)

$$I \equiv \int dq_1 \int dq_2 \, e^{\imath q_1 F(t_1-s_1)} \, e^{\imath q_2 F(t_2-s_2)} \, U(q_1,q_2) \; . \tag{B.60}$$

We can now express the correlator more concisely

$$C_A^{(1)} = 2D^2 \int dk_3 \, e^{-\sigma k_3^2 t_1} \int_0^{t_1} ds_1 \, e^{\sigma k_3^2 s_1} \int dk_4 \, e^{\imath k_4(x_1-x_2)} e^{-\sigma k_4^2 t_1} \int_0^{t_1} ds_2 \, e^{\sigma k_4^2 s_2} \, \partial_{w_1^2} I \tag{B.61}$$

We have let the differential operator $\partial_{w_1^2}$ to act on I which is evaluated in App. B.7 (Eq. (B.177)):

$$I = \frac{\sqrt{2}\pi}{\sqrt{a_1}w_2} \exp\left(-\frac{F^2(t_2-s_2)^2}{2w_2^2} + \frac{a_2^2}{a_1}\right) \ , \tag{B.62}$$

where we have introduced new functions

$$\begin{aligned} a_1(x_1-x_2,t_1,t_2) &\equiv \frac{1}{2}\left[w_1^2(t_1) - \frac{S^2(x_1-x_2,t_1,t_2)}{w_1^2(t_2)}\right] && \text{(B.63)} \\ a_2(x_1-x_2,t_1,t_2,s_1.s_2) &\equiv \frac{\imath F}{2}\left[(t_1-s_1) - (t_2-s_2)\frac{S(x_1-x_2,t_1,t_2)}{w_1^2(t_2)}\right] \ . && \text{(B.64)} \end{aligned}$$

Indices have been written out explicitly to see which parts will be affected by a spatial Fourier transform. The fact that only differences of the form $x_1 - x_2$ appear in the arguments means that the Fourier transformed correlator will be proportional to $\delta(k_1 + k_2)$. To perform the transformation

$$\int dx_1 \int dx_2 \, e^{-\imath(k_1x_1+k_2x_2)} f(x_1-x_2) \ , \tag{B.65}$$

we change variables of integration as $x_1 - x_2 = x$; $x_1 + x_2 = 2X$. Inversely, $x_1 = X + x/2$; $x_2 = X - x/2$. The Jacobian of the transformation is unity: $\partial(x_1, x_2)/\partial(x, X) = 1$. The argument of the exponential becomes

$$k_1x_1 + k_2x_2 = k_1(X + x/2) + k_2(X - x/2) = X(k_1 + k_2) + x(k_1 - k_2)/2 \ . \tag{B.66}$$

Since the integrand is independent of X we can perform the integration over it yielding

$$\begin{aligned} &\int dx_1 \int dx_2 \, e^{-\imath(k_1x_1+k_2x_2)} f(x_1-x_2) \\ &\quad = \delta(k_1+k_2)\int dx \, e^{-\imath x(k_1-k_2)/2} f(x) = \delta(k_1+k_2)\int dx \, e^{-\imath x k_1} f(x) \ . \end{aligned} \tag{B.67}$$

Utilizing this result we transform $C_i^{(1)}(k, t_1; k', t_2)$ $(i = A, B, C, D)$:

$$C_i^{(1)}(k,t_1;k',t_2) \equiv \int dx_1 \int dx_2 \, e^{-\imath(kx_1+k'x_2)} \, C_i^{(1)}(x_1,t_1;x_2,t_2) \equiv \delta(k+k') \, \tilde{C}_i^{(1)}(k,t_1;k',t_2) \ , \tag{B.68}$$

where for simplicity we have introduced new notation $\tilde{C}_i^{(1)}$ to be used in the rest of the text. Hence,

$$\begin{aligned} \tilde{C}_A^{(1)} = \; & 2D^2 \int dx \, e^{-\imath kx} \int dk_3 \, e^{-\sigma k_3^2 t_1} \int_0^{t_1} ds_1 \, e^{\sigma k_3^2 s_1} \int dk_4 \, e^{\imath k_4 x} e^{-\sigma k_4^2 t_1} \int_0^{t_1} ds_2 \, e^{\sigma k_4^2 s_2} \\ & \frac{\pi\sqrt{2}}{4w_2} a_1(x)^{-3/2} \left[-1 - 2\frac{a_2^2(x)}{a_1(x)}\right] \exp\left(-\frac{F^2(t_2-s_2)^2}{2w_2^2} + \frac{a_2^2(x)}{a_1(x)}\right) \end{aligned} \tag{B.69}$$

To be able to see the relevant scaling behaviour of different terms we extract the dimensionfull quantities by rescaling time arguments as $t_i \equiv tp_i$, $s_i \equiv ts'_i$, $i = 1, 2$. The idea is to divide the analysis into domains where the expressions contain as few dimensionless variables as possible. New dimensionless length $x' \equiv x/\sqrt{\sigma t}$. Rescaling arguments of S (Eq. (B.44)) gives

$$S(\sqrt{\sigma t}\, x', tp_1, tp_2, \sqrt{\sigma t}/L) = W_t^2 g(x', p_1, p_2, \sqrt{\sigma t}/L) \ , \tag{B.70}$$

where

$$g(x', p_1, p_2, \sqrt{\sigma t}/L) \equiv \int_{\sqrt{\sigma t}/L} dk_1 \, e^{\imath k_1 x'} \, e^{-k_1^2 |p_1 - p_2|} \frac{1 - e^{-2k_1^2 \min\{p_1, p_2\}}}{2k_1^2} \; . \tag{B.71}$$

The last argument of g will be explicitly written out when system size dependence is important for the analysis. In the infinite system limit it will be dropped from the argument list. The symbol W_t^2 is determined by scaling of $w_1^2(tp_i, L)$ $(i = 1, 2)$, see Eq. (B.43):

$$w_1^2(tp_i, L) = \frac{D}{F\sigma}(\sigma t p_i)^{2\beta_1} \int_{\frac{\sqrt{\sigma t p_i}}{L}} dk \, \frac{1 - e^{-2k^2}}{2k^2} \rightarrow \left\{ \begin{array}{ll} W_t^2 p_i^{2\beta_1} f_w(0) & \text{, for } \frac{\sqrt{\sigma t}}{L} \ll 1 \\ W_L^2 & \text{, for } \frac{\sqrt{\sigma t}}{L} \gg 1 \; . \end{array} \right. \tag{B.72}$$

Defining the growth exponent $\beta_1 = (2 - d)/4$ and the roughness exponent $\chi_1 = (2 - d)/2$ allows us to write the prefactors as

$$W_t^2 \equiv \frac{D}{F\sigma}(\sigma t)^{2\beta_1} \; ; \; W_L^2 \equiv \frac{D}{F\sigma} L^{2\chi_1} \tag{B.73}$$

In the following we will be interested in taking the limit where the dimensionless variable $\sigma k^2 t$ becomes large. To derive the hidden dimensionless scales we will scale perform a similar scaling of arguments for a_1 and a_2 as we did for w_i and S. To simplify the resulting expressions and to be able to see more clearly, how the expressions behave as a function $\sigma k^2 t$ only, we'll require that $\sqrt{\sigma t}/L \ll 1$, which is obviously true in the infinite system size limit $L \rightarrow \infty$. However, the results should apply for finite systems as well. Setting the lower boundary of k integrals $\sigma t / L^2 \ll 1 = 0$ means that in the spherical coordinate system we start integrating the radial k-mode from zero onwards. In rectangular coordinates the notation means that there will be no infrared cut-off. Extraction of time dependent factors yields

$$\begin{aligned} a_1(\sqrt{\sigma t}\, x', tp_1, tp_2) &= \frac{1}{2}\left(W_t^2 p_1^{2\beta_1} f_w(0) - \frac{W_t^4 g^2(x', p_1, p_2)}{W_t^2 p_2^{2\beta_1} f_w(0)} \right) && \text{(B.74)} \\ &= \frac{W_t^2}{2}\left(p_1^{2\beta_1} f_w(0) - \frac{g^2(x', p_1, p_2)}{p_2^{2\beta_1} f_w(0)} \right) \; . && \text{(B.75)} \\ a_2(\sqrt{\sigma t}\, x', tp_1, tp_2, ts_1', ts_2') &= \frac{\imath F t}{2}\left((p_1 - s_1') - (p_2 - s_2') \frac{W_t^2 g(x', p_1, p_2)}{W_t^2 p_2^{2\beta_1} f_w(0)} \right) && \text{(B.76)} \\ &= \frac{\imath F t}{2}\left((p_1 - s_1') - (p_2 - s_2') \frac{g(x', p_1, p_2)}{p_2^{2\beta_1} f_w(0)} \right) \; . && \text{(B.77)} \end{aligned}$$

The hidden scale reveals itself since the ratio a_2^2/a_1 can be seen to be proportional to $(Ft/W_t)^2$. Depending on the size of it different noise correlator terms will dominate.

$$\frac{a_2^2}{a_1} = \left(\frac{Ft}{W_t}\right)^2 m_1(x', p_1, p_2, s_1', s_2') \; , \tag{B.78}$$

and

$$m_1(x', p_1, p_2, s_1', s_2') \equiv -\frac{\left[(p_1 - s_1') - (p_2 - s_2') p_2^{-2\beta_1} f_w^{-1}(0) g(x', p_1, p_2) \right]^2}{\left[p_1^{2\beta_1} - p_2^{-2\beta_1} g^2(x', p_1, p_2) \right]} \tag{B.79}$$

The same is true for the argument of the exponential in Eq. (B.69) which can be written in a more symmetrical form (App. B.7):

$$-\frac{F^2(tp_2 - ts_2')^2}{2w_1^2(tp_2)} + \frac{a_2^2(\sqrt{\sigma t}\,x', tp_1, tp_2, ts_1'.ts_2')}{a_1(\sqrt{\sigma t}\,x', tp_1, tp_2)} = -\frac{1}{2}\left(\frac{Ft}{W_t}\right)^2 m_2(x', p_1, p_2, s_1', s_2') \ , \tag{B.80}$$

where

$$m_2(x', p_1, p_2, s_1', s_2') \equiv \frac{p_1^{2\beta_1} f_w(0)(p_1 - s_1')^2 + p_2^{2\beta_1} f_w(0)(p_2 - s_2')^2 - 2(p_1 - s_1')(p_2 - s_2')g(x', p_1, p_2)}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2)} . \tag{B.81}$$

Knowing the scaling of the individual parts of $C_A^{(1)}$ we are now ready to compute the scaling behaviour of the whole.

Noise correlator $C_A^{(1)}$

Rewrite Eq. (B.69) in scaled variables: $t_i = tp_i$, $s_i = ts_i'$ $x' = x/\sqrt{\sigma t}$. Placing the dimension-full quantities in front gives

$$\tilde{C_A}^{(1)}(k, tp_1; k', tp_2) = 2\pi D^2 t^2 (\sigma t)^{-d/2}\, W_t^{-4} \int dx'\, e^{-\imath k\sqrt{\sigma t} x'} \tag{B.82}$$

$$\int dk_3'\, e^{-(k_3')^2 p_1} \int_0^{p_1} ds_1'\, e^{(k_3')^2 s_1'} \int dk_4'\, e^{\imath k_4' x'} e^{-(k_4')^2 p_1} \int_0^{p_1} ds_2'\, e^{(k_4')^2 s_2'}\ p_2^{-\beta_1} f_w^{-\frac{1}{2}}(0)$$
$$\left[p_1^{2\beta_1} f_w(0) - \frac{g^2(x', p_1, p_2)}{p_2^{2\beta_1} f_w(0)}\right]^{-\frac{3}{2}} \left[-1 - 2\left(\frac{Ft}{W_t}\right)^2 m_1(x', p_1, p_2, s_1', s_2')\right]$$
$$\exp\left(-\frac{1}{2}\left(\frac{Ft}{W_t}\right)^2 m_2(x', p_1, p_2, s_1', s_2')\right) \ . \tag{B.83}$$

Now we start considering the limits in the previous expression. When $M_w \equiv Ft/W_t \ll 1$ the exponential term and the expression in the square brackets can be approximated as

$$\exp(-M_w^2 m_2/2) \approx 1 \ ; \ [-1 - 2M_w^2 m_1] \approx -1 \ . \tag{B.84}$$

In the opposite limit, $M_w \gg 1$ second term in the square brackets dominates $[-1-2M_w^2 m_1] \approx -2M_w^2 m_1$, and the factor M_w^2 together with $\exp(-M_w^2 m_2/2)$ forms a two dimensional representation of the delta function. This can be seen by forming new integration variables $s_i'' \equiv p_i - s_i'$ and diagonalizing the quadratic form in variables s_i'', $i = 1, 2$, more details in App. B.8 In other words, the limit $M_w \to \infty$ is well defined. Letting also $k\sqrt{\sigma t} \to \infty$ leads to vanishing of the whole expression because of rapidly oscillating integrand. This is true for other noise correlators (C_B, C_C, C_D), too.

Noise correlator $C_B^{(1)}$

Repeating the steps that lead to Eq. (B.69) and using Eq. (B.56) together with Eq. (B.180) we have for the Fourier transformed $C_B^{(1)}$:

$$C_B^{(1)}(k, t_1; k', t_2) \equiv \int dx_1 \int dx_2\, e^{-\imath(kx_1 + k'x_2)}\, C_B^{(1)}(x_1, t_1; x_2, t_2) \tag{B.85}$$

$$= 2D^2\,\delta(k+k')\int dx\,e^{-\imath kx}\int dk_3\,e^{-\sigma k_3^2 t_1}\int_0^{t_1} ds_1\,e^{\sigma k_3^2 s_1}\int dk_4\,e^{-\sigma k_4^2 t_2}\int_0^{t_2} ds_2\,e^{\sigma k_4^2 s_2}$$

$$\frac{\pi\sqrt{2}}{w_2}a_1^{-3/2}\left[\frac{S}{2w_2^2} - a_2\frac{\imath F(t_2-s_2)}{w_2^2} + \frac{Sa_2^2}{w_2^2 a_1}\right]\exp\left(-\frac{F^2(t_2-s_2)^2}{2w_2^2} + \frac{a_2^2(x)}{a_1(x)}\right) \tag{B.86}$$

Next, we write the expression in square brackets in a more symmetrical form with respect to interchange of time indices using Eq. (B.184).

$$\frac{S}{2w_2^2} - a_2\frac{\imath F(t_2-s_2)}{w_2^2} + \frac{Sa_2^2}{w_2^2 a_1} = \frac{S}{2w_2^2} + \frac{F^2}{2w_2^2}\Delta_1\Delta_2 + \frac{S}{w_2^2}\left(\frac{a_2^2}{a_1} - \frac{F^2\Delta_2^2}{2w_2^2}\right) \tag{B.87}$$

$$= \frac{W_t^2 g(x',p_1,p_2)}{2W_t^2 p_2^{2\beta_1} f_w(0)} + \frac{F^2(tp_1 - ts_1')(tp_2 - ts_2')}{2W_t^2 p_2^{2\beta_1} f_w(0)} + \frac{W_t^2 g(x',p_1,p_2)}{W_t^2 p_2^{2\beta_1} f_w(0)}\left(-M_w^2\frac{m_2}{2}\right) \tag{B.88}$$

$$= \frac{g(x',p_1,p_2)}{2p_2^{2\beta_1} f_w(0)} + M_w^2\frac{(p_1-s_1')(p_2-s_2')}{2p_2^{2\beta_1} f_w(0)} - M_w^2\frac{g(x',p_1,p_2)}{p_2^{2\beta_1} f_w(0)}m_2\ . \tag{B.89}$$

All arguments in the previous equation (including function m_2) are expressed in scaled quantities. We have also set $\sqrt{\sigma t}/L \to 0$. Defining a new function

$$m_3(x',p_1,p_2,s_1',s_2') \equiv \frac{(p_1-s_1')(p_2-s_2')}{2p_2^{2\beta_1} f_w(0)} - \frac{g(x',p_1,p_2)}{p_2^{2\beta_1} f_w(0)}m_2(x',p_1,p_2,s_1',s_2')\ , \tag{B.90}$$

we can write

$$\frac{S}{2w_2^2} - a_2\frac{\imath F(t_2-s_2)}{w_2^2} + \frac{Sa_2^2}{w_2^2 a_1} = \frac{g(x',p_1,p_2)}{2p_2^{2\beta_1} f_w(0)} + M_w^2\,m_3(x',p_1,p_2,s_1',s_2')\ . \tag{B.91}$$

Extracting dimensionfull variables and using Eq. (B.91) yields

$$\tilde{C_B}^{(1)}(k,tp_1;k',tp_2) = 8\pi D^2 t^2(\sigma t)^{-d/2}\,W_t^{-4}\int dx'\,e^{-\imath k\sqrt{\sigma t}x'} \tag{B.92}$$

$$\int dk_3'\,e^{-(k_3')^2 p_1}\int_0^{p_1} ds_1'\,e^{(k_3')^2 s_1'}\int dk_4'\,e^{-(k_4')^2 p_2}\int_0^{p_2} ds_2'\,e^{(k_4')^2 s_2'}\ p_2^{-\beta_1} f_w^{-\frac{1}{2}}(0)$$

$$\left[p_1^{2\beta_1} f_w(0) - \frac{g^2(x',p_1,p_2)}{p_2^{2\beta_1} f_w(0)}\right]^{-\frac{3}{2}}\left[\frac{g(x',p_1,p_2)}{2p_2^{2\beta_1} f_w(0)} + M_w^2\,m_3(x',p_1,p_2,s_1',s_2')\right]$$

$$\exp\left(-\frac{1}{2}M_w^2\,m_2(x',p_1,p_2,s_1',s_2')\right)\ . \tag{B.93}$$

Limit $M_w \to \infty$ is well defined as for $C_A^{(1)}$. In the opposite case, $M_w \ll 1$ we can approximate the exponential by one and leave out the part in the square brackets which is proportional to M_w^2. Scaling behaviour of $C_B^{(1)}$ in time is obviously the same as that of $C_A^{(1)}$. It should also be noted that taking $\sigma k^2 t \to \infty$ makes $C_B^{(1)}$ go to zero.

Noise correlator $C_C^{(1)}$

Calculation of the remaining noise correlator $C_C^{(1)}$ is straightforward now. Utilizing Eq. (B.57) the Fourier transform gives

$$C_C^{(1)}(k,t_1;k',t_2) \equiv \int dx_1\int dx_2\,e^{-\imath(kx_1+k'x_2)}\,C_C^{(1)}(x_1,t_1;x_2,t_2) \tag{B.94}$$

$$= 2D^2\,\delta(k+k')\int dx\, e^{-\imath kx}\int dk_3\, e^{-\imath k_3 x} e^{-\sigma k_3^2 t_2}\int_0^{t_2} ds_1\, e^{\sigma k_3^2 s_1}\int dk_4\, e^{\imath k_4 x} e^{-\sigma k_4^2 t_1}\int_0^{t_1} ds_2\, e^{\sigma k_4^2 s_2}$$
$$\frac{\pi\sqrt{2}}{w_2} a_1^{-\frac{3}{2}}\left[\frac{S}{2w_2^2} - a_2\frac{\imath F(t_2-s_2)}{w_2^2} + \frac{S a_2^2}{w_2^2 a_1}\right]\exp\left(-\frac{F^2(t_2-s_2)^2}{2w_2^2} + \frac{a_2^2(x)}{a_1(x)}\right) \tag{B.95}$$

Notice that the time indices (integrals over s_1 and s_2) are different from those of $C_A^{(1)}$ and $C_B^{(1)}$. With the aid of Eq. (B.91) we can extract the dimensionfull variables of $C_C^{(1)}$. Placing them in the front gives

$$\tilde{C_C}^{(1)}(k, tp_1; k', tp_2) = 8\pi D^2 t^2 (\sigma t)^{-d/2}\, W_t^{-4}\int dx'\, e^{-\imath k\sqrt{\sigma t}x'} \tag{B.96}$$
$$\int dk_3'\, e^{-\imath k_3' x'} e^{-(k_3')^2 p_2}\int_0^{p_2} ds_1'\, e^{(k_3')^2 s_1'}\int dk_4'\, e^{\imath k_4' x'} e^{-(k_4')^2 p_1}\int_0^{p_1} ds_2'\, e^{(k_4')^2 s_2'}\; p_2^{-\beta_1} f_w^{-\frac{1}{2}}(0)$$
$$\left[p_1^{2\beta_1} f_w(0) - \frac{g^2(x', p_1, p_2)}{p_2^{2\beta_1} f_w(0)}\right]^{-\frac{3}{2}}\left[\frac{g(x', p_1, p_2)}{2p_2^{2\beta_1} f_w(0)} + M_w^2\, m_3(x', p_1, p_2, s_1', s_2')\right]$$
$$\exp\left(-\frac{1}{2}M_w^2 m_2(x', p_1, p_2, s_1', s_2')\right)\ . \tag{B.97}$$

Limiting case $M_w \to \infty$ is analogous to $C_A^{(1)}$ and $C_B^{(1)}$. The power law scaling in time is the same as well. Limit $\sigma k^2 t \to \infty$ causes $C_C^{(1)}$ to vanish. Finally, since $C_D^{(1)}$ behaves as $C_A^{(1)}$ with time and spatial arguments interchanged, we conclude the all the four noise correlators $C_i^{(1)}$ $(i = A, B, C, D)$ share the same scaling form and vanish in the limit $\sigma k^2 t \to \infty$.

B.5 Structure factors

In this section we will determine the scaling behaviour of the structure factors C_i $(i = A, B, C)$ for $Ft/W_t \ll 1$. The opposite limit has been considered in App. B.4.

Structure factor $S_A^{(1)}$

When $Ft/W_t \ll 1$, Eq. (B.69) reduces to

$$\tilde{C}_A^{(1)} \approx -2D^2\int dx\, e^{-\imath kx}\int dk_3\, e^{-\sigma k_3^2 t_1}\int_0^{t_1} ds_1\, e^{\sigma k_3^2 s_1}\int dk_4\, e^{-\sigma k_4^2 t_1}\int_0^{t_1} ds_2\, e^{\sigma k_4^2 s_2}\,\frac{\pi\sqrt{2}}{4w_2}\, a_1^{-\frac{3}{2}}\ . \tag{B.98}$$

Performing the time integrations over s_i $(i = 1, 2)$ and including the system size dependence gives

$$\tilde{C}_A^{(1)} = -2D^2\int^L dx\, e^{-\imath kx}\int_{\frac{1}{L}} dk_3\,\frac{1-e^{-\sigma k_3^2 t_1}}{\sigma k_3^2}\int_{\frac{1}{L}} dk_4\, e^{\imath k_4 x}\,\frac{1-e^{-\sigma k_4^2 t_1}}{\sigma k_4^2}\,\frac{\pi\sqrt{2}}{4w_2 a_1^{3/2}} \tag{B.99}$$
$$= -2D^2\pi\, w_1^{-3}(t_1, L)\, w_1^{-1}(t_2, L)\int_{\frac{1}{L}} dk_3\,\frac{1-e^{-\sigma k_3^2 t_1}}{\sigma k_3^2}\int^L dx\, e^{-\imath kx}$$
$$\int_{\frac{1}{L}} dk_4\; e^{\imath k_4 x}\frac{1-e^{-\sigma k_4^2 t_1}}{\sigma k_4^2}\left[1 - \frac{S^2(x, t_1, t_2)}{w_1^2(t_1, L)\, w_1^2(t_2, L)}\right]^{-\frac{3}{2}}\ . \tag{B.100}$$

Further simplifications of the form of the noise correlator can be obtained by considering various limits of the dimensionless variables ($\sigma k^2 t$, $\sigma t/L^2$ etc.). Next, we will construct the structure factor $S_A^{(1)}$ whose relation to $\tilde{C}_A^{(1)}$ is very simple:

$$S_A^{(1)}(k,t) = e^{-2\sigma k^2 t} \int_0^t ds_1 \int_0^t ds_2 \, e^{\sigma k^2 (s_1+s_2)} \, \tilde{C}_A^{(1)}(k, s_1, s_2) \ . \tag{B.101}$$

Limits will be easier to consider if we transform the time variables as $s_i = t(1-p_i)$ ($i = 1, 2$). Hence,

$$S_A^{(1)}(k,t) = e^{-2\sigma k^2 t} \int_1^0 (-t) \, dp_1 \int_1^0 (-t) \, dp_2 \ e^{\sigma k^2 t(2-p_1-p_2)} \, \tilde{C}_A^{(1)}(k, t(1-p_1), t(1-p_2)) \ . \tag{B.102}$$

Place the dimensionfull numbers in front:

$$S_A^{(1)}(k,t) = t^2 \int_0^1 dp_1 \int_0^1 dp_2 \ e^{-\sigma k^2 t(p_1+p_2)} \, \tilde{C}_A^{(1)}(k, t(1-p_1), t(1-p_2)) \ . \tag{B.103}$$

Owing to the change of variables a dimensionless combination $\sigma k^2 t$ has appeared in the argument of the exponential making it easier for us to consider limits of this variable being much larger or smaller than one. Writing out the arguments explicitly and substituting $\tilde{C}_A^{(1)}$ from Eq. (B.100) leads to a rather lengthy expression:

$$\begin{gathered} S_A^{(1)}(k,t) = -2D^2 \pi \, t^2 \int_0^1 dp_1 \int_0^1 dp_2 \ e^{-\sigma k^2 t(p_1+p_2)} \, w_1^{-3}(t(1-p_1)) \, w_1^{-1}(t(1-p_2)) \int^L dx \ e^{-\imath k x} \\ \int_{\frac{1}{L}} dk_3 \ \frac{1 - e^{-\sigma k_3^2 t(1-p_1)}}{\sigma k_3^2} \int_{\frac{1}{L}} dk_4 \ e^{\imath k_4 x} \, \frac{1 - e^{-\sigma k_4^2 t(1-p_1)}}{\sigma k_4^2} \left[1 - \frac{S^2(x, t(1-p_1), t(1-p_2))}{w_1^2(t(1-p_1)) \, w_1^2(t(1-p_2))} \right]^{-\frac{3}{2}} \end{gathered} \tag{B.104}$$

Note that w_i ($i = 1, 2$) always depends on the system size even though we have dropped L from the argument list. In order to condense the notation we introduce some new notation. The early time scaling of the correlation function S we have determined in Eq. (B.70).

$$\begin{aligned} & S(x, t(1-p_1), t(1-p_2)) \\ & \quad = W_t^2 \int_{\frac{\sqrt{\sigma t}}{L}} dk_1 \, e^{\imath k_1 x/\sqrt{\sigma t}} \, e^{-\imath k_1^2 |p_1-p_2|} \, \frac{1 - e^{-2k_1^2 \min\{1-p_1, 1-p_2\}}}{2k_1^2} && \text{(B.105)} \\ & \quad = W_t^2 \, g(x/\sqrt{\sigma t}, 1-p_1, 1-p_2, \sqrt{\sigma t}/L) \ . && \text{(B.106)} \end{aligned}$$

We are first going to study the limit $\sigma k^2 t \ll 1$ and we are further simplifying the algebra by assuming that $\sqrt{\sigma t}/L \to 0$. The integrals over k_3 and k_4 appearing in Eq. (B.104) can be denoted more compactly by first changing variables

$$\int_{\frac{1}{L}} dk_4 \ e^{\imath k_4 x} \, \frac{1 - e^{-\sigma k_4^2 t(1-p_1)}}{\sigma k_4^2} = \frac{(\sigma t)^{2\beta_1}}{\sigma} \int dk_4' \ e^{\imath k_4' x/\sqrt{\sigma t}} \ \frac{1 - e^{-(k_4')^2 (1-p_1)}}{(k_4')^2} \ , \tag{B.107}$$

and then defining new scaling function R_2 through

$$R_2(x/\sqrt{\sigma t}, p_1) \equiv \int dk_4' \ e^{\imath k_4' x/\sqrt{\sigma t}} \ \frac{1 - e^{-(k_4')^2 (1-p_1)}}{(k_4')^2} \ . \tag{B.108}$$

The other integral over k_3 appearing in the expression of $S_A^{(1)}$ is expressed in terms of R_2 in the limit $\sqrt{\sigma t}/L \to 0$:

$$\int_{\frac{1}{L}} dk_3 \, \frac{1 - e^{-\sigma k_3^2 t(1-p_1)}}{\sigma k_3^2} \to \frac{(\sigma t)^{2\beta_1}}{\sigma} R_2(0, p_1) \ . \tag{B.109}$$

The scaling of the width is goes as $w_1^2(t(1-p)) = W_t^2 f_w(0)$ for early times ($\sigma k^2 t(1-p)/L \to 0$ if $\sigma k^2 t/L \to 0$ and Eq. (B.72) can be used). We also note that in Eq. (B.104) the exponential $\exp(-\sigma k^2 t(1-p_1)) \approx 1$ in the early time regime $\sigma k^2 t \ll 1$. In terms of the new scaling functions we obtain

$$S_A^{(1)}(k,t) = -2D^2 \pi \, t^2 \int_0^1 dp_1 \int_0^1 dp_2 \, W_t^{-3} f_w^{-\frac{3}{2}}(0) \, W_t^{-1} f_w^{-\frac{1}{2}}(0) \int^L dx \ e^{-\imath k x} \tag{B.110}$$

$$\frac{(\sigma t)^{2\beta_1}}{\sigma} R_2(0, p_1) \frac{(\sigma t)^{2\beta_1}}{\sigma} \ R_2(x/\sqrt{\sigma t}, p_1) \left[1 - \frac{W_t^4 g^2(x/\sqrt{\sigma t}, 1-p_1, 1-p_2)}{W_t^2 f_w(0) \, W_t^2 f_w(0)} \right]^{-\frac{3}{2}} \tag{B.111}$$

We perform next the transformation $x/\sqrt{\sigma t} \equiv x'$ to obtain a dimensionless parameter of the correct form $\sigma k^2 t$. Time dependent terms and constants are placed in front of the integrals:

$$S_A^{(1)}(k,t) = -2D^2 \pi \, t^2 W_t^{-3} f_w^{-\frac{3}{2}}(0) \, W_t^{-1} f_w^{-\frac{1}{2}}(0) \frac{(\sigma t)^{4\beta_1}}{\sigma^2} (\sigma t)^{\frac{d}{2}} \int_0^1 dp_1 \int_0^1 dp_2$$

$$\int dx \ e^{-\imath k \sqrt{\sigma t} x'} R_2(0, p_1) \, R_2(x', p_1) \left[1 - \frac{g^2(x/\sqrt{\sigma t}, 1-p_1, 1-p_2, 0)}{f_w^2(0)} \right]^{-\frac{3}{2}} \ . \tag{B.112}$$

Notice that the upper integration limit of the x' integral, $L/\sqrt{\sigma t}$, has been taken to infinity which is consitent with the choice of setting the lower integration limit $\sqrt{\sigma t}/L$ to zero in the definition of R_2 above. Therefore, $S_A^{(1)}$ scales in the early time regime like

$$S_A^{(1)}(k,t) \sim -D^2 t^2 W_t^{-3} W_t^{-1} \frac{(\sigma t)^{4\beta_1}}{\sigma^2} \, (\sigma t)^{\frac{d}{2}} = -(F/\sigma)^2 \, (\sigma t)^{4 - \frac{d}{2} - 4\beta_1} \ . \tag{B.113}$$

The limit $\sigma k^2 t \ll 1$ is needed to make the integral over x' only weakly dependent on the dimensionless variable $\sigma k^2 t$. I.e. the leading power law behaviour of $S_A^{(1)}$ is not affected by making $\sigma k^2 t$ smaller. Interestingly, the D dependence of the noise correlator vanishes at this order of iterative approximation signalling that indeed the we cannot simply interpret the current approach as perturbative expansion in the noise strength D. At least, the powers of D are not the same for all moments corresponding to the same order of iteration. For example, $C_0^{(1)} \propto D/W_t \propto D^{1/2}$. However, it is clear that different powers of D will be generated by continuing the iterations.

The scaling of the correlator in long time saturated limit will be studied next. This means that $\sigma t/L^2 \gg 1$ which implies $\sigma k^2 t \gg 1$ because $k_{\text{min}} = 1/L$. Our starting point is Eq. (B.104). As we are assuming that $M \equiv \sigma k^2 t \gg 1$, we notice that the time integrals obtain significant contribution only from small times $p_i < c/M$ $(i = 1, 2)$ c being some (small) constant. Therefore the upper limits of time integrals are set to c/M where $M \equiv \sigma k^2 t$. Subsequent transformation of integration variables $p_i \equiv (c/M) p_i'$ $(i = 1, 2)$ gives

$$S_A^{(1)}(k,t) \ \ \approx \ \ t^2 \, (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2' \ e^{-c(p_1' + p_2')} \, \tilde{C}_A^{(1)}(k, t\,(1 - \tfrac{cp_1'}{M}), t\,(1 - \tfrac{cp_2'}{M})) \tag{B.114}$$

$$\begin{aligned} = \;& -2D^2\pi\, t^2 (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\; e^{-c(p_1'+p_2')}\, w_1^{-3}(t(1-\tfrac{cp_1'}{M}))\, w_1^{-1}(t(1-\tfrac{cp_2'}{M})) \\ & \int^L dx\; e^{-\imath kx} \int_{\frac{1}{L}} dk_3\; \frac{1-e^{-\sigma k_3^2 t(1-\frac{cp_1'}{M})}}{\sigma k_3^2} \int_{\frac{1}{L}} dk_4\; e^{\imath k_4 x}\, \frac{1-e^{-\sigma k_4^2 t(1-\frac{cp_1'}{M})}}{\sigma k_4^2} \\ & \Big[1 - S^2(x, t(1-\tfrac{cp_1'}{M}), t(1-\tfrac{cp_2'}{M}))/(w_1^2(t(1-\tfrac{cp_1'}{M}))\, w_1^2(t(1-\tfrac{cp_2'}{M})))\Big]^{-\frac{3}{2}} \end{aligned} \tag{B.115}$$

Determining the scaling properties is our next task. Surface width (whose explicit L dependence has been suppressed above) behaves like $w_1^2(t\,(1-\frac{cp_i'}{M}), L) \approx w_1^2(t, L) \sim \frac{D}{F\sigma} L^{2\chi_1}$ for times greater than the saturation time $t \gg L^2/\sigma$. The integral over k_4 scales as

$$\int_{\frac{1}{L}} dk\; e^{\imath k_4 x}\, \frac{1-e^{-\sigma k_4^2 t(1-(c/M)p_1')}}{\sigma k_4^2} \approx \int_{\frac{1}{L}} dk_4\; e^{\imath k_4 x}\, \frac{1-e^{-\sigma k_4^2 t}}{\sigma k_4^2} \approx \int_{\frac{1}{L}} dk_4\; e^{\imath k_4 x}\, \frac{1}{\sigma k_4^2}\;. \tag{B.116}$$

For times greater than saturation time $t \gg L^2/\sigma$ the integral over k_4 can be conveniently expressed with the aid of a new scaling function R_2' which is obtained by making the last expression of Eq. (B.116) dimensionless:

$$\sigma^{-1} L^{2-d} \int_1 dk_4'\, \frac{e^{\imath k_4' x/L}}{(k_4')^2} \equiv \sigma^{-1} L^{2-d}\, R_2'(x/L)\;. \tag{B.117}$$

Obviously, $R_2 \to R_2'$ for $\sigma t/L^2 \gg 1$. In terms of R_2' we can also express the scaling of the integral over k_3:

$$\int_{\frac{1}{L}} dk\; \frac{1-e^{-\sigma k_3^2 t(1-(c/M)p_1')}}{\sigma k_3^2} \approx \int_{\frac{1}{L}} dk_3\; \frac{1-e^{-\sigma k_3^2 t}}{\sigma k_3^2} \approx \int_{\frac{1}{L}} dk_3\; \frac{1}{\sigma k_3^2} = \sigma^{-1} L^{2-d}\, R_2'(0)\;, \tag{B.118}$$

Thus, the scaling behaviour of these integrals is identical to that of the surface width. As shown in previous Sect. B.5, S scales as

$$S(x, t(1-\tfrac{cp_1'}{M}), t(1-\tfrac{cp_2'}{M})) \approx W_L^2\, g'(x/L, p_1', p_2')\;, \tag{B.119}$$

where the definition $DL^{2\chi_1}/(F\sigma) \equiv W_L^2$ was used. Substituting these scaling forms into Eq. (B.115) gives

$$\begin{aligned} S_A^{(1)}(k,t) = -2D^2\pi\, t^2 (c/M)^2 & \int_0^1 dp_1' \int_0^1 dp_2'\; e^{-c(p_1'+p_2')} \left(W_L^2\right)^{-\frac{3}{2}} \left(W_L^2\right)^{-\frac{1}{2}} \\ & \int^L dx\, \sigma^{-1} L^{2-d} R_2'(0)\, \sigma^{-1} L^{2-d} R_2'(x/L) \left[1 - \frac{W_L^4\, g'^2(x/L, p_1', p_2')}{W_L^2\, W_L^2}\right]^{-\frac{3}{2}}. \end{aligned} \tag{B.120}$$

Finally, we transform the integration variable $x/L \equiv x'$ and study the structure factor as a function of the smallest wave vector $k_{\text{min}} = 1/L$. The system size dependence will come out correctly for *all* modes since $k_n = 2\pi n/L$ in a finite system, only prefactors will change.

$$\begin{aligned} S_A^{(1)}(1/L, t) = -2D^2\pi\, t^2\, (c/M_L)^2 & \left(W_L^2\right)^{-2} L^d \left(\sigma^{-1} L^{2-d}\right)^2 R_2'(0) \\ & \int_0^1 dp_1' \int_0^1 dp_2'\; e^{-c(p_1'+p_2')} \int dx'\, R_2'(0)\, R_2'(x') \left[1 - g'^2(x', p_1', p_2')\right]^{-\frac{3}{2}}\;, \end{aligned} \tag{B.121}$$

where we have defined $M_L \equiv \sigma t/L^2$ to remind us of the fact that we are in the saturated regime. All in all,

$$S_A^{(1)}(1/L,t) \propto -D^2 t^2\, M_L^{-2} W_L^{-4} L^d \left(\sigma^{-1} L^{2-d}\right)^2 = -(F/\sigma)^2\, L^{8-d-4\chi_1} \tag{B.122}$$

In $d = 1$ we have $S_A^{(1)} \sim L^5$. As a function of the system size the structure factor obeys scaling $S(1/L) \sim L^{2\chi_2+d}$ giving us $\chi_2 = 2$. However, the requirement $Ft/W_t \ll 1$, which is the assumption we have made here, will actually make $S_0^{(1)}$ dominant giving us a smaller global roughness exponent $\chi_2 = 5/4$.

Structure factor $S_B^{(1)}$

When $Ft/W_t \ll 1$, Eq. (B.86) reduces to

$$\tilde{C}_B^{(1)} \approx 2D^2 \!\int\! dx\, e^{-\imath kx} \int dk_3\, e^{-\sigma k_3^2 t_1} \int_0^{t_1}\! ds_1\, e^{\sigma k_3^2 s_1} \int dk_4\, e^{-\sigma k_4^2 t_2} \int_0^{t_2}\! ds_2\, e^{\sigma k_4^2 s_2}\, \frac{\pi\sqrt{2}}{w_2}\, a_1^{-\frac{3}{2}} \frac{S}{2w_2^2} \tag{B.123}$$

Performing the time integrations over s_i $(i = 1, 2)$ and including the system size dependence gives

$$\begin{aligned}
\tilde{C}_B^{(1)} &= 2D^2 \int^L\! dx\, e^{-\imath kx} \int_{\frac{1}{L}}\! dk_3\, \frac{1-e^{-\sigma k_3^2 t_1}}{\sigma k_3^2} \int_{\frac{1}{L}}\! dk_4\, \frac{1-e^{-\sigma k_4^2 t_2}}{\sigma k_4^2}\, \frac{\pi}{\sqrt{2}}\, \frac{S(x,t_1,t_2)}{w_2^3\, a_1^{3/2}} && \text{(B.124)}\\
&= 4D^2\pi\, w_1^{-3}(t_1)\, w_1^{-3}(t_2) \int_{\frac{1}{L}}\! dk_3\, \frac{1-e^{-\sigma k_3^2 t_1}}{\sigma k_3^2} \int_{\frac{1}{L}}\! dk_4\, \frac{1-e^{-\sigma k_4^2 t_2}}{\sigma k_4^2} \\
&\qquad \int^L\! dx\, e^{-\imath kx}\, S(x,t_1,t_2) \left[1 - S^2(x,t_1,t_2)/(w_1^2(t_1)\, w_1^2(t_2))\right]^{-\frac{3}{2}} \; . && \text{(B.125)}
\end{aligned}$$

As for $C_A^{(1)}$ it is possible to further reduce the complexity of the correlator $C_B^{(1)}$ by considering various limits of dimensionless variables. We shall directly work with the structure factor in the following. As before (Eq. (B.103)), we find it convenient to change the time variables as $s_i = t(1 - p_i)$ $(i = 1, 2)$:

$$\begin{aligned}
S_B^{(1)}(k,t) &= e^{-2\sigma k^2 t} \int_0^t ds_1 \int_0^t ds_2\; e^{\sigma k^2 (s_1+s_2)}\, \tilde{C}_B^{(1)}(k,s_1,s_2) && \text{(B.126)}\\
&= t^2 \int_0^1 dp_1 \int_0^1 dp_2\; e^{-\sigma k^2 t (p_1+p_2)}\, \tilde{C}_B^{(1)}(k, t(1-p_1), t(1-p_2)) \; . && \text{(B.127)}
\end{aligned}$$

Substitution of the noise correlator yields

$$\begin{aligned}
S_B^{(1)}(k,t) &= 4D^2\pi\, t^2 \int_0^1 dp_1 \int_0^1 dp_2\, e^{-\sigma k^2 t(p_1+p_2)}\, w_1^{-3}(t(1-p_1))\, w_1^{-3}(t(1-p_2)) \\
&\qquad \int_{\frac{1}{L}}\! dk_3\, \frac{1-e^{-\sigma k_3^2 t(1-p_1)}}{\sigma k_3^2} \int_{\frac{1}{L}}\! dk_4\, \frac{1-e^{-\sigma k_4^2 t(1-p_2)}}{\sigma k_4^2} \int^L\! dx\; e^{-\imath kx} \\
&\qquad S(x, t(1-p_1), t(1-p_2)) \left[1 - \frac{S^2(x, t(1-p_1), t(1-p_2))}{w_1^2(t(1-p_1))\, w_1^2(t(1-p_2))}\right]^{-\frac{3}{2}} \; . && \text{(B.128)}
\end{aligned}$$

In the early time regime, $\sigma k^2 t \ll 1$, the surface width $w_1(t(1-p_i)) \sim W_t$ $(i = 1, 2)$. Moreover, the argument of the first exponential in Eq. (B.128) is small for early times and we set $\exp(-\sigma k^2 t(p_1 + p_2)) \approx 1$. Thus,

$$S_B^{(1)}(k,t) \approx 4D^2 \pi\, t^2 \int_0^1 dp_1 \int_0^1 dp_2 \left(W_t^{-3} f_w^{-3/2}(0)\right)^2 \frac{(\sigma t)^{2\beta_1}}{\sigma} R_2(0,p_1) \frac{(\sigma t)^{2\beta_1}}{\sigma} R_2(0,p_2)$$

$$\int^L dx\ e^{-\imath k x}\, W_t^2\, g(x/\sqrt{\sigma t}, 1-p_1, 1-p_2) \left[1 - \frac{W_t^4\, g^2(x/\sqrt{\sigma t}, 1-p_1, 1-p_2)}{W_t^2 f_w(0)\, W_t^2 f_w(0)}\right]^{-\frac{3}{2}} \tag{B.129}$$

Replace x by a scaled variable $x/\sqrt{\sigma t} \equiv x'$ and extract time dependent factors:

$$S_B^{(1)}(k,t) \approx 4D^2 \pi\, t^2 \left(W_t^{-3} f_w^{-3/2}(0)\right)^2 \frac{(\sigma t)^{4\beta_1}}{\sigma^2} W_t^2 (\sigma t)^{\frac{d}{2}} \int_0^1 dp_1 \int_0^1 dp_2 \tag{B.130}$$

$$\int dx\ e^{-\imath k \sqrt{\sigma t} x'}\ g(x', 1-p_1, 1-p_2) \left[1 - \frac{g^2(x', 1-p_1, 1-p_2)}{f_w^2(0)}\right]^{-\frac{3}{2}}. \tag{B.131}$$

In other words,

$$S_B^{(1)}(k,t) \propto D^2 t^2 W_t^{-6} (\sigma t)^{4\beta_1} \sigma^{-2}\, W_t^2\, (\sigma t)^{\frac{d}{2}} = (F/\sigma)^2\, (\sigma t)^{4-\frac{d}{2}-4\beta_1}\ , \tag{B.132}$$

which is the same as the scaling behaviour of $S_A^{(1)}$ in the early time regime except that the overall sign has changed from minus to plus.

In the late time saturated regime $\sigma k^2 t \gg 1$ and $\sigma t/L^2 \gg 1$. Begin with Eq (B.128) and make a transformation of the time variables $p_i \equiv (c/M) p_i'$:

$$\begin{aligned} S_B^{(1)}(k,t) &= t^2 (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\ e^{-c(p_1'+p_2')}\, \tilde{C}_B^{(1)}(k, t(1-\tfrac{cp_1}{M}), t(1-\tfrac{cp_2}{M})) && \text{(B.133)} \\ &= 4D^2 \pi\, t^2 (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\, e^{-c(p_1'+p_2')}\, w_1^{-3}(t(1-\tfrac{cp_1'}{M}))\, w_1^{-3}(t(1-\tfrac{cp_2'}{M})) \\ &\quad \int_{\frac{1}{L}} dk_3\, \frac{1-e^{-\sigma k_3^2 t(1-\frac{cp_1'}{M})}}{\sigma k_3^2} \int_{\frac{1}{L}} dk_4\, \frac{1-e^{-\sigma k_4^2 t(1-\frac{cp_2'}{M})}}{\sigma k_4^2} \int^L dx\ e^{-\imath k x} \\ &\quad S(x, t(1-\tfrac{cp_1'}{M}), t(1-\tfrac{cp_2'}{M})) \left[1 - \frac{S^2(x, t(1-\frac{cp_1'}{M}), t(1-\frac{cp_2'}{M}))}{w_1^2(t(1-\frac{cp_1'}{M}))\, w_1^2(t(1-\frac{cp_2'}{M}))}\right]^{-\frac{3}{2}}. && \text{(B.134)} \end{aligned}$$

Plugging the scaling forms from Eqs. (B.117,B.119) into Eq. (B.134) gives

$$S_B^{(1)}(k,t)\ = 4D^2 \pi\, t^2\, (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\, e^{-c(p_1'+p_2')} \left(W_L^{-3}\right)^2 \left[\sigma^{-1} L^{2-d}\, R_2'(0)\right]^2$$

$$\int^L dx\ e^{-\imath k x}\, W_L^2\, g'(x/L, p_1', p_2') \left[1 - \frac{W_L^4\, g'^2(x/L, p_1', p_2')}{W_L^2\, W_L^2}\right]^{-\frac{3}{2}}. \tag{B.135}$$

Transforming $x' \equiv x/L$ we have the following behaviour for $k = 1/L$:

$$S_B^{(1)}(1/L,t) = 4D^2 \pi\, t^2\, (c/M_L)^2\, W_L^{-6} L^d \left(\sigma^{-1} L^{2-d} R_2'(0)\right)^2 W_L^2$$

$$\int_0^1 dp_1' \int_0^1 dp_2'\ e^{-c(p_1'+p_2')} \int^1 dx'\ e^{-\imath x'}\ g'(x', p_1', p_2') \left[1 - g'^2(x', p_1', p_2')\right]^{-\frac{3}{2}}. \tag{B.136}$$

The apparent t dependence is cancelled by $M_L \equiv \sigma t/L^2$, and we have

$$S_B^{(1)}(1/L,t) \propto D^2 t^2\, M_L^{-2} W_L^{-6} L^d \left(\sigma^{-1} L^{2-d}\right)^2 W_L^2 = (F/\sigma)^2\, L^{8-d-4\chi_1}\ . \tag{B.137}$$

The scaling behaviour is identical to that of $C_A^{(1)}$ apart from the sign of the correlator.

Structure factor $S_C^{(1)}$

Simplify correlator in the limit $Ft/W_t \ll 1$ (Eq. (B.95)). Performing the time integrations over s_i $(i = 1, 2)$ and including the system size dependence we have

$$\tilde{C}_C^{(1)} = 2D^2 \int^L dx\, e^{-\imath kx} \int_{\frac{1}{L}} dk_3\, e^{-\imath k_3 x}\, \frac{1-e^{-\sigma k_3^2 t_2}}{\sigma k_3^2} \int_{\frac{1}{L}} dk_4\, e^{\imath k_4 x}\, \frac{1-e^{-\sigma k_4^2 t_1}}{\sigma k_4^2}\, \frac{\pi\, S(x,t_1,t_2)}{\sqrt{2}\, w_2^3\, a_1^{3/2}}\ . \tag{B.138}$$

With arguments fully shown, the previous expression reads as

$$\begin{aligned} \tilde{C}_C^{(1)} \;&=\; 4D^2\pi\, w_1^{-3}(t_1)\, w_1^{-3}(t_2) \int^L dx\, e^{-\imath kx} \int_{\frac{1}{L}} dk_3\, e^{-\imath k_3 x}\, \frac{1-e^{-\sigma k_3^2 t_2}}{\sigma k_3^2} \\ &\int_{\frac{1}{L}} dk_4\, e^{\imath k_4 x}\, \frac{1-e^{-\sigma k_4^2 t_1}}{\sigma k_4^2}\, S(x,t_1,t_2) \left[1 - \frac{S^2(x,t_1,t_2)}{w_1^2(t_1) w_1^2(t_2)}\right]^{-\frac{3}{2}}. \end{aligned} \tag{B.139}$$

Calculation of the structure factor proceeds in the familiar manner:

$$S_C^{(1)}(k,t) \;=\; e^{-2\sigma k^2 t} \int_0^t ds_1 \int_0^t ds_2\; e^{\sigma k^2 (s_1+s_2)}\, \tilde{C}_C^{(1)}(k,s_1,s_2) \tag{B.140}$$

$$\;=\; t^2 \int_0^1 dp_1 \int_0^1 dp_2\; e^{-\sigma k^2 t(p_1+p_2)}\, \tilde{C}_C^{(1)}(k, t(1-p_1), t(1-p_2))\ . \tag{B.141}$$

Substitution of the noise correlator yields

$$\begin{aligned} S_C^{(1)}(k,t) \;&=\; 4D^2\pi\, t^2 \int_0^1 dp_1 \int_0^1 dp_2\; e^{-\sigma k^2 t(p_1+p_2)}\, w_1^{-3}(t(1-p_1))\, w_1^{-3}(t(1-p_2)) \\ &\int^L dx\; e^{-\imath kx} \int_{\frac{1}{L}} dk_3\; e^{-\imath k_3 x}\, \frac{1-e^{-\sigma k_3^2 t(1-p_2)}}{\sigma k_3^2} \int_{\frac{1}{L}} dk_4\; e^{\imath k_4 x}\, \frac{1-e^{-\sigma k_4^2 t(1-p_1)}}{\sigma k_4^2} \\ &S(x, t(1-p_1), t(1-p_2)) \left[1 - \frac{S^2(x, t(1-p_1), t(1-p_2))}{w_1^2(t(1-p_1))\, w_1^2(t(1-p_2))}\right]^{-\frac{3}{2}}. \end{aligned} \tag{B.142}$$

Surface width follows the scaling $w(t(1-p_i)) \sim W_t$ for small enough times t. For the same reason we can set $\exp(-\sigma k^2 t(p_1+p_2)) \approx 1$ in Eq. (B.141). Thus,

$$\begin{aligned} S_C^{(1)}(k,t) \;&=\; 4D^2\pi\, t^2 \int_0^1 dp_1 \int_0^1 dp_2\, W_t^{-3} f_w^{-3/2}(0)\; W_t^{-3} f_w^{-3/2}(0) \\ &\int^L dx\; e^{-\imath kx}\, \frac{(\sigma t)^{2\beta_1}}{\sigma} R_2(x/\sqrt{\sigma t}, p_2)\; \frac{(\sigma t)^{2\beta_1}}{\sigma} R_2(x/\sqrt{\sigma t}, p_1) \\ &W_t^2\, g(x/\sqrt{\sigma t}, 1-p_1, 1-p_2) \left[1 - \frac{W_t^4\, g^2(x/\sqrt{\sigma t}, 1-p_1, 1-p_2)}{W_t^2 f_w(0)\, W_t^2 f_w(0)}\right]^{-\frac{3}{2}}. \end{aligned} \tag{B.143}$$

As a final step we transform $x/\sqrt{\sigma t} \equiv x'$ and pull out the time dependent terms to obtain

$$\begin{aligned} S_C^{(1)}(k,t) &= 4D^2 \pi\, t^2 \left(W_t^{-3} f_w^{-3/2}(0)\right)^2 \frac{(\sigma t)^{4\beta_1}}{\sigma^2}\, W_t^2\, (\sigma t)^{\frac{d}{2}} \int_0^1 dp_1 \int_0^1 dp_2 \int dx'\; e^{-\imath k \sqrt{\sigma t} x'} \\ & \qquad R_2(x', p_2)\, R_2(x', p_1)\, g(x', 1-p_1, 1-p_2) \left[1 - \frac{g^2(x', 1-p_1, 1-p_2)}{f_w^2(0)}\right]^{-\frac{3}{2}} && \text{(B.144)} \\ &\propto D^2\, t^2\, W_t^{-6}\, (\sigma t)^{2-d}\, \sigma^{-2}\, W_t^2\, (\sigma t)^{\frac{d}{2}} = (F/\sigma)^2\, (\sigma t)^{4-\frac{d}{2}-4\beta_1}\ . && \text{(B.145)} \end{aligned}$$

Again, we should take the limit $\sigma k^2 t \ll 1$ in which case the function $\exp(-\imath k \sqrt{\sigma t} x')$ in the previous formula affects the value of the integral very weakly. The time scaling of $C_C^{(1)}$ is seen to be the same as that of $C_A^{(1)}$ and $C_B^{(1)}$.

The scaling of the correlator in long time saturated limit $\sigma k^2 t \gg 1$, or $\sigma t/L^2 \gg 1$, can be obtained in the familiar manner. Starting from Eq. (B.142) we set the upper limits of time integrals to c/M where $M \equiv \sigma k^2 t$. Subsequent transformation $p_i \equiv (c/M) p_i'$ $(i = 1, 2)$ gives

$$\begin{aligned} S_C^{(1)}(k,t) &\approx t^2\, (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\; e^{-c(p_1'+p_2')}\, \tilde{C}_C^{(1)}(k, t\,(1 - \tfrac{cp_1'}{M}), t\,(1 - \tfrac{cp_2'}{M})) && \text{(B.146)} \\ &= 4D^2 \pi\, t^2\, (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\; e^{-c(p_1'+p_2')}\, w_1^{-3}(t(1 - \tfrac{cp_1'}{M}))\, w_1^{-3}(t(1 - \tfrac{cp_2'}{M})) \\ & \qquad \int^L dx\; e^{-\imath k x} \int_{\frac{1}{L}} dk_3\; e^{-\imath k_3 x}\, \frac{1 - e^{-\sigma k_3^2 t (1 - \frac{cp_2'}{M})}}{\sigma k_3^2} \int_{\frac{1}{L}} dk_4\; e^{\imath k_4 x}\, \frac{1 - e^{-\sigma k_4^2 t (1 - \frac{cp_1'}{M})}}{\sigma k_4^2} \\ & \qquad S(x, t(1 - \tfrac{cp_1'}{M}), t(1 - \tfrac{cp_2'}{M})) \left[1 - \frac{S^2(x, t(1 - \frac{cp_1'}{M}), t(1 - \frac{cp_2'}{M}))}{w_1^2(t(1 - \frac{cp_1'}{M}))\, w_1^2(t(1 - \frac{cp_2'}{M}))}\right]^{-\frac{3}{2}} . && \text{(B.147)} \end{aligned}$$

Plugging the scaling forms from Eqs. (B.117,B.119) into Eq. (B.147) gives

$$S_C^{(1)}(k,t) \approx 4D^2 \pi\, t^2\, (c/M)^2 \int_0^1 dp_1' \int_0^1 dp_2'\; e^{-c(p_1'+p_2')} \left(W_L^{-3}\right)^2 \int^L dx\; e^{-\imath k x} \tag{B.148}$$

$$\left[\sigma^{-1} L^{2-d} R_2'(x/L)\right]^2 W_L^2\, g'(x/L, p_1', p_2') \left[1 - \frac{W_L^4\, g'^2(x/L, p_1', p_2')}{W_L^2\, W_L^2}\right]^{-\frac{3}{2}} \tag{B.149}$$

Transform variable $x' \equiv x/L$ and study scaling of the smallest k-mode:

$$\begin{aligned} & S_C^{(1)}(1/L, t) = 4D^2 \pi\, t^2\, (c/M_L)^2 W_L^{-6} L^d \left(\sigma^{-1} L^{2-d}\right)^2 W_L^2 && \text{(B.150)} \\ & \int_0^1 dp_1' \int_0^1 dp_2'\, e^{-c(p_1'+p_2')} \int^1 dx'\; e^{-\imath x'}\, \left[R_2'(x')\right]^2 g'(x', p_1', p_2') \left[1 - g'^2(x', p_1', p_2')\right]^{-\frac{3}{2}} \end{aligned}$$

Remembering that $M_L \equiv \sigma t/L^2$ we see that

$$S_C^{(1)}(1/L, t) \propto D^2\, t^2\, M_L^{-2} W_L^{-4} L^d \left(\sigma^{-1} L^{2-d}\right)^2 = (F/\sigma)^2\, L^{8-d-4\chi_1}\ . \tag{B.151}$$

This is consistent with the system size scaling of correlators $C_A^{(1)}$ and $C_B^{(1)}$.

B.6 Non-Gaussian features

Using the cumulant expansion we can evaluate the noise average of the first term in Eq. (B.11) exactly for any statistics of α, at least in principle. For white noise we have

$$\langle e^{\imath q_1 \Delta_H} \rangle_\alpha = \langle e^{\imath q_1 \Delta_H} \rangle_H = \exp\left(\sum_{n=0}^{\infty} \frac{(\imath q_1)^n}{n!} \kappa_n(\Delta_H) \right) , \tag{B.152}$$

where we have defined $\Delta_H \equiv H(1) - H(2)$ and $\kappa_n(x) \equiv \langle x^n \rangle_c$ denotes the nth cumulant of x. To justify the first equality of Eq. (B.152) we note that having two stochastic variables α and H related to each other implicitly as $H = H(\alpha)$ we can perform average of expression $R(H)$ in two ways:

$$\begin{aligned} \langle R(H) \rangle_H &\equiv \int R(H) g(H) dH = \int R(H(\alpha)) g(H(\alpha)) (dH/d\alpha) d\alpha && \text{(B.153)} \\ &\equiv \int R(H(\alpha)) f(\alpha) d\alpha \equiv \langle R(H(\alpha)) \rangle_\alpha \; . && \text{(B.154)} \end{aligned}$$

The probability densities of specific realizations of α and H have been denoted by $f(\alpha)$ and $g(H)$ respectively. They are related to each other through $f(\alpha)d\alpha = g(H)dH$. Thus, the averaging in Eqs. (B.20,B.23) when regarded as over α gives rise to the functional determinant when averaging over H. For example,

$$\langle (H(\alpha(1)) - H(\alpha(2))) \rangle_\alpha = \int (H(1) - H(2)) (d\alpha/dH) dH = \langle (H(1) - H(2)) \rangle_H \tag{B.155}$$

For practical calculations we always average over the noise field α since we its probability distribution from the outset where as that for H has to be constructed perturbatively.

Because of the quenched noise field the full solution to Eq. (12.15) is an infinite set of coupled nonlinear equations for the different moments (cumulants) of H. Writing the nth cumulant of H as κ_n we obtain a BBGKY hierarchy of the type

$$\begin{aligned} \kappa_1 &= \kappa_1[-, \kappa_2, \kappa_3, \kappa_4, \ldots] && \text{(B.156)} \\ \kappa_2 &= \kappa_2[\kappa_1, -, \kappa_3, \kappa_4, \ldots] && \text{(B.157)} \\ \kappa_3 &= \kappa_3[\kappa_1, \kappa_2, -, \kappa_4, \ldots] && \text{(B.158)} \\ \kappa_4 &= \kappa_4[\kappa_1, \kappa_2, \kappa_3, -, \ldots] && \text{(B.159)} \\ &\vdots \end{aligned}$$

As usual, we have to truncate the hierarchy. In all of our examples we will be closing the moment hierarchy after the second moment. Since the higher moments are expected to be expressible via the first and second, we are trying to mimic a very complicated nonlinear stochastic process with a Gaussian process when we make specific computations. This limitation is in principle easily lifted and higher order closures can be constructed straightforwardly at the expense of calculational effort.

B.7 Some integrals

Performing q_2-integration first,

$$I \equiv \int dq_1 \int dq_2 \, e^{\imath q_1 F(t_1 - s_1)} \, e^{\imath q_2 F(t_2 - s_2)} \, U(q_1, q_2) \tag{B.160}$$

$$= \int dq_1\, e^{\imath q_1 F(t_1-s_1) - w_1^2 q_1^2/2} \int dq_2\, e^{\imath q_2 F(t_2-s_2) - w_2^2 q_2^2/2 - S q_1 q_2} \ . \tag{B.161}$$

Completing square in the latter integral gives

$$\begin{aligned} &\int dq_2\, e^{-(w_2^2/2)(q_2^2 - 2w_2^{-2}(\imath F(t_2-s_2) - S q_1))} \\ &\quad = \int dq_2\, e^{-(w_2^2/2)(q_2^2 - 2Aq_2 + A^2 - A^2)} = (2\pi/w_2^2)^{\frac{1}{2}} e^{(w_2 R)^2/2} \ , \end{aligned} \tag{B.162}$$

where we have used $R \equiv (\imath F(t_2 - s_2) - S q_1)/w_2^2$. Gaussian integration is valid when $w_2^2 > 0$. Plugging the results back into Eq. (B.161) gives

$$I = (2\pi/w_2^2)^{\frac{1}{2}} \int dq_1\, \exp(\imath q_1 F(t_1 - s_1) - w_1^2 q_1^2/2)\, \exp((w_2 R)^2/2) \ . \tag{B.163}$$

Time differences will be abbreviated as $t_i - s_i \equiv \Delta_i$ $(i = 1, 2)$. Regrouping the terms in the exponential and completing the square yields

$$\begin{aligned} &\imath q_1 F \Delta_1 - w_1^2 q_1^2/2 + [-F^2 \Delta_2^2 - 2\imath F \Delta_2 S q_1 + S^2 q_1^2]/(2w_2^2) \\ &= -F^2 \Delta_2^2/(2w_2^2) - w_1^2 q_1^2/2 + \imath q_1 F \Delta_1 - \imath F \Delta_2 S q_1/w_2^2 + s^2 q_1^2/(2w_2^2) && \text{(B.164)} \\ &= -F^2 \Delta_2^2/(2w_2^2) - (w_1^2 - S^2/w_2^2)\, q_1^2/2 + \imath F[\Delta_1 - \Delta_2 S/w_2^2]\, q_1 && \text{(B.165)} \\ &= -F^2 \Delta_2^2/(2w_2^2) - a_1 q_1^2 + 2a_2 q_1 \ , && \text{(B.166)} \end{aligned}$$

where we define

$$a_1 \equiv (1/2)(w_1^2 - S^2/w_2^2) \quad ; \quad a_2 \equiv (\imath F/2)[(t_1 - s_1) - (t_2 - s_2) S/w_2^2] \ . \tag{B.167}$$

The last remaining Gaussian integral gives

$$\begin{aligned} I &= (2\pi/w_2^2)^{1/2} \exp(-F^2 (t_2 - s_2)^2/(2w_2^2)) \int dq_1\, \exp(-a_1 q_1^2 + 2a_2 q_2^2) && \text{(B.168)} \\ &= \frac{\pi\sqrt{2}}{w_2 \sqrt{a_1}} \exp\left(-\frac{F^2 (t_2 - s_2)^2}{2w_2^2} + \frac{a_2^2}{a_1} \right) \ . && \text{(B.169)} \end{aligned}$$

The validity of this result obviously depends on the positivity of a_1. It is easy to show that $a_1 > 0$ except when $t_1 = t_2$.

Next, we will rewrite the argument of the exponential in Eq. (B.169) in a more symmetrical form to show that times t_1 and t_2 can be interchanged.

$$\begin{aligned} &-\frac{F^2}{2w_2^2}\Delta_2^2 + \frac{a_2^2}{a_1} = -\frac{F^2}{2w_2^2}\Delta_2^2 - \frac{1}{a_1}\frac{F^2}{4}\left(\Delta_1 - \Delta_2 \frac{S}{w_2^2}\right)^2 && \text{(B.170)} \\ &= -\frac{F^2}{4a_1 w_2^2}\left[2a_1 \Delta_2^2 + w_2^2 \left(\Delta_1 - \Delta_2 \frac{S}{w_2^2}\right)^2\right] && \text{(B.171)} \\ &= -\frac{F^2}{4a_1 w_2^2}\left[w_1^2 \Delta_2^2 - \frac{S^2}{w_2^2}\Delta_2^2 + w_2^2 \left(\Delta_1^2 - 2\Delta_1 \Delta_2 \frac{S}{w_2^2} + \Delta_2^2 \frac{S^2}{w^4}\right)\right] && \text{(B.172)} \\ &= -\frac{F^2\,(w_1^2 \Delta_1^2 + w_2^2 \Delta_1^2 - 2\Delta_1 \Delta_2 S)}{2(w_1^2 w_2^2 - S^2)} \ . && \text{(B.173)} \end{aligned}$$

In the last line we used the definition of $a_1 \equiv \frac{1}{2}(w_1^2 - S^2/w_2^2)$.

Finally, we take derivatives of I with respect to w_1^2 (w_2^2) which is need for calculation of noise correlator C_A (C_D):

$$\partial_{w_1^2} I = \frac{\pi\sqrt{2}}{w_2} \exp\left(-\frac{F^2\Delta_2^2}{2w_2^2}\right) \partial_{w_1^2}\left[a_1^{-\frac{1}{2}} \exp\left(a_2^2/a_1\right)\right] \ . \tag{B.174}$$

Performing the latter differentiation

$$\partial_{w_1^2}\left[a_1^{-\frac{1}{2}} \exp\left(a_2^2/a_1\right)\right] = \left[\partial_{w_1^2}(a_1^{-\frac{1}{2}}) + a_1^{-\frac{1}{2}}\partial_{w_1^2}\left(a_2^2/a_1\right)\right] \exp\left(a_2^2/a_1\right) \tag{B.175}$$

$$= \left[-\partial_{w_1^2}(a_1)/(2a_1^{\frac{3}{2}}) - (a_2^2/a_1^{\frac{5}{2}})\,\partial_{w_1^2}(a_1)\right] \exp\left(a_2^2/a_1\right) \ . \tag{B.176}$$

Combining the Eq. (B.174) with Eq. (B.176) yields

$$\partial_{w_1^2} I = \frac{\pi\sqrt{2}}{4w_2} a_1^{-\frac{3}{2}} \left(-1 - 2a_2^2/a_1\right) \exp\left(-\frac{F^2\Delta_2^2}{2w_2^2} + \frac{a_2^2}{a_1}\right) \ . \tag{B.177}$$

Differentiation of I with respect to S is needed for calculation of noise correlators C_B and C_A. Instead of Eq. (B.175) we get now

$$\partial_S\left[a_1^{-\frac{1}{2}} \exp\left(a_2^2/a_1\right)\right] = \left[\partial_S(a_1^{-\frac{1}{2}}) + a_1^{-\frac{1}{2}}\partial_S\left(a_2^2/a_1\right)\right] \exp\left(a_2^2/a_1\right) \tag{B.178}$$

$$= \left[-\partial_S(a_1)/(2a_1^{\frac{3}{2}}) + a_1^{-\frac{1}{2}}\left(2\frac{a_2}{a_1}\partial_S(a_2) - \frac{a_2^2}{a_1^2}\partial_S(a_1)\right)\right] \exp\left(a_2^2/a_1\right) \ . \tag{B.179}$$

Thus,

$$\partial_S I = \frac{\pi\sqrt{2}}{w_2} a_1^{-\frac{3}{2}} \left[\frac{S}{2w_2^2} - a_2\frac{\imath F\Delta_2}{w_2^2} + \frac{Sa_2^2}{w_2^2 a_1}\right] \exp\left(-\frac{F^2\Delta_2^2}{2w_2^2} + \frac{a_2^2}{a_1}\right) \ . \tag{B.180}$$

Again, we should be able to put the result in a symmetric form since we know that the time and spatial arguments of noise correlators C_B and C_C can be interchanged.

$$\partial_S I = \frac{\pi\sqrt{2}}{w_2^3} a_1^{-3/2} \left[\frac{S}{2} - a_2 \imath F\Delta_2 + \frac{Sa_2^2}{a_1}\right] \tag{B.181}$$

$$= \frac{\pi\sqrt{2}}{w_2^3} a_1^{-3/2} \left[\frac{S}{2} - a_2 \imath F\Delta_2 + S\left(\frac{a_2^2}{a_1} - \frac{F^2\Delta_2^2}{2w_2^2} + \frac{F^2\Delta_2^2}{2w_2^2}\right)\right] \tag{B.182}$$

$$= \frac{\pi\sqrt{2}}{w_2^3} a_1^{-3/2} \left[\frac{S}{2} - a_2 \imath F\Delta_2 + \frac{SF\Delta_2^2}{2w_2^2} + S\left(\frac{a_2^2}{a_1} - \frac{F^2\Delta_2^2}{2w_2^2}\right)\right] \tag{B.183}$$

$$= \frac{\pi\sqrt{2}}{w_2^3} a_1^{-3/2} \left[\frac{S}{2} + \frac{F^2}{2}\Delta_1\Delta_2 + S\left(\frac{a_2^2}{a_1} - \frac{F^2\Delta_2^2}{2w_2^2}\right)\right] \tag{B.184}$$

$$= \frac{4\pi}{w_1^2 w_2^3} \left(1 - \frac{S^2}{w_1^2 w_2^2}\right)^{-3/2} \left[\frac{S}{2} + \frac{F^2}{2}\Delta_1\Delta_2 + S\left(\frac{a_2^2}{a_1} - \frac{F^2\Delta_2^2}{2w_2^2}\right)\right] \ . \tag{B.185}$$

This form is clearly symmetric since the expression $(a_2^2/a_1 - F^2\Delta_2^2/(2w_2^2))$ is the argument of the exponential function, the symmetry of which we have demonstrated in App. B.4.

B.8 Delta functions in correlators

We shall demonstrate below that taking the limit $M \equiv Ft/W_t \to \infty$ noise correlator C_0 reduces to a delta function correlator characteristic of Edwards-Wilkinson model. We use the following representation of the delta function

$$\lim_{M\to\infty} Me^{-M^2x^2} \to \delta(x) \ , \tag{B.186}$$

where the limit is understood to be taken after integration. How to cast the correlator $C_0^{(1)}$ into this form?

$$\tilde{C}_0(k, ts_1; k', ts_2) = D[G_c^{(1)}(0, ts_1, ts_2)]^{-1/2} \exp\left(\frac{(Ft)^2(s_1 - s_2)^2}{G_c^{(1)}(0, ts_1, ts_2)}\right) \tag{B.187}$$

Using Eq. (12.29) and Eq. (12.30) we can write the correlation function as

$$G_c^{(1)}(0, ts_1, ts_2) \propto \left[s_1^{2\beta_1} f_w(0) + s_2^{2\beta_1} f_w(0) - 2g(0, s_1, s_2, 0)\right] \tag{B.188}$$

$$= s_1^{2\beta_1}\int dk\, \frac{1 - e^{-2k^2 s_1}}{2k^2}\left[1 - e^{-k^2(s_2 - s_1)}\right] + s_2^{2\beta_1}\int dk\, \frac{1 - e^{-2k^2 s_2}}{2k^2}\left[1 - e^{-k^2(s_1 - s_2)}\right]$$

where the definition of $f_w(0)$ was also utilized (Eq. (B.45)). When $s_1 \approx s_2$, we can expand the exponentials. This shows that $G_c^{(1)} \sim \sqrt{s_1 - s_2}$ and the argument of the exponential goes as

$$\frac{(Ft)^2(s_1 - s_2)^2}{G_c^{(1)}(0, ts_1, ts_2)} \sim (s_1 - s_2)^{1/2} \tag{B.189}$$

Changing the variables in the familiar manner as $s_1 - s_2 \equiv u$ and $s_1 + s_2 \equiv 2U$ and concentrating on the limit $u \to 0$ we see that Eq. (B.189) goes effectively like $c\sqrt{u}$. Making the argument of the emerging delta function linear in u is readily done: $\delta(c\sqrt{u}) = (2/c)\sqrt{u}\,\delta(u)$. The prefactor is cancelled by the term $[G_c^{(1)}(0, ts_1, ts_2)]^{-1/2}$ multiplying the exponential leaving us just with $\delta(u) = \delta(s_1 - s_2)$ when s_1 is very close to s_2. Hence, we confirm that $C_0^{(1)}$ gives rise to the annealed noise term when $M \gg 1$.

Next, we wish to demonstrate that the limit $M \to \infty$ is well defined for noise correlators C_i ($i = A, B, C, D$). Part of the their integrand consists of expression of the form $M^2 \exp(-(M^2/2)m_2)$. First, we introduce the representation of a *two dimensional* delta function:

$$\lim_{M\to\infty} M^2 e^{-M^2(x^2+y^2)} = \lim_{M\to\infty} Me^{-M^2x^2} \lim_{M\to\infty} Me^{-M^2y^2} \to \delta(x)\delta(y) \ . \tag{B.190}$$

In the case of noise correlators C_i ($i = A, B, C, D$) we have essentially this situation. The only thing that remains to be done is to show that we can separate the arguments of the exponentials in such a way that the quadratic combinations only contain independent variables (like x and y). This is easily done by first defining new time variables: $s_i'' \equiv p_i - s_i'$, $i = 1, 2$. Then $m_2(x', p_1, p_2, s_1', s_2')$ (Eq. (B.81)) transforms as,

$$\frac{p_1^{2\beta_1} f_w(0)(p_1 - s_1')^2 + p_2^{2\beta_1} f_w(0)(p_2 - s_2')^2 - (p_1 - s_1')(p_2 - s_2')g(x', p_1, p_2)}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2)} \tag{B.191}$$

$$= \frac{p_1^{2\beta_1} f_w(0)(s_1'')^2 + p_2^{2\beta_1} f_w(0)(s_2'')^2 - (s_1'')(s_2'')g(x', p_1, p_2)}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2)} = a(s_1'')^2 + b(s_2'')^2 - cs_1''s_2''$$

where the coefficients are defined as

$$a \equiv \frac{p_1^{2\beta_1} f_w(0)}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2, 0)} \; . \tag{B.192}$$

$$b \equiv \frac{p_2^{2\beta_1} f_w(0)}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2, 0)} \; . \tag{B.193}$$

$$c \equiv \frac{2g(x', p_1, p_2, 0)}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2, 0)} \; . \tag{B.194}$$

In terms of matrices the quadratic form is expressible as $a(s_1'')^2 + b(s_2'')^2 - c s_1'' s_2'' = \underline{s}^T A \underline{s}$, where $\underline{s}^T \equiv [s_1'', s_2'']$, and

$$A \equiv \begin{pmatrix} a & -c/2 \\ -c/2 & b \end{pmatrix} \tag{B.195}$$

We find the eigenvalues λ_i and eigenvectors $\underline{r}_i$ $(i = 1, 2)$ of the symmetric matrix A. With the aid of these we can construct a diagonalizing orthogonal matrix Q satisfying

$$(Q\underline{s})^T Q A Q^T (Q\underline{s}) = (Q\underline{s})^T D (Q\underline{s}) \; , \tag{B.196}$$

where $D = \mathrm{diag}\{\lambda_1, \lambda_2\}$ is a diagonal matrix. The eigenvalues are $\lambda_1 = (1/2)(a+b) + (1/2)\sqrt{(a-b)^2 + c^2}$ and $\lambda_2 = (1/2)(a+b) - (1/2)\sqrt{(a-b)^2 + c^2}$. The diagonalizing matrix

$$Q = \frac{1}{2\sqrt{(a-b)^2 + c^2}} \begin{pmatrix} c & c \\ (a-b) - \sqrt{(a-b)^2 + c^2} & (a-b) + \sqrt{(a-b)^2 + c^2} \end{pmatrix} \tag{B.197}$$

In the new coordinates $\underline{r} = Q\underline{s}$ we have

$$\lim_{M_w \to \infty} M_w^2 \exp\left(-M_w^2 m_2/2\right) \tag{B.198}$$

$$= \lim_{M_w \to \infty} M_w^2 \exp\left(-\frac{M_w^2}{2} \frac{\lambda_1 r_1^2 + \lambda_2 r_2^2}{p_1^{2\beta_1} p_2^{2\beta_1} f_w^2(0) - g^2(x', p_1, p_2, 0)}\right) \tag{B.199}$$

This is of the same form as Eq. (B.190) showing that the limit can be safely taken. In other words, the factor $M_w^2 \equiv (Ft/W_t)^2$ multiplying the exponential doesn't change the scaling behaviour of $C_A^{(1)}$ in the limit $M \to \infty$ since it can be absorbed into the definition of the delta function. The powerlaw behaviour $C_A^{(1)} \sim t^{2-d/2-4\beta_1}$ of the regime $M_w \ll 1$ will remain the same.

Appendix C

Details of contact line model

C.1 Miscellanea on projection

The projection can be carried out at least in two different ways. One possibility [337] is to use project both sides of the equation of motion for the bulk order parameter field ϕ *after* performing the functional derivative. For Model A we have:

$$\int dz\, \partial_z \phi\, \partial_t \textsc{h} = \int dz\, \partial_z \phi \left[-\nabla^2 \phi + \partial V(\phi)/\partial \phi \right] \ , \tag{C.1}$$

where the functional form of the free energy $F_{3D} = \int dV dt\, [\, |\nabla \phi|/2 + V(\phi)\,]$. The other possibility is not to perform the functional derivative with respect to ϕ but with respect to a new collective coordinate $\textsc{h}$ for which we first have to get an effective free energy for. Expressing ϕ in terms of the collective coordinate $\textsc{h}$ gives approximately

$$\phi_{\mathrm{H}}(\mathbf{r}, \textsc{h}(\mathbf{r},t), t) \approx \tanh\left(\frac{\textsc{h}(\mathbf{r},t) - z}{\xi} \right) \ , \tag{C.2}$$

where ξ is the width of the interface (approaches zero in the sharp interface limit) and $\mathbf{r} = (x, y)$. Thus,

$$F_{3D}[\phi_{\mathrm{H}}] \equiv F_{2D}[\textsc{h}], \tag{C.3}$$

which in terms of densities f_{3D} and f_{2D} reads

$$\int dz\, f_{3D}(\phi_{\mathrm{H}}) = f_{2D}(\textsc{h}) \ . \tag{C.4}$$

We note that the condition $\phi_{\mathrm{H}}(x, y, \textsc{h}, t) = 0$ defines $\textsc{h}(x, y, t)$. Of course, we could also use some other level set to define the position of the phase boundary: $\phi(x, y, \textsc{h}, t) = \mathit{const} \neq 0$ would do equally well. The defining condition is nonlinear as opposed to the connection between the meniscus $\textsc{h}(x, y, t)$ and the contact line $\textsc{c}(x, t)$: $\textsc{h}(x, 0, t) \equiv \textsc{c}(x, t)$. After this step, we can effect the projection on the functional differentiation operator in the equation of motion as follows:

$$\int dz\, \partial_z \phi\, \partial_t \textsc{h} = \int dz\, \partial_z \phi\, \frac{\delta}{\delta \phi(x, y, z, t)} F_{3D}[\phi] = \frac{\delta}{\delta \textsc{h}(x, y, t)} F_{2D}[\textsc{h}] \ . \tag{C.5}$$

Even though $\phi(x,y,\mathrm{H},t)=0$ by definition, the *variation* $\delta\phi(x,y,\mathrm{H},t)\neq 0$. In other words, projection removes the z-dependence, which is supposed to be rather non-interesting at distances larger than ξ, the correlation length, from the interface. Only the interesting interfacial degrees of freedom survive the projection.

The same formalism goes through for both for Model A and Model B, only the form of the Rayleigh dissipation functional, to be specified below, changes. The equation of motion for the phase field is given by

$$\frac{\delta R_{3D}[\partial_t\phi]}{\delta(\partial_t\phi)} = -\frac{\delta F_{3D}[\phi]}{\delta\phi} \tag{C.6}$$

In case of the non-conserved Model A we define the Rayleigh dissipation functional as follows:

$$R_{3D} \equiv \int dV \int dt\, \frac{1}{2}(\partial_t\phi)^2\ . \tag{C.7}$$

When order parameter ϕ is conserved, Eq. (C.6) gives still the dynamics, but for the dissipation functional we should write

$$R_{3D} \equiv \int dV \int dV' \int dt \int dt'\ \frac{1}{2}\,\partial_t\phi\, G_{3D}\,\partial_{t'}\phi\ , \tag{C.8}$$

where G_{3D} is the Green function resulting from the inversion of the Laplacian and it has been further assumed that Green's boundary terms vanish all together.

To obtain the equation of motion of the meniscus, we can either project the individual terms arising from the functional differentiation in Eq. (C.6) and recast the whole equation into the familiar variational form:

$$\frac{\delta R_{2D}[\partial_t\mathrm{H}]}{\delta(\partial_t\mathrm{H})} = -\frac{\delta F_{2D}[\mathrm{H}]}{\delta\mathrm{H}} \tag{C.9}$$

The other possibility is to use functional methods briefly described at the end of this appendix. For computational purposes it is useful to go over to a curvilinear $(u,\mathbf{s})$-coordinate system. Above (Eq. (C.5)) we approximated $z\approx u$, the liquid-gas interface being almost horizontal. Having just a single wall we can think of a curvilinear coordinate system where u is perpendicular to all three phase boundaries (if the liquid-gas interface is just a straight line, we could use polar coordinates (r,θ) with the identification $\theta=u$, and place the origin at the contact point (line) of the three phases.) For two vertical walls we have to invent a more complicated curvilinear coordinate system such that u-axis coincides with the normal directions of each phase boundaries at any particular boundary point, For a single wall the intuitively clear effective free energy which doesn't contain any bulk contribution any more is given by

$$\begin{aligned} F_{2D} &= \int dt \int dV \left(\sigma\sqrt{1+|\nabla\mathrm{H}|^2}\,\delta_{LG} + (\sigma_{sl}(x,z)-\sigma_{sg}(x,z))\,\delta_{SF}\right) \\ &= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dx \int_{0}^{\infty} dy\, \sigma\sqrt{1+|\nabla\mathrm{H}(x,y,t)|^2} + \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dx \int_{0}^{\mathrm{C}(x,t)} dz\, (\sigma_{sl}(x,z)-\sigma_{sg}(x,z))\ . \end{aligned} \tag{C.10}$$

In the first line the delta functions δ_{LG} and δ_{SF} define where the liquid-gas and solid-fluid (solid-gas or solid-liquid) interfaces are located. The square root contribution arises in the capillary wave approximation. For more detailed descriptions of the effective Hamiltonian of the liquid-vapour interfaces one can consult Refs. [352, 353]. Taking a variation of F_{2D} with respect to $\textsc{h}$ *and keeping the contact line position* $\textsc{c}(x,t)$ *fixed at the same time* yields the final equality in Eq. (8.43). This is analogous to the two stage minimization procedure of Ref. [285] Notice also the obvious analogy with the wall potential of conventional wetting theory where the free energy has the form [353]:

$$F[m] = \int d\mathbf{y} \left\{ \int_0^{\infty} dz \, \left[\frac{1}{2} |\nabla m|^2 + \Phi(m) \right] + \frac{g}{2} m_1^2 - m_1 h_1 \right\} \ . \tag{C.11}$$

The bulk order parameter is m, bulk potential is Φ, and the parameters h_1 and g denote the surface field and enhancement respectively. The value of the order parameter at the wall is $m_1(\mathbf{y}) = m(\mathbf{y}, 0)$. Integrating out the z-coordinate in Eq. (C.10) we can see the latter term (local surface tension fluctuations) as a nonlinear analogue of the surface field term of Eq. (C.11): Making σ_{sl} and σ_{sg} independent of z gives $\int^{\textsc{c}} dz \, (\sigma_{sl} - \sigma_{sg}) = h_1 \textsc{c}$, where $h_1 = \sigma_{sl} - \sigma_{sg}$ and $\textsc{c}$ is the surface value of the 'bulk' field $\textsc{h}$: $\textsc{c}(x) = \textsc{h}(x, 0)$.

Using a more proper projection in curvilinear coordinate system for a system with one vertical wall placed at $y = 0$ results in the following set of coupled equations of motion for the different interfaces. Denoting the solid-liquid interface with $\textsc{h}_A(x, z, t)$, solid-gas by $\textsc{h}_B(x, z, t)$ and the liquid-gas interface with $\textsc{h}(x, y, t)$ gives three distinct equations, which are produced by hitting the bulk evolution equation with projectors onto interfaces $\textsc{h}$, $\textsc{h}_A$ and $\textsc{h}_B$. Projection onto interface $\textsc{h}(x, y, t)$ $(y \geq 0)$ gives

$$\begin{aligned}
&\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, G_{3D}(x, y, \textsc{h}(x, y, t); x_1, y_1, \textsc{h}(x_1, y_1, t)) \, \partial_t \textsc{h}(x_1, y_1, t) + \\
&\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\textsc{c}(x_1,t)} dz_1 \, G_{3D}(x, y, \textsc{h}(x, y, t); x_1, \textsc{h}_A(x_1, z_1, t), z_1) \, \partial_t \textsc{h}_A(x_1, z_1, t) + \\
&\int_{-\infty}^{\infty} dx_1 \int_{\textsc{c}(x_1,t)}^{\infty} dz_1 \, G_{3D}(x, y, \textsc{h}(x, y, t); x_1, \textsc{h}_B(x_1, z_1, t), z_1) \, \partial_t \textsc{h}_B(x_1, z_1, t) \\
&= \frac{\sigma}{4} \left(\partial_x^2 + \partial_y^2 \right) \textsc{h}(x, y, t) + \tilde{\Lambda}(x, y, \textsc{h}(x, y, t), t) \ .
\end{aligned} \tag{C.12}$$

Interfaces $\textsc{h}_A$ and $\textsc{h}_B$ are assumed to meet each other at $z = \textsc{c}(x, t)$. Projecting onto interface $\textsc{h}_A(x, z, t)$ $(z \leq \textsc{c}(x, t))$ gives

$$\begin{aligned}
&\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\textsc{c}(x_1,t)} dz_1 \, G_{3D}(x, \textsc{h}_A(x, z, t), z; x_1, \textsc{h}_A(x_1, z_1, t), z_1) \, \partial_t \textsc{h}_A(x_1, z_1, t) + \\
&\int_{-\infty}^{\infty} dx_1 \int_{\textsc{c}(x_1,t)}^{\infty} dz_1 \, G_{3D}(x, \textsc{h}_A(x, z, t), z; x_1, \textsc{h}_B(x_1, z_1, t), z_1) \, \partial_t \textsc{h}_B(x_1, z_1, t) + \\
&\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, G_{3D}(x, \textsc{h}_A(x, z, t), z; x_1, y_1, \textsc{h}(x_1, y_1, t)) \, \partial_t \textsc{h}(x_1, y_1, t) \\
&= \frac{\sigma_{sl}}{4} \left(\partial_x^2 + \partial_z^2 \right) \textsc{h}_A(x, z, t) + \tilde{\Lambda}_{sl}(x, \textsc{h}_A(x, z, t), z, t) \ .
\end{aligned} \tag{C.13}$$

Finally, we have the projection onto the solid-gas interface $\textsc{h}_B(x, z, t)$ $(z > \textsc{c}(x, t))$:

$$\begin{aligned}
&\int_{-\infty}^{\infty} dx_1 \int_{\textsc{c}(x_1,t)}^{\infty} dz_1 \, G_{3D}(x, \textsc{h}_B(x, z, t), z; x_1, \textsc{h}_B(x_1, z_1, t), z_1) \, \partial_t \textsc{h}_B(x_1, z_1, t) + \\
&\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\textsc{c}(x_1,t)} dz_1 \, G_{3D}(x, \textsc{h}_B(x, z, t), z; x_1, \textsc{h}_A(x_1, z_1, t), z_1) \, \partial_t \textsc{h}_A(x_1, z_1, t) +
\end{aligned}$$

$$\int_{-\infty}^{\infty} dx_1 \int_{0}^{\infty} dy_1\, G_{3D}(x, \mathrm{H}_B(x,z,t), z; x_1, y_1, \mathrm{H}(x_1,y_1,t))\, \partial_t \mathrm{H}(x_1,y_1,t)$$
$$= \frac{\sigma_{sg}}{4}\left(\partial_x^2 + \partial_z^2\right) \mathrm{H}_B(x,z,t) + \tilde{\Lambda}_{sg}(x, \mathrm{H}_B(x,z,t), z, t)\ . \tag{C.14}$$

To simplify things further, we assume that the boundary conditions for the chemical potential μ have been chosen in such a way that the Green's surface terms Λ, Λ_{sl} and Λ_{sg} vanish. In addition, the physical fact that the normal velocities $\partial_t \mathrm{H}_A$ and $\partial_t \mathrm{H}_B$ should be zeroes since both these boundaries are fixed by the position of the solid wall for all times. Thus, Eq. (C.12) reduces to

$$\int_{-\infty}^{\infty} dx_1 \int_{0}^{\infty} dy_1\, G_{3D}(x, y, \mathrm{H}(x,y,t); x_1, y_1, \mathrm{H}(x_1,y_1,t))\, \partial_t \mathrm{H}(x_1,y_1,t)$$
$$= \frac{\sigma}{4}\left(\partial_x^2 + \partial_y^2\right) \mathrm{H}(x,y,t)\ . \tag{C.15}$$

This is the fundamental equation of motion (Eq. (8.43)) in the sense that the morphology of H changes considerably in the course of time as compared to H_A and H_B, which are slightly curved close to the contact line but otherwise they conform to the planar wall interface by construction. The other phase boundaries evolution is given by

$$\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\mathrm{C}(x_1,t)} dz_1\, G_{3D}(x, \mathrm{H}_A(x,z,t), z; x_1, \mathrm{H}(x_1,z_1,t), z_1)\, \partial_t \mathrm{H}(x_1,z_1,t)$$
$$= \frac{\sigma_{sl}}{4}\left(\partial_x^2 + \partial_z^2\right) \mathrm{H}_A(x,z,t)\ . \tag{C.16}$$

$$\int_{-\infty}^{\infty} dx_1 \int_{\mathrm{C}(x_1,t)}^{\infty} dz_1\, G_{3D}(x, \mathrm{H}_B(x,z,t), z; x_1, \mathrm{H}(x_1,z_1,t), z_1)\, \partial_t \mathrm{H}(x_1,z_1,t)$$
$$= \frac{\sigma_{sg}}{4}\left(\partial_x^2 + \partial_z^2\right) \mathrm{H}_B(x,z,t)\ . \tag{C.17}$$

By not setting the curvature terms on the right hand side of Eq. (C.16) and Eq. (C.17) equal to zero we are allowing for small deviation from a perfectly flat planar solution close to the contact line. Although we are anticipating a plane like solution $\mathrm{H}_i \approx 0$ $(i = A, B)$ away from the contact line, it is important not to set *both* $\mathrm{H}_i = 0$ *and* $\nabla^2 \mathrm{H}_i = 0$ because then Eq. (C.16) and Eq. (C.17) reduce to a single equation which acts as an extra condition for the meniscus H. There is no guarantee that this extra constraint is compatible with the fundamental Eq. (C.15). Within the current approximation it is possible to solve both H_A and H_B once the solution H of Eq. (C.15) is known, *i.e.* no extra constraint equations for H are generated.

Based on the previous arguments we construct the functionals $R_{2D}[\partial_t \mathrm{H}]$ and $F_{2D}[\mathrm{H}]$ and leave H_A and H_B out of the subsequent analysis. Extremization of these functionals with respect to the meniscus fluctuations yields the equation of motion of the meniscus for a *fixed* contact line position, which acts as a boundary condition for H. Substituting the formal solution of H (which depends on the unknown $\mathrm{C}(x,t)$) back into R_{2D} and F_{2D}, and extremizing the resulting expressions with respect to the contact line C gives an equation of motion for the contact line itself. Mathematically we can express this by projecting $\delta F_{2D}/\delta \mathrm{H}$ onto plane $y = 0$ with the result

$$\frac{\delta F_{2D}[\mathrm{H}_\mathrm{C}]}{\delta \mathrm{H}_\mathrm{C}(x,0,t)} = \int dx' \int dt'\, \frac{\delta \mathrm{C}(x',t')}{\delta \mathrm{H}_\mathrm{C}(x,0,t)} \frac{\delta F_{2D}[\mathrm{H}_\mathrm{C}]}{\delta \mathrm{C}(x',t')} = \frac{\delta F_{1D}[\mathrm{C}]}{\delta \mathrm{C}(x,t)}\ , \tag{C.18}$$

where we have used the fact that $\delta\textsc{c}(x',t')/\delta\textsc{h}_{\mathrm{C}}(x,0,t) = \delta(x-x')\delta(t-t')$ by definition. We have also set $F_{2D}[\textsc{h}_{\mathrm{C}}] \equiv F_{1D}[\textsc{c}]$ where $\textsc{h}_{\mathrm{C}}$ denotes the solution of Eq. (8.43) for the fixed contact line $\textsc{c}(x,t)$. More precisely, we should write

$$\int_0^L dy\, f_{2D}\left(\textsc{h}_{\mathrm{C}}(x,y,t)\right) = f_{1D}(\textsc{c}(x,t)) \ , \tag{C.19}$$

where f_{1D} and f_{2D} denote the free energy densities in one and two dimensions, respectively. Similar arguments hold for the Rayleigh dissipation functional. Finally, it is pointed out that the formal projection of meniscus equation can be cast into a form which is equivalent to Eq. (C.18) by transforming into a curvilinear coordinate system (u, s_1, s_2) from the Cartesian coordinates (x,y,z). In the new coordinates u specifies the distance from the phase boundary (that is, condition $u=0$ is equivalent to $\phi(x,y,H(x,y))=0$), the vector $\mathbf{s} \equiv (s_1, s_2)$ specifies the point on the phase boundary. We obtain

$$\frac{\delta F_{3D}[\phi_{\mathrm{H}}]}{\delta\phi(\mathbf{s},t)} = \int d\mathbf{s}' \int du' \int dt' \, \frac{\delta\textsc{h}(\mathbf{s}',t')}{\delta\phi_{\mathrm{H}}(\mathbf{s},0,t)} \frac{\delta F_{3D}[\phi_{\mathrm{H}}]}{\delta\textsc{h}(\mathbf{s}',t')} = \frac{\delta F_{2D}[\textsc{h}]}{\delta\textsc{h}(\mathbf{s},t)} \ , \tag{C.20}$$

The previous equation enables us to see the formal similarity to Eq. (C.18) at the cost of introduction of more complicated coordinates. What is different with Eq. (C.20) is that unlike $\delta\textsc{c}(x',t')/\delta\textsc{h}_{\mathrm{C}}(x,0,t) = \delta(x-x')\delta(t-t')$ the functional derivative

$$\delta\textsc{h}(\mathbf{s}',t')/\delta\phi_{\mathrm{H}}(\mathbf{s},0,t) = \ ? \ . \tag{C.21}$$

The reason for this is probably easier to see in the Cartesian coordinates. The contact line and the meniscus satisfy a linear relationship: $\textsc{h}_{\mathrm{C}}(x,0,t) = \textsc{c}(x,t)$ whereas the bulk phase field and meniscus are related through a nonlinear condition, $\phi_{\mathrm{H}}(x,y,\textsc{h}(x,y,t),t) = 0$. To calculate the variation in Eq. (C.21) utilize the approximation in Eq. (C.2). Then,

$$\begin{aligned} \frac{\delta\textsc{h}(\mathbf{r}',t')}{\delta\phi_{\mathrm{H}}(\mathbf{r},t)} &= \left[-\xi\, \phi'_{\mathrm{H}} \frac{\delta\textsc{h}(\mathbf{r},t)}{\delta\textsc{h}(\mathbf{r}',t')}\right]^{-1} && \text{(C.22)} \\ &= -\xi^{-1}\cosh^2(0)\, \frac{\delta\textsc{h}(\mathbf{r}',t')}{\delta\textsc{h}(\mathbf{r},t)} = -\xi^{-1}\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t') \ . && \text{(C.23)} \end{aligned}$$

The operation $[\cdot]^{-1}$ means the inverse operator and $\phi'_{\mathrm{H}} = \partial_z\phi_{\mathrm{H}}(z)|_{z=\textsc{h}(\mathbf{r},t)}$. The factor $-\xi^{-1}$ is exactly cancelled by the factor arising from the projection of the velocities on the left hand side of the equation of motion:

$$\frac{\delta\dot{\textsc{h}}(\mathbf{r}',t')}{\delta\dot{\phi}_{\mathrm{H}}(\mathbf{r},t)} = \left[-\xi\, \phi'_{\mathrm{H}} \frac{\delta\dot{\textsc{h}}(\mathbf{r},t)}{\delta\dot{\textsc{h}}(\mathbf{r}',t')}\right]^{-1} = -\xi^{-1}\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t') \ , \tag{C.24}$$

where we have used $\dot{\phi}_{\mathrm{H}}(\mathbf{r},t) \equiv \partial_t\phi_{\mathrm{H}}(\mathbf{r},t) = -\xi\,\phi'_{\mathrm{H}}\,\partial_t\textsc{h}(\mathbf{r},t)$. Direct projection of Cancelling out the common factors on both sides of Eq. (C.6) which arise when changing from the collective coordinate $\phi_{\mathrm{H}}(\mathbf{r},\textsc{h}(\mathbf{r}),t),t$ to $\textsc{h}(\mathbf{r},t)$ using the functional chain rule, we obtain Eq. (C.9).

A word of warning is appropriate as what comes to the apparent reduction of dimensionality of the variable (field) with respect to which the variation is taken. For example, in Eq. (C.18) we have a variation $\delta F_{2D}[\textsc{h}_{\mathrm{C}}]/\delta\textsc{h}_{\mathrm{C}}(x,0,t)$ which we could have formally written as

$$\int dy\, \delta(y) \frac{\delta F_{2D}[\textsc{h}_{\mathrm{C}}]}{\delta\textsc{h}_{\mathrm{C}}(x,y,t)} \equiv P_0 \frac{\delta F_{2D}[\textsc{h}_{\mathrm{C}}]}{\delta\textsc{h}_{\mathrm{C}}(x,y,t)} \tag{C.25}$$

But we cannot interpret the projection operator P_0 as the one which constrains the variation to be performed with respect to the boundary value $\text{H}(x,0,t)$ instead of $\text{H}(x,y,t)$. In other words,

$$P_0 \frac{\delta F_{2D}[\text{H}_\text{C}]}{\delta \text{H}_\text{C}(x,y,t)} \neq \frac{\delta F_{2D}[\text{H}_\text{C}]}{\delta \text{H}_\text{C}(x,0,t)} \ . \tag{C.26}$$

This is easy to understand since we do not get the same result if we first perform the variation $\text{H}(x,y,t)$ and set $y=0$, or if we perform the variation right a way with respect to $\text{H}(x,0,t)$. For this purpose we have to define a new operator $\mathcal{P}_b$ the action of whose is to project variational expressions in such a way that only boundary variation of the field is allowed to vary on the boundary b, which in our case can take the values $b = \text{C}$ or $b = \text{H}$ corresponding to projection onto the contact line and meniscus, respectively. Thus,

$$\mathcal{P}_\text{C} \frac{\delta F_{2D}[\text{H}_\text{C}]}{\delta \text{H}_\text{C}(x,y,t)} \equiv \frac{\delta F_{2D}[\text{H}_\text{C}]}{\delta \text{H}_\text{C}(x,0,t)} \ \ ; \ \ \mathcal{P}_\text{C} \frac{\delta R_{2D}[\dot{\text{H}}_\text{C}]}{\delta \dot{\text{H}}_\text{C}(x,y,t)} \equiv \frac{\delta R_{2D}[\dot{\text{H}}_\text{C}]}{\delta \dot{\text{H}}_\text{C}(x,0,t)} \tag{C.27}$$

Similarly, operating with $\mathcal{P}_\text{H}$ on both sides of the phase field Eq. (C.6) yields Eq. (C.9). Hence, we can identify

$$\mathcal{P}_\text{C} \frac{\delta}{\delta \text{H}(x,y,t)} = \frac{\delta}{\delta \text{H}(x,0,t)} \ \ ; \ \ \mathcal{P}_\text{C} \frac{\delta}{\delta \dot{\text{H}}(x,y,t)} = \frac{\delta}{\delta \dot{\text{H}}(x,0,t)} \ . \tag{C.28}$$

Thus, the operation of $\mathcal{P}_\text{C}$ is the same irrespective of the type of field (velocity or position) it acts on. Projecting the meniscus equation out of the three dimensional bulk evolution equation for the phase field is achieved in an analogous manner:

$$\mathcal{P}_\text{H} \frac{\delta}{\delta \phi(x,y,z,t)} = \frac{\delta}{\delta \phi(x,y,\text{H}(x,y,t),t)} \ \ ; \ \ \mathcal{P}_\text{H} \frac{\delta}{\delta \dot{\phi}(x,y,z,t)} = \frac{\delta}{\delta \dot{\phi}(x,y,\text{H}(x,y,t),t)} \ . \tag{C.29}$$

By transforming the coordinate system we can make the previous definitions look similar to those given in Eq. (C.28). In curvilinear coordinates where u denotes the normal to the equipotential surface $\text{H}(\mathbf{s},t)$ parametrized by coordinates $\mathbf{s} = (s_1, s_2)$ we obtain

$$\mathcal{P}_\text{H} \frac{\delta}{\delta \phi(\mathbf{s},u,t)} = \frac{\delta}{\delta \phi(\mathbf{s},0,t)} \ \ ; \ \ \mathcal{P}_\text{H} \frac{\delta}{\delta \dot{\phi}(\mathbf{s},u,t)} = \frac{\delta}{\delta \dot{\phi}(\mathbf{s},0,t)} \ . \tag{C.30}$$

Since we do not have a general procedure of determining the dynamics of lower dimensional phase boundaries starting from the higher dimensional bulk evolution equation, we have extended the two stage extremization procedure valid in equilibrium to cover the nonequilibrium case using the same philosophy as in the equilibrium case: the first stage of the hierarchy (meniscus equation) can be derived in various ways, which are consistent with the variational ansatz, so we find that reliable. The derivation of the contact line equation is based on the fact that we can obtain nontrivial information about the system when we allow the new degree of freedom (contact line configuration $\text{C}(x,t)$) to participate in the variation. At the meniscus level we kept C fixed when performing the variation with respect to H. To focus on the variations of the contact line we need the operator $\mathcal{P}_\text{C}$ which hits the meniscus equation on both sides such that only the variation of the velocity field of the meniscus at plane $y=0$ (contact line velocity) in the Rayleigh functional and the variation of the meniscus at $y=0$ (contact line position) in the free energy are taken into account. In other words,

$$P_0 \neq \mathcal{P}_\text{C} \ , \tag{C.31}$$

because the spaces on which the two operators are defined are quite different from each other: P_0 is defined to operate on the class of projectable functions whereas $\mathcal{P}_{\mathrm{C}}$ can be said to act on variations directly as far as Eq. (C.28) and Eq. (C.29) are taken as mnemonic rules only. To proceed more rigorously, we could introduce a functional projector $\tilde{\mathcal{P}}_b$ which projects out the parts of the functionals which do not vary in the subspace spanned by the collective coordinate indicated by the subindex b. For example,

$$\tilde{\mathcal{P}}_{\mathrm{H}} F_{3D}[\phi] \equiv F_{2D}[\textsc{h}] \ . \tag{C.32}$$

This is analogous to using the function projector P_{H} to project out the degrees of freedom of the field U_{3D} living in 3D space which are orthogonal to $\partial_z\phi$, which is assumed to be a sharply peaked function at $z = \textsc{h}$:

$$P_{\mathrm{H}} U_{3D} \equiv \int dz\, \partial_z \phi(z - \textsc{h}(x,y)) U_{3D}(x,y,z) \approx U_{3D}(x,y,\textsc{h}(x,y)) \equiv U_{2D}(\textsc{h}) \ . \tag{C.33}$$

The last identity defines a new function U_{2D} analogous to functional $F_{2D}[\textsc{h}]$ above. Assuming that the variations which are orthogonal to the new functional vanish, we are aiming at something like

$$\frac{\delta}{\delta\phi(x,y,z,t)} \tilde{\mathcal{P}}_{\mathrm{H}} F_{3D}[\phi] \simeq \frac{\delta}{\delta\phi(x,y,z,t)} F_{2D}[\textsc{h}] \simeq \frac{\delta}{\delta\phi(x,y,\textsc{h}(x,y,t),t)} F_{2D}[\textsc{h}] \ . \tag{C.34}$$

Symbol $\simeq$ has been used instead of $=$ because the meaning of the first two expressions has to be clarified. To find out the corresponding function projector (which acts on ordinary functions) we should solve

$$P_{\mathrm{H}} \frac{\delta F_{3D}[\phi]}{\delta\phi(x,y,z,t)} = \frac{\delta}{\delta\phi(x,y,\textsc{h}(x,y,t),t)} F_{2D}[\textsc{h}] \ . \tag{C.35}$$

This equation can be taken to define the operator P_{H}. Vice versa, knowing P_{H} we can use the previous relation to define $\tilde{\mathcal{P}}_{\mathrm{H}}$ more rigorously. For simplicity, let us approximate the true operator $\tilde{\mathcal{P}}_{\mathrm{H}}$ with an operator which replaces the field ϕ and any variation of it $\delta\phi$ with the mean field solutions ϕ_{H} and $\delta\phi_{\mathrm{H}}$, respectively. Then, the argumentation goes like

$$\begin{aligned} \tilde{\mathcal{P}}_{\mathrm{H}} \left(F_{3D}[\phi + \delta\phi] - F_{3D}[\phi] \right) &= \tilde{\mathcal{P}}_{\mathrm{H}} \int dV \!\int dt\ F'_{3D}[\phi]\, \delta\phi = \int dV \!\int dt\ F'_{3D}[\phi_{\mathrm{H}}]\, \delta\phi_{\mathrm{H}} && \text{(C.36)} \\ &= \int dV \!\int dt\ F'_{2D}[\textsc{h}] \int dV' \!\int dt'\ \delta\textsc{h}\, J(V,t;V',t') \propto \int dV \!\int dt\ F'_{2D}[\textsc{h}]\, \delta\textsc{h} \ . && \text{(C.37)} \end{aligned}$$

On the second line J denotes the Jacobian of the transformation of variables given in Eq. (C.22). The first equality on the second line defines the mean field approximation of the free energy functional of meniscus fluctuations. Notice that the assumption that $\delta\phi$ in the argument of the free energy functional transforms into $\delta\phi_{\mathrm{H}}$ means that the projector $\tilde{\mathcal{P}}_{\mathrm{H}}$ automatically restricts the allowed variations into the right subspace.

C.2 Units

Since the units will play an important role in many of the considerations to come, let us define our unital system properly. It should be remembered that for all numerical and analytical work we have used dimensionless variables by measuring time in units Mr^2/K and length in units $\sqrt{K/r}$ [4] which is the intrinsic width of the interface, or bulk correlation length. Since this is true for the fundamental order parameter equation (8.36) it holds true for all the projected quantities such as H and C as well. For some idea of the size of the model parameters of the free energy in dimensionless units one can consult Ref. [354] where the authors studied a completely different system, namely ordering kinetics in solid alloys. Nevertheless, the form of the Landau free energy is of ϕ^4-type, the same as in this work.

Let us determine now the dimensions of the different quantities appearing in our theory. In the fluid phases our free energy functional reduces to the familiar ϕ^4-form:

$$F = \int d^dx \Big((\gamma/2)\, |\nabla\phi(\mathbf{x})|^2 + (a/2)\, \phi^2(\mathbf{x}) + (b/4)\, \phi^4(\mathbf{x}) \Big) \ . \tag{C.38}$$

The physical units of F are those of energy E: $[F] = [E] = Nm$. Then, the units of the parameters of the free energy are fixed by the units of F: $[\gamma] = m^{2-d}[F]$, $[a] = [b] = m^{-d}[F]$. For clarity's sake, we define below another quantity A which is has the same form as F but there is an extra integral over time as the argument fields can now depend on time, too:

$$A = \int d^dx \int dt \, \Big((\gamma/2)\, |\nabla\phi(\mathbf{x},t)|^2 + (a/2)\, \phi^2(\mathbf{x},t) + (b/4)\, \phi^4(\mathbf{x},t) \Big) \ . \tag{C.39}$$

The units of A are those of action: $[A] = [E]s = Nms$. We have decorated the terms with dimensionfull prefactors γ, a and b. Let the phase field ϕ be dimensionless:

$$[\phi] = 1 \ . \tag{C.40}$$

Using the action, we have to divide by the units of time: $[\gamma] = m^{2-d}[A]/s$, $[a] = [b] = m^{-d}[A]/s$. These formulae still have to be modified since the contain redundant units of density, which in our current system has been set equal to one. For further comments, see Sect. 10.4.1. After simplification, the units become $[\gamma] = m^4/s^2$, $[a] = [b] = m^2/s^2$.

The units of the mobility are found from the equation of motion. Nonconserved dynamics of the phase field is given by Model A:

$$\partial_t\phi = -M_A \frac{\delta A[\phi]}{\delta\phi} = M_A \left(\gamma\nabla^2\phi - a\phi - b\phi^3 \right) \ . \tag{C.41}$$

It should be noted that the use of action is mandatory when the argument of ϕ contains time. Otherwise units do not match. Equating the dimensions on both sides of the previous equation yields three equations anyone of which can be used to fix the dimension of the mobility M_A:

$$\frac{[\phi]}{s} = \frac{[M_A][\gamma][\phi]}{m^2} = [M_A][a][\phi] = [M_A][b][\phi]^3 \ . \tag{C.42}$$

Choosing the first equality gives: $[M_A] = m^2/(s[\gamma]) = m^d/[A] = s/m^2$, where we have discarded the units of mass density. This means that we can not naively set $[\delta A/\delta\phi] = [A]/[\phi]$. Instead, we have

$$\left[\frac{\delta A}{\delta\phi}\right] = \frac{[A]}{m^d s} = \frac{m^2}{s^2} \ . \tag{C.43}$$

That is, the units of the variational derivative of A are the units of action density. Of course, the notation has been misused in the second equality of the previous equation: The obsolete factor kg/m^d must be set equal to one to obtain the correct units of the current unit system where $[phi] = 1$. The factor of s in the denominator arises from the time integral. Let us now see how the dimensions change if we use conserved dynamics for the phase field (Model B):

$$\partial_t \phi = M_B \nabla^2 \frac{\delta A[\phi]}{\delta \phi} = M_B \nabla^2 \left(-\gamma \nabla^2 \phi + a\phi + b\phi^3 \right) \ . \tag{C.44}$$

Instead of Eq. (C.42) we now have the following set of relations

$$\frac{[\phi]}{s} = \frac{[M_B][\gamma][\phi]}{m^4} = \frac{[M_B][a][\phi]}{m^2} = \frac{[M_B][b][\phi]^3}{m^2} \ . \tag{C.45}$$

Choosing again the first equality above to fix the dimension of M_B, we obtain $[M_B] = m^{2+d}/[A] = s$. In conclusion, going from Model A to Model B only changes the dimensionality of the diffusive coefficient: $[M_A] \neq [M_B]$.

Next we focus on the projected equation of motion for the liquid-gas interface. Upon projection a new dimensionfull quantity, the surface tension, appears. Surface tension σ is determined in general through the formula $\sigma \equiv (F_{int} - F_{pure})/L^{d-1}$, where F_{int} is the free energy of the configuration with one planar interface separating two coexisting phases, F_{pure} is the reference free energy of either one of the pure phases (their free energies should be the same in this formulation), and L^{d-1} is the interfacial area. Clearly, in one dimensional time independent situation (interface is just a point) with calibration $F_{pure} = 0$, $\sigma = F = \int dx\, (\gamma |\partial_x \phi|^2/2 + a\phi^2/2 + b\phi^4/4)$. In two d-dimensional situation with translational symmetry broken with respect to the x-direction only, we get

$$F = L^{d-1} \int dx\, (\gamma\, |\partial_x \phi|^2/2 + a\phi^2/2 + b\phi^4/4) \ , \tag{C.46}$$

which is consistent with our definition. On the other hand, in the one dimensional case we can utilize the special form of the free energy and write $\sigma = \gamma \int dx\, (\partial_x \phi)^2$. Dimensions of σ become $[\sigma] = [\gamma] m [\phi]^2/m^2 = [F]/m^{d-1}$ with the units of γ determined from the time independent free energy $[\gamma] = m^{2-d}[F]$ in Eq. (C.46). Equivalently, one can have the time integral included in the definition of the free energy, in which case we call it the action. Mathematically speaking, the time integral should be part of the definition of the free energy functional, because the equation of motion of the phase field involves functional differentiation with respect to $\phi(x, y, z, t)$ which depends on time coordinate t explicitly. Eq. (C.46) gets modified:

$$F = L^{d-1}\, \mathrm{t} \int dx\, (\gamma\, |\partial_x \phi|^2/2 + a\phi^2/2 + b\phi^4/4) \ , \tag{C.47}$$

where t is the extent of the time interval, which we treat as an extra dimension. In fact, we should use the symbol A instead of F but since the fields ϕ are only functions of the spatial position and not time (which has been integrated out in Eq. (C.47), we continue to use the symbol F. The dimension of γ in Eq. (C.46) is $m^{2-d}[F]$ whereas in Eq. (C.47) $[\gamma] = m^{2-d}[F]/s$. Consequently, in the latter case we have to define the surface tension parameter $\sigma \equiv F/(L^{d-1}\mathrm{t})$. This is to say that when using the generalized free energy having time dependent fields as its arguments, the units σ become $[F]/(m^{d-1}s) = m^3/s^2$.

For Model A, the interface equation of motion is obtained by hitting both sides of Eq. (C.41) with the projection operator $\int dz\, \partial_z \phi$ where z is the direction orthogonal to the interface. After projection and linearization we obtain

$$\sigma \partial_t h(x, t) = M_A \gamma \partial_x^2 h(x, t) \ , \tag{C.48}$$

where the surface tensions on both sides cancel out. Dimensional consistency requires that $[M_A][\gamma] = m^2/s$, which is obviously true. For Model B, we invert the Laplacian operator with the aid of the Green's function G after which we project:

$$\int dx_1 \int dy_1\, G_{3D}(x,y,h(x,y,t);x_1,y_1,h(x_1,y_1,t))\, \partial_t h(x_1,y_1,t) \propto \frac{M_B\sigma}{4}\nabla^2 h(x,t)\ . \qquad \text{(C.49)}$$

The Green's function depends on h explicitly but this does not change its dimensionality. Consistency of units requires that $m^{d-1}[G_{3D}][h(x,t)]/s = [M_B][\sigma][h(x,t)]/m^2$. Since $[h(x,t)] = m$, $[\phi(x,t)] = 1$, $[M_B] = m^{2+d}/[A]$, we can solve for the units of the Green's function: $[G_{3D}] = m^{-1}$. More generally, we could write the left hand side of Eq. (C.49) as $\int d^d x\, G\partial_t\phi$ whose dimension is $m^d[G]/s$, which means that the units of the Green's function in general dimension is m^{2-d}. This is readily seen to hold by computing the dimensions of the infinite space Green's functions: $G_{3D} \sim 1/r$, $G_{2D} \sim \ln(r/r_0)$ and $G_{1D} \sim |r|$.

C.3 Linearization of the Green's function

The derivation presented in Sect. 8.4 applies only to systems where the fluid-fluid (liquid-gas) interface (H) behaves well in the sense that it possesses a normal vector whose direction only experiences small fluctuations around some well defined reference direction. The extent of the system perpendicular to the reference direction should be infinite, otherwise periodic boundary conditions should be used. Clearly some of these conditions are violated if we are modelling a system having solid wall(s). Because of the walls the system is not infinite (liquid-gas boundary does not have infinite extent), nor can periodicity be imposed. Moreover, when observing the three phase contact region, which is diffuse in reality and in computer simulations, it is difficult to tell where exactly does the liquid-gas interface end and where does the liquid-solid (or gas-solid) interface begin: dealing with several interconnected phase boundaries can be awkward. On the other hand, if one decides to build a theory which uses just a single interface, say the outer boundary of the liquid domain, the traditional projection method will fail in the vicinity of the contact line where this single interface makes a rapid turn.

These difficulties can be avoided by using the sharp interface approximation and by restricting our focus only on the region where the liquid-gas interface is well-defined and modelling the effect of other interfaces through the action of the contact line common to the liquid-gas interface and the disregarded ones. In the case of a single vertical wall located at $y = 0$ we should consider only the region $x \in (-\infty,\infty)$; $y \in [0,\infty)$; $z \in [0,\infty)$. Similarly, in the case of two vertical walls at $y = 0$ and $y = L$ the restricted domain, in which the fluid-fluid boundary is well-defined, is $y \in [0,L]$. Therefore, we should also find out what are the boundary conditions for the chemical potential at the boundaries of the restricted domain to be able to invert the Laplacian properly within this domain. This is, however, easier said than done: because of the diffusiveness of the phase boundaries the chemical potential will not take its equilibrium bulk value immediately at the interfaces between solid and fluid phases. Consequently, the naive choice of $\mu = 0$ at the boundaries of the restricted domain is not correct. Knowing the values of μ there gives us an extra term in the equation of motion (8.39) denoted by Λ:

$$M^{-1}\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \int_0^{\infty} dz_1\, G_{3D}(\mathbf{r};\mathbf{r}_1)\, \partial_t\phi(\mathbf{r}_1,t) = \mu(\mathbf{r},t) + \Lambda(\mathbf{r},t)\ , \qquad \text{(C.50)}$$

where $\mathbf{r} \equiv (x, y, z)$, $\mathbf{r}_1 \equiv (x_1, y_1, z_1)$, and the Green's theorem fixes the form of the boundary term

$$\Lambda \equiv \int dS \left[\partial_n G_{3D}\, \mu - \partial_n \mu\, G_{3D}\right] \ . \tag{C.51}$$

The normal derivative symbol is ∂_n and S denotes the boundary region where the solid phase meets the fluid phases. Notice also the lower limit of the y-integral in Eq. (C.50) signifying the presence of a single vertical wall at $y = 0$ (Having another wall at $y = L$ would also change the upper limit of the integral). Even though it is a bit elaborate to find out what the boundary values of μ are, we can still proceed since the explicit functional form of Λ is not needed in the following.

To ease the extraction of the physics, we linearize the Green function G_{3D}. Physical condition for the validity of the linearization is derived in App. C.4. We assume that without any *random* inhomogeneities on the wall(s), the meniscus takes the shape given by function $\textsc{h}_0$. It can be a function of both spatial coordinates x and y, but assuming that the wall is completely homogeneous, $\textsc{h}_0 = \textsc{h}_0(y, t)$, where y marks the coordinate perpendicular to the wall. The fluctuating contribution caused by randomly distributed pinning centers of the solid walls is denoted by $h = h(x, y, t)$ and the full solution of the meniscus profile is denoted by $\textsc{h}$. In other words,

$$\textsc{h}(x, y, t) = \textsc{h}_0(y, t) + h(x, y, t) \ . \tag{C.52}$$

In the following the forms of $\textsc{h}_0$ and h will be kept arbitrary. Linearization means that terms with second or higher powers of fluctuations h are dropped (such as $h\,\partial_t h$, for example). First, Taylor expand the Green function of on the left hand side of the meniscus equation (8.47):

$$M^{-1}\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\; G_{3D}(x, y, \textsc{h}(x, y, t); x_1, y_1, \textsc{h}(x_1, y_1, t))\, \partial_t \textsc{h}(x_1, y_1, t) \approx \tag{C.53}$$

$$\begin{aligned} M^{-1}\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\; &\Big[G_{3D} + \partial_z G_{3D}|_{\textsc{h}_0}\, h(x, y, t) + \partial_{z_1} G_{3D}|_{\textsc{h}_0}\, h(x_1, y_1, t)\Big] \\ &\times \Big[\partial_t \textsc{h}_0(y_1, t) + \partial_t h(x_1, y_1, t)\Big] = \frac{\delta F_{2D}[\textsc{h}]}{\delta \textsc{h}} + \tilde{\Lambda}_{\textsc{h}}(x, y, t) \ , \end{aligned} \tag{C.54}$$

where $\tilde{\Lambda}_{\textsc{h}}(x, y, t) \equiv \Lambda(x, y, \textsc{h}(x, y, t), t)$ is the projection of $\Lambda(x, y, z, t)$ onto the liquid-gas phase boundary. The short-hand notation introduced for the expansion of the Green function G_{3D} above is the following:

$$\begin{aligned} G_{3D} &= G_{3D}(x, y, \textsc{h}_0(y, t); x_1, y_1, \textsc{h}_0(y_1, t)) \ ; && \text{(C.55)} \\ \partial_z G_{3D}|_{\textsc{h}_0} &= \partial_z G_{3D}(x, y, z; x_1, y_1, \textsc{h}_0(y_1, t))|_{\textsc{h}_0(y,t)} \ ; && \text{(C.56)} \\ \partial_{z_1} G_{3D}|_{\textsc{h}_0} &= \partial_{z_1} G_{3D}(x, y, \textsc{h}_0(y, t); x_1, y_1, z_1)|_{\textsc{h}_0(y_1,t)} \ . && \text{(C.57)} \end{aligned}$$

Expanding the product of the terms in square brackets and keeping the terms of order zero or one in h gives

$$I_A + I_B + I_C + I_D = -\frac{M}{4}\frac{\delta F_{2D}[\textsc{h}]}{\delta \textsc{h}} + \tilde{\Lambda}_{\textsc{h}} \ . \tag{C.58}$$

The different terms appearing in Eq. (C.58) are tabulated below:

$$I_A \equiv \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, G_{3D}(x, y, \textsc{h}_0(y, t); x_1, y_1, \textsc{h}_0(y_1, t))\, \partial_t \textsc{h}_0(y_1, t) \ ; \tag{C.59}$$

$$I_B \equiv \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, \partial_z G_{3D}(x, y, z; x_1, y_1, \textsc{h}_0(y_1, t))|_{\textsc{h}_0(y,t)}\, h(x, y, t)\, \partial_t \textsc{h}_0(y_1, t) \ ; \tag{C.60}$$

$$I_C \equiv \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, \partial_{z_1} G_{3D}(x, y, \mathrm{H}_0(y,t); x_1, y_1, z_1)|_{\mathrm{H}_0(y_1,t)}\, h(x_1, y_1, t)\, \partial_t \mathrm{H}_0(y_1, t) \ ; \quad \text{(C.61)}$$

$$I_D \equiv \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, G_{3D}(x, y, \mathrm{H}_0(y,t); x_1, y_1, \mathrm{H}_0(y_1,t))\, \partial_t h(x_1, y_1, t) \ . \qquad \text{(C.62)}$$

Next, we can partition the terms in Eq. (C.58) into two groups based on the fact that if the walls of our set-up are clean (no chemical inhomogeneities) we expect the fluctuation term h to vanish. In other words, we assume that $h = h(A)$, where A is the noise field, *i.e.* the projected wall potential appearing in Eq. (8.61). In the limit of vanishing noise only the term I_A survives as it contains no fluctuation terms h. How this happens as a function of the noise strength D can be answered using the results of App. (B). Thus, split the terms in Eq. (C.58) as

$$\begin{aligned} I_A &= (M\sigma/4)\, \partial_y^2 \mathrm{H}_0 + \tilde{\Lambda}_{\mathrm{H}_0} \ ; & \text{(C.63)} \\ I_B + I_C + I_D &= -\frac{M}{4} \frac{\delta F_{2D}[h]}{\delta h} + \tilde{\Lambda}'_{\mathrm{H}_0,\, h} \ . & \text{(C.64)} \end{aligned}$$

The first equation corresponds to homogeneous walls, the second describes fluctuation corrections arising from spatial variation of the local wetting properties. Green's boundary term has been split in the following way: $\tilde{\Lambda}_{\mathrm{H}} \approx \tilde{\Lambda}_{\mathrm{H}_0} + \tilde{\Lambda}'_{\mathrm{H}_0,\, h}$, where the first term on the right is the equilibrium contribution and the second one contains contribution from the linearized fluctuations. However, the physically motivated assumption of zero mass flux through the solid walls (which will be used later on as well) renders $\tilde{\Lambda}$ rigorously zero. Thus, in practice we set $\tilde{\Lambda}_{\mathrm{H}} = 0$ and use Eq. (C.63) to fix the unknown fitting factors of an ansatz like Eq. (8.52). The form of the ansatz for H_0 can be justified by numerics and the analysis of the quasi-static limit of the present model.

C.4 Condition for linearization of Green's function

Validity of the linearization is studied in this section. For clarity's sake, we first find out what are the physical units of the terms in the equation of motion. We shall not use the full Eq. (8.58, 8.61) but a simplified representative form, which allows us to determine the units and scaling more easily:

$$\frac{1 - e^{-\mathrm{C}_0 |k|}}{k^2}\, \partial_t c(k,t) = -\sigma_1 |k|\, c(k,t) + A_1(k,t) \ , \qquad \text{(C.65)}$$

where we have chosen to use a simplified form of the restoring force, $\sigma_1 |k|\, c(k,t)$, on the right hand side. For infinite wall separation L the restoring force, which we have derived in Sect. C.14.5, has a linear dependence on $|k|$. Thus, the scaling behaviour should be correctly reproduced by the simplified force term on the right hand side of Eq. (C.65). The form of the kernel $\sigma_1 |k|$ is identical to the JdG [355] kernel for the restoring force as far as the wave-vector behaviour is concerned: $\Gamma_{JdG}(k) = \gamma |k|$ with $\gamma \equiv \theta_0^2 \sigma$, and σ is the bare surface tension. Moreover, we have defined

$$\sigma_1 \equiv M\sigma \ \ ; \ \ A_1(k,t) \equiv M A(k,t) \ . \qquad \text{(C.66)}$$

Redimensionalizing yields the following units (notation $[f]$ means the physical unit of f):

$$[c(k,t)] = m^{1+d} \ \ ; \ \ [\sigma_1] = m^3/s \ \ ; \ \ [A_1(k,t)] = m^{3+d}/s \ \ ; \ \ [D] = m^{7+d}/s^2 \ . \qquad \text{(C.67)}$$

In general dimension d the function and its Fourier transform have different units, of course. For example, $[c(x,t)] = m$ but $[c(k,t)] = m^{1+d}$. In case of the contact line the spatial dimensionality $d = 1$ and we have

$$[c(k,t)] = m^2 \;\; ; \;\; [\sigma_1] = m^3/s \;\; ; \;\; [A_1(k,t)] = m^4/s \;\; ; \;\; [D] = m^8/s^2 \; . \tag{C.68}$$

The units of σ_1 are fixed by balancing the dimensions on both sides of Eq. (C.65). Determining the dimensionality of the noise strength D of A requires more work. In Sect. (12.3) it is shown that effective noise correlator $\langle A_1 A_1' \rangle$ behaves like

$$\langle A_1(k,t) A_1(k',t') \rangle \approx \delta(k+k') \frac{D}{\sqrt{G_c(0,t,t')}} \; . \tag{C.69}$$

The correlation function G_c is defined through

$$G_c(x_1 - x_2, t_1, t_2) \equiv \langle (h(x_1,t_1) - h(x_1,t_1))^2 \rangle - \langle (h(x_1,t_1) - h(x_1,t_1)) \rangle^2 \; , \tag{C.70}$$

and it clearly behaves similarly to the surface width $W^2 \equiv \langle (h(x,t) - \langle h(x,t) \rangle)^2 \rangle$. Therefore, its unit is the unit of length: $[G_c(x,t)] = [W] = m$. Using this result in Eq. (C.69),

$$[\langle A_1 A_1' \rangle] \sim m^d \frac{[D]}{[W]} = [D] m^{d-1} \; . \tag{C.71}$$

Plugging in the known dimensions of $A_1(k,t)$ from Eq. (C.67) to the left hand side of the previous equation and solving for the units of D gives $[D] \sim m^{1-d} m^{6+2d}/s^2 = m^{7+d}/s^2$. Thus, we obtain the results given in Eq. (C.67).

The minimum requirement which our perturbation series should satisfy, is the smallness of the first term dropped from the analysis compared to those kept. In other words we should find out when

$$\int dx_1 \int dy_1 \; \partial_z G_{3D}(x,y,z;x_1,y_1,\mathrm{H}_0(y_1,t))\Big|_{\mathrm{H}_0(y,t)} c(x,t) \tag{C.72}$$

$$\gg \int dx_1 \int dy_1 \;\; \partial_z^2 G_{3D}(x,y,z;x_1,y_1,\mathrm{H}_0(y_1,t))\Big|_{\mathrm{H}_0(y,t)} [c(x,t)]^2 \tag{C.73}$$

To evaluate the gross magnitude of the terms we find it convenient to replace the exact requirement appearing in the previous equation with its dimensional equivalent:

$$\left[\int dx_1 \int dy_1 \, \partial_z G_{3D}\right] [c(x,t)] \gg \left[\int dx_1 \int dy_1 \, \partial_z^2 G_{3D}\right] \left[\langle c^2(x,t) \rangle\right] \; , \tag{C.74}$$

We will first estimate the magnitude of the contact line height c from the representative equation of motion (C.65). In the following the calculations will be performed in the regime where $\mathrm{c}_0|k| \ll 1$, which makes the left hand side of Eq. (C.65) equal to $(\mathrm{c}_0(t)/|k|)\, \partial_t c(k,t)$. Dividing both sides with $\mathrm{c}_0(t)/|k|$ and neglecting the time dependence of c_0, we can write the formal solution, which is sufficient to study scaling, as

$$c(k,t) = \int_0^t ds \, J(k,t-s) A_1(k,s) \sim \frac{\bar{A}}{\sigma_1 |k|} \;\; \Rightarrow \;\; c(x,t) \sim \frac{\bar{A}}{\sigma_1} \; . \tag{C.75}$$

In the previous equation we defined the kernel $J(k,t) \equiv (|k|/\mathrm{C}_0)\exp(-\sigma_1 k^2 t/\mathrm{C}_0)$. The average noise field is denoted by $\bar{A}$. The dimensionality of $\bar{A}$ is the same as that of $A_1(k,t)$. Let us evaluate the magnitude of $c^2(x,t)$ by computing the magnitude of $\langle c^2(x,t)\rangle$:

$$\begin{aligned}\langle c^2(x,t)\rangle &= \int dk_1 \int dk_2\, e^{-\imath(k_1+k_2)x} \int_0^t ds_1 \int_0^t ds_2\, J(k_1, t-s_1) J(k_2, t-s_2) \langle A_1(k_1,s_1) A_1(k_2,s_2)\rangle \\ &= \int dk\, \frac{k^2}{\mathrm{C}_0^2}\, e^{-2(\sigma_1 k^2/\mathrm{C}_0)\,t} \int_0^t ds_1 \int_0^t ds_2\, e^{(\sigma_1 k^2/\mathrm{C}_0)(s_1+s_2)}\, \frac{D}{W} \qquad \text{(C.76)} \\ &\sim \frac{D}{W}\int dk\, \frac{1}{\sigma_1^2 k^2} \sim \frac{D}{W\sigma_1^2 k}\ . \qquad \text{(C.77)}\end{aligned}$$

The integrals over k_1 and k_2 are one dimensional in the previous equation. What about the dimensionality of the derivatives of the Green's function G_{3D}?

$$\partial_z G_{3D} \sim \partial_z \frac{1}{r} \sim \frac{1}{r^2} \ \ ; \ \ \partial_z^2 G_{3D} \sim \frac{1}{r^3}\ , \qquad \text{(C.78)}$$

where we have used $r \equiv [\,(x-x')^2 + (y-y')^2 + (z-z')^2\,]^{1/2}$. Taking into account the dimensionality of the integrals we get dimensionally that

$$\left[\int dx_1 \int dy_1\, \partial_z G_{3D}\right] \sim 1 \ \ ; \ \ \left[\int dx_1 \int dy_1\, \partial_z^2 G_{3D}\right] \sim 1/[r] \sim [k]\ . \qquad \text{(C.79)}$$

We can now express the requirement (Eq. (C.73)) dimensionally in terms of the model parameters as

$$\frac{\bar{A}}{\sigma_1} \gg k\, \frac{D}{W\sigma_1^2 k} \ \Rightarrow W \ \gg \frac{D}{\bar{A}\sigma_1}\ . \qquad \text{(C.80)}$$

The expansion is seen to valid when the fluctuations of the contact line width W are large enough compared to the ratio of the noise strength to the product of the average noise and the surface tension. Values of $\bar{A}$ and D must be determined from the experiment.

C.5 Variational derivation of the meniscus dynamics

We first derive the equation of motion for the liquid-gas boundary through a variational approach. Then, we study the commutativity of linearization and variation and arrive at separate equations for the zeroeth order meniscus solution H_0 describing the effect of pure walls and another equation for the fluctuating modes h accounting for the random impurities.

C.5.1 Derivation

Equation of motion for the meniscus can be derived through direct application of the project operator on both sides of the bulk phase field equation (8.36). This method will be abbreviated as DirP. Another possibility is to define two functionals, called Rayleigh's dissipation functional R_{3D} and free energy functional F_{3D} the form of which we are already familiar with. Analogously to Lagrange's mechanics for point particles we write the equation of motion in the variational form (VarF for short):

$$\frac{\delta R_{3D}[\dot{\phi}]}{\delta\dot{\phi}(\mathbf{r},t)} = -\frac{\delta F_{3D}[\phi]}{\delta\phi(\mathbf{r},t)}\ . \qquad \text{(C.81)}$$

Let us define R_{3D} in such a way that Eq. (8.43) will be reproduced. The domain of three dimensional spatial integration will be called V and

$$\int dV_i \equiv \int_{-\infty}^{\infty} dx_i \int_0^L dy_i \int_0^{\infty} dz_i \ , \tag{C.82}$$

where $i = 1, 2$. This is the volume for the set-up with two vertical solid walls situated at $y = 0$ and $y = L$. If we want to model a single wall at $y = 0$, we take the upper integration limit L of the integral over y_i to infinity. Time integrals are interpreted as $\int dt_i \equiv \int_{-\infty}^{\infty} dt_i$. With these notations we can write

$$R_{3D}[\dot{\phi}] \equiv \frac{1}{2} M^{-1} \int dV_1 \int dt_1 \int dV_2 \int dt_2 \, \dot{\phi}(1, t_1) \, G_{3D}(1; 2) \delta(t_1 - t_2) \, \dot{\phi}(2, t_2) \ , \tag{C.83}$$

where we have introduced a short hand notation for the arguments of the the functions $\dot{\phi}$ and G_{3D}: $f(i, t) \equiv f(x_i, y_i, z_i, t)$, $i = 1, 2$. Spatial and time arguments are separated and the number of components in the spatial argument list is fixed by the available entries of the function f. Thus, for example $\phi(1, t_1) \equiv \phi(x_1, y_1, z_1, t_1)$, $\mathrm{H}(2, t) \equiv \mathrm{H}(x_2, y_2, t)$ and $G_{3D}(1, \mathrm{H}(1, t_1); 2, \mathrm{H}(2, t_2)) \equiv G_{3D}(x_1, y_1, \mathrm{H}(x_1, y_1, t_1); x_2, y_2, \mathrm{H}(x_2, y_2, t_2))$.

It is immediately seen that performing the variations of the functionals R_{3D} defined in Eq. (C.83) and F_{3D} defined in Eq. (8.37) produces the phase field equation of motion given in Eq. (8.39). To produce the meniscus equation (8.43) substitute the approximation of the order parameter field given in Eq. (8.42) into the expression for R_{3D}:

$$\begin{aligned} R_{2D}[\dot{\mathrm{H}}] \equiv R_{3D}[\dot{\phi}_{\mathrm{H}}] = \frac{1}{2M} \int dV_1 \int dt_1 \int dV_2 \int dt_2 \, \{ & 2\delta(\mathrm{H}(1, t_1) - z_1) \, \dot{\mathrm{H}}(1, t_1) \, G_{3D}(1; 2) & \text{(C.84)} \\ & \times \delta(t_1 - t_2) \, 2\delta(\mathrm{H}(2, t_2) - z_2) \, \dot{\mathrm{H}}(2, t_2) \} \\ = \frac{2}{M} \int dA_1 \int dt_1 \int dA_2 \int dt_2 \, & \dot{\mathrm{H}}(1, t_1) \, G_{3D}(1, \mathrm{H}(1, t_1); 2, \mathrm{H}(1, t_2)) \, \delta(t_1 - t_2) \, \dot{\mathrm{H}}(2, t_2) \ , & \text{(C.85)} \end{aligned}$$

where $\int dA_i \equiv \int_{-\infty}^{\infty} dx_i \int_0^L dy_i$, $i = 1, 2$. By writing $\dot{\phi}_{\mathrm{H}}$ instead of just $\dot{\phi}$ in the first line we want to indicate the dependence of the order parameter on the meniscus profile H defined in a lower dimensional space, which calls for integration over the z-coordinate in the functional. There is no guarantee in the general case that the procedure we have just employed to derive R_{2D} will preserve the positivity of the functional. Clearly, R_{3D} is a positive definite quadratic functional in the field $\dot{\phi}$. This is easy to see in the Fourier space where the kernel of R_{3D} is simply $1/k^2 \geq 0$ where zero eigenvalue can be removed by proper choice of boundary conditions. It is, however, more difficult to analyze projected expressions such as the kernel of R_{2D}. Luckily, we can derive the meniscus equation by the direct projection method DirP, which confirms that our result really is the correct one. To finish the derivation of Eq. (8.43) we write down also the free energy functional F_{2D}, which has been derived in App. C.1.

$$F_{2D}[\mathrm{H}] = \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dx \int\limits_{0}^{\infty} dy \, \sigma \sqrt{1 + |\nabla \mathrm{H}(x, y, t)|^2} + \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dx \int\limits_{0}^{\mathrm{C}(x,t)} dz \, (\sigma_{sl}(x, z) - \sigma_{sg}(x, z)) \ . \tag{C.86}$$

This form holds for a set-up with a single vertical wall situated at $y = 0$. Generalizations of F_{2D}, which go beyond capillary wave approximation have been derived in Ref. [352]. The second term on the right hand side of Eq. (C.86) gives the interface energy of the wall due to random fluctuations of the surface energies arising from chemical inhomogeneities. If we have second wall at $y = L$, the free energy assumes the following form

$$F_{2D}[\mathrm{H}] = \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dx \int\limits_{0}^{L} dy\, \sigma \sqrt{1 + |\nabla \mathrm{H}(x,y,t)|^2} + \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dx \int\limits_{0}^{\mathrm{C}_a(x,t)} dz\, \Big(\sigma_{sl}^a(x,z) - \sigma_{sg}^a(x,z)\Big)$$
$$+ \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dx \int\limits_{0}^{\mathrm{C}_b(x,t)} dz\, \Big(\sigma_{sl}^b(x,z) - \sigma_{sg}^b(x,z)\Big) \tag{C.87}$$

The contact line profiles on the walls at $y = 0$ and $y = L$ are denoted as C_a and C_b, respectively. Similar identification applies to the superscripts of the surface tensions. To make contact with the three dimensional bulk free energy, we can associate the surface tension fluctuations with the wall potential A, *i.e.*

$$A(x,0,z) = \sigma_{sl}^a(x,z) - \sigma_{sg}^a(x,z) \;\; ; \;\; A(x,L,z) = \sigma_{sl}^b(x,z) - \sigma_{sg}^b(x,z) \; . \tag{C.88}$$

When we are dealing with one wall only, the y-coordinate of the wall potential plays no role and it will be dropped. Considering only such variations of the order parameter field, which take place at the liquid-gas phase boundary, we obtain from Eq. (C.81) the meniscus equation of motion as shown in App. C.1:

$$\mathcal{P}_{\mathrm{H}} \frac{\delta R_{3D}[\dot{\phi}]}{\delta \dot{\phi}(x,y,z,t)} = -\mathcal{P}_{\mathrm{H}} \frac{\delta F_{3D}[\phi]}{\delta \phi(x,y,z,t)} \quad \Rightarrow \quad \frac{\delta R_{2D}[\dot{\mathrm{H}}]}{\delta \dot{\mathrm{H}}(x,y,t)} = -\frac{\delta F_{2D}[\mathrm{H}]}{\delta \mathrm{H}(x,y,t)} \tag{C.89}$$

It is important to note that the variation with respect to H on the right hand side of the previous equation is such that the contact line profiles, C_a and C_b, stay fixed. This enables nontrivial information to be withdrawn from the functional F_{2D} at the final projection stage when the contact line equation is derived (see App. C.14.6). The variations are easily computed:

$$\frac{\delta R_{2D}[\dot{\mathrm{H}}]}{\delta \dot{\mathrm{H}}(x,y,t)} = \frac{4}{M} \int dx_1 \int dy_1\, G_{3D}(x,y,\mathrm{H}(x,y,t);x_1,y_1,H(x_1,y_1,t))\, \partial_t \mathrm{H}(x_1,y_1,t) \; , \tag{C.90}$$

where the factor of four arises from the combined effect of the miscibility gap (factor of two in Eq. (8.42)) and the functional derivative hitting the field $\dot{\mathrm{H}}$ which appears twice in $R_{2D}[\dot{\mathrm{H}}]$. The variation which is taken with respect to H will always be such that it does not alter the position of the contact line C, *i.e.* C stays fixed under the variation $\delta\mathrm{H}$. Therefore, we can leave out the random surface energy contribution to F_{2D} (Eq. (C.86)) when discussing meniscus dynamics. When contact line equation is formed, the random part will have to be taken into account, of course. Variation of the free energy gives

$$-\frac{\delta F_{2D}[\mathrm{H}]}{\delta \mathrm{H}(x,y,t)} \approx \sigma \nabla^2 \mathrm{H} \; , \tag{C.91}$$

where we have used the small slope approximation $\sigma\sqrt{1 + |\nabla \mathrm{H}|^2} \approx \mathit{const} + \sigma |\nabla \mathrm{H}|^2/2$. Finally, equating Eq. (C.91) with Eq. (C.90) produces the equation of motion for the meniscus (Eq. (8.47)):

$$\frac{4}{M} \int dx_1 \int dy_1\, G_{3D}(x,y,\mathrm{H}(x,y,t);x_1,y_1,H(x_1,y_1,t))\, \partial_t \mathrm{H}(x_1,y_1,t) = \sigma \nabla^2 \mathrm{H} \; . \tag{C.92}$$

This is our fundamental equation of motion, which has been obtained by projecting the three dimensional bulk equation of motion onto the liquid-gas interface. Mathematically, we have expressed this fact in Eq. (C.89) by forcing the variations of the bulk fields $\dot{\phi}$ and ϕ to live on the interface region only.

C.5.2 Non-commutativity of variation and linearization

What we would ultimately like to do is to solve $\textsc{h}$ from Eq. (C.92) as a function(al) of the unknown contact line profile $\textsc{c}$ and derive $R_{1D}[\dot{\textsc{c}}] \equiv R_{2D}[\dot{\textsc{h}}_{\textsc{c}}]$ and $F_{1D}[\textsc{c}] \equiv F_{2D}[\textsc{h}_{\textsc{c}}]$ analogously to the way the 2D meniscus dynamics was deduced from the 3D phase field evolution equation in the previous section. Unfortunately the nonlinearities make it difficult to find how $\textsc{h}$ depends on $\textsc{c}$, so we have to resort to linearization. This, however, induces a few extra complications which we will talk about below.

Variation after linearization

We demonstrate first what happens if we linearize the meniscus profile first and take the variation with respect to linearized variables afterwards. We assume that the meniscus can be represented as

$$\textsc{h}(x,y,t) = \textsc{h}_0(y,t) + h(x,y,t) \ . \tag{C.93}$$

The zeroeth order meniscus solution, $\textsc{h}_0$, describes the profile which is confined by one or two pure, homogeneous walls. It does not depend on the x-coordinate. The effect of random impurities causing fluctuations of the local surface tensions (see previous section) is given by h, which is assumed to have a small amplitude, such that we can only consider the lowest order terms in h in the following calculations. Substitution of the decomposition given in Eq. (C.93) into the expression of R_{2D} gives

$$\begin{aligned} R_{2D}[\dot{\textsc{h}}_0, \dot{h}] = 2\int dA_1 \int dt_1 \int dA_2 \int dt_2 \Big\{ [\dot{\textsc{h}}_0(1,t_1) + \dot{h}(1,t_1)]\, G_{3D}(1, \textsc{h}(1,t_1); 2, \textsc{h}(1,t_2)) \\ \times\, \delta(t_1 - t_2)\, [\dot{\textsc{h}}_0(2,t_2) + \dot{h}(2,t_2)] \Big\} \ . \end{aligned} \tag{C.94}$$

Eventually $\textsc{h}$ in the argument of the Green's function will also be split into $\textsc{h}_0 + h$ but at the moment this representation is more convenient. Introducing a short-hand symbols $G^{\mathrm{H}}_{3D}(1;2) \equiv G_{3D}(1, \textsc{h}(1,t_1); 2, \textsc{h}(2,t_2))$ and $\delta_{a|b} \equiv \delta(a-b)$, we can rewrite the previous equation as

$$\begin{aligned} R_{2D}[\dot{\textsc{h}}_0, \dot{h}] = 2\int dA_1 \int dt_1 \int dA_2 \int dt_2 \Big\{ \dot{\textsc{h}}_0(1,t_1) G^{\mathrm{H}}_{3D}(1;2) \dot{\textsc{h}}_0(2,t_2) \\ + \dot{h}(1,t_1) G^{\mathrm{H}}_{3D}(1;2) \dot{h}(2,t_2) + 2\dot{\textsc{h}}_0(1,t_1) G^{\mathrm{H}}_{3D}(1;2) \dot{h}(2,t_2) \ \Big\} \delta_{t_1|t_2} \ . \end{aligned} \tag{C.95}$$

Let us see what kind of equations of motion are generated if we treat $\dot{\textsc{h}}_0$ and $\dot{h}$ as independent variables. Taking first the variation with respect to $\dot{\textsc{h}}_0$ yields

$$\delta R_{2D}[\dot{\textsc{h}}_0, \dot{h}] / \delta \dot{\textsc{h}}_0(y,t) = \tag{C.96}$$

$$2\int dx_1 \int dt_1 \int dx_2 \int dt_2 \ \delta_{t_1|t_2} \Big\{ \int dy_1 \int dy_2 \, \delta_{y_1|y} \, \delta_{t_1|t} \, G^{\mathrm{H}}_{3D}(1;2) \dot{\textsc{h}}_0(2,t_2)$$

$$+\int dy_1 \int dy_2\, \dot{\textsc{h}}_0(1,t_1) G^{\mathrm{H}}_{3D}(1;2)\, \delta_{y_2|y}\, \delta_{t_2|t} + \int dy_1 \int dy_2\, 2\, \delta_{y_1|y}\, \delta_{t_1|t}\, G^{\mathrm{H}}_{3D}(1;2) \dot{\textsc{h}}_0(2,t_2) \Big\} \; .$$

$$= 4 \int dx_1 \int dx_2 \int dy_2 \left\{ G^{\mathrm{H}}_{3D}(1;2) \dot{\textsc{h}}_0(2,t_2) + G^{\mathrm{H}}_{3D}(1;2) \dot{h}(2,t_2) \right\} \tag{C.97}$$

The first two terms on the right hand side of Eq. (C.96) arise from taking variation of the quadratic term in $\dot{\textsc{h}}_0$. Owing to the symmetry of the Green's function, $G_{3D}(1,2) = G_{3D}(2,1)$ the entries can be swapped around showing that the first two terms are equal to each other. Taking variation of R_{2D} with respect to $\dot{h}$ we obtain an equation similar to above:

$$\delta R_{2D}[\dot{\textsc{h}}_0, \dot{h}]/\delta \dot{h}(x,y,t) = 4 \int dx_2 \int dy_2 \left\{ G^{\mathrm{H}}_{3D}(1;2) \dot{h}(2,t_2) + G^{\mathrm{H}}_{3D}(1;2) \dot{\textsc{h}}_0(2,t_2) \right\} \; , \tag{C.98}$$

where the only difference as compared to Eq. (C.97) is that the x_1-integral is missing. The reason for this is the abundance of x dependence in $\dot{\textsc{h}}_0(y,t)$: when we take functional derivative with respect to $\dot{h}(x,y,t)$ there is an extra delta function generated ($\delta_{x|x_1}$) which kills the x_1-integral.

Having calculated the left hand sides of the equations of motion for $\textsc{h}_0$ and h above, we can compute the variations of the free energy $F_{2D}[\textsc{h}_0, h]$ in order to get the right hand sides. Leaving the random part of F_{2D} out for simplicity, we get

$$F_{2D}[\textsc{h}_0, h] = \frac{1}{2} \int dA_1 \int dt_1 \int dA_2 \int dt_2 \left\{ [\textsc{h}_0(1,t_1) + h(1,t_1)] \left(-\sigma \nabla^2\, \delta_{x_1|x_2} \delta_{y_1|y_2} \delta_{t_1|t_2} \right) \right.$$
$$\left. \times\; [\textsc{h}_0(2,t_2) + h(2,t_2)] \right\} \; . \tag{C.99}$$

Variation $F_{2D}[\textsc{h}_0, h]$ with respect to $\textsc{h}_0$ and h independently gives rise to coupling between the zeroeth order solution and the fluctuation. We notice immediately the same thing from Eq. (C.97) and Eq. (C.98): the motion of the zeroeth order solution $\textsc{h}_0$ is coupled with the fluctuation induced contribution h and vice versa. This is a consequence of the fact that the functional R_{2D} (F_{2D}) has a nonlinear dependence on its arguments. If we now linearize the expressions $\delta R_{2D}[\dot{\textsc{h}}_0, \dot{h}]/\delta \dot{\textsc{h}}_0$ and $\delta R_{2D}[\dot{\textsc{h}}_0, \dot{h}]/\delta \dot{h}$ by expanding the Green's function G^{H}_{2D} and throwing a way terms which are of higher than first order in fluctuations h (or $\dot{h}$), we do not obtain the same result that we get by linearizing the equation of motion (C.92), which we regard as the fundamental equation.

Linearization after variation

Let us now compare the results derived above to those presented in App. C.3. There we linearized the Green's function G_{3D} which appeared on the left hand side of the bulk equation of motion, which had been projected onto the interface at $z = \textsc{h}$. In Sect. C.5.1 we explained how the projection and taking variations can be combined by introducing the concept of restricted variation, which lives on the interface separating two phases. Linearization of the Green's function in Eq. (C.92) yields

$$I_A \;=\; (M\sigma/4)\, \partial_y^2 \textsc{h}_0 \; ; \tag{C.100}$$

$$I_B + I_C + I_D \;=\; -\frac{M}{4} \frac{\delta F_{2D}[h]}{\delta h} \; , \tag{C.101}$$

where we have set the Green's boundary $\tilde{\Lambda}_{\mathrm{H}}$ term to zero. The rest of the abbreviations are collected below:

$$I_A \equiv \int dx_1 \int dy_1\, G_{3D}(x, y, \textsc{h}_0(y,t); x_1, y_1, \textsc{h}_0(y_1,t))\, \partial_t \textsc{h}_0(y_1,t) \; ; \tag{C.102}$$

$$I_B \equiv \int dx_1 \int dy_1 \, \partial_z G_{3D}(x,y,z;x_1,y_1,\mathrm{H}_0(y_1,t))|_{\mathrm{H}_0} \, h(x,y,t) \, \partial_t \mathrm{H}_0(y_1,t) \; ; \tag{C.103}$$

$$I_C \equiv \int dx_1 \int dy_1 \, \partial_{z_1} G_{3D}(x,y,\mathrm{H}_0(y,t);x_1,y_1,z_1)|_{\mathrm{H}_0} \, h(x_1,y_1,t) \, \partial_t \mathrm{H}_0(y_1,t) \; ; \tag{C.104}$$

$$I_D \equiv \int dx_1 \int dy_1 \, G_{3D}(x,y,\mathrm{H}_0(y,t);x_1,y_1,\mathrm{H}_0(y_1,t)) \, \partial_t h(x_1,y_1,t) \; . \tag{C.105}$$

In Eq. (C.103) the substitution $|_{\mathrm{H}_0} \equiv |_{\mathrm{H}_0}(y,t)$ and in Eq. (C.104), $|_{\mathrm{H}_0} \equiv |_{\mathrm{H}_0}(y_1,t)$. As before, the limits of the integrals depend whether we are modelling a single or double wall geometry. Treating the linearized equations (C.100) and (C.101) as fundamental we notice that there should be no coupling in the equation of motion of the pure system to the random one. In other words, H_0 (Eq. (C.100)) does not depend on h (Eq. (C.101)), but h does depend on H_0.

How to separate the random part from the pure

Because of the quadratic (nonlinear) nature of the functionals R_{2D} and F_{2D}, some coupling terms, which are not present in the linearized meniscus equations (C.100) and (C.101), will always arise, if we write the meniscus dynamics as follows

$$\frac{\delta R_{2D}[\dot{\mathrm{H}}_0, \dot{h}]}{\delta \dot{\mathrm{H}}_0(y,t)} = -\frac{\delta F_{2D}[\mathrm{H}_0, h]}{\delta \mathrm{H}_0(y,t)} \; ; \tag{C.106}$$

$$\frac{\delta R_{2D}[\dot{\mathrm{H}}_0, \dot{h}]}{\delta \dot{h}(x,y,t)} = -\frac{\delta F_{2D}[\mathrm{H}_0, h]}{\delta h(x,y,t)} \; . \tag{C.107}$$

Therefore, we will now *design* new dissipation and free energy functionals in such a way that the zeroeth order meniscus dynamics (H_0) and the dynamics of the fluctuations (h) given in Eq. (C.100) and Eq. (C.101), are reproduced through the variational approach. This means that we have to find R^p_{2D}, F^p_{2D}, R^f_{2D}, and F^f_{2D} such that Eq. (C.100) and Eq. (C.101) can be equivalently written in the following form:

$$\frac{\delta R^p_{2D}[\dot{\mathrm{H}}_0]}{\delta \dot{\mathrm{H}}_0(y,t)} = -\frac{\delta F^p_{2D}[\mathrm{H}_0]}{\delta \mathrm{H}_0(y,t)} \; ; \tag{C.108}$$

$$\frac{\delta R^r_{2D}[\dot{h}]}{\delta \dot{h}(x,y,t)} = -\frac{\delta F^r_{2D}[h]}{\delta h(x,y,t)} \; , \tag{C.109}$$

where the superscripts p and r refer to the pure and fluctuating random contributions of the functionals. The construction of the new functionals will be presented in more detail below. It turns out that Eq. (C.109) is just the same as Eq. (C.107), which means that $R^r_{2D} = R_{2D}$ and $F^r_{2D} = F_{2D}$. The essential thing is that the fluctuations h are coupled with the zeroeth order solution H_0 through this equation. In contrary, there is no such coupling present in Eq. (C.108) because it is missing from Eq. (C.100) which we want to reproduce. Therefore, functionals R^p_{2D} and F^p_{2D} are obtained from R_{2D} and F_{2D} by ignoring the coupling terms. Thus, Eq. (C.108) is a self-contained equation of mean-field type for H_0.

C.5.3 Pure system

There are different possibilities among which one can choose the functionals $R^p_{2D}[\dot{\mathrm{H}}_0]$ and $F^p_{2D}[\mathrm{H}_0]$ such that the correct dynamics is generated through Eq. (C.108). The Rayleigh dissipation functional can be presented for example in the following form:

$$R^p_{2D}[\dot{\mathrm{H}}_0] = \frac{2}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2 \ \dot{\mathrm{H}}_0(1,t_1)\left(G^{\mathrm{H}_0}_{3D}(1;2)\,\delta_{t_1|t_2} 2\delta_{-x_1|x_2}\right)\dot{\mathrm{H}}_0(2,t_2) \tag{C.110}$$

The factor of two in the front is due to the miscibility gap. The Green's function is defined as $G^{\mathrm{H}_0}_{3D}(1;2) \equiv G_{3D}(x_1, y_1, \mathrm{H}_0(y_1,t_1); x_2, y_2, \mathrm{H}_0(y_2,t_2))$. The other factor of two multiplying the delta function $\delta_{-x_1|x_2} = \delta(x_1 + x_2)$ inside the big parenthesis allows us to get rid of one of the x-integrals (if H_0 would be a function of x, too, it would not be needed). Let us show this:

$$\begin{aligned}\frac{\delta R^p_{2D}[\dot{\mathrm{H}}_0]}{\delta \dot{\mathrm{H}}_0(y,t)} &= \frac{4}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2 \ \delta_{y|y_1}\delta_{t|t_1}\left(G^{\mathrm{H}_0}_{3D}(1;2)\,\delta_{t_1|t_2}\delta_{-x_1|x_2}\right)\dot{\mathrm{H}}_0(2,t_2) \\ &+ \frac{4}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2 \ \dot{\mathrm{H}}_0(1,t_1)\left(G^{\mathrm{H}_0}_{3D}(1;2)\,\delta_{t_1|t_2}\delta_{-x_1|x_2}\right)\delta_{y|y_2}\delta_{t|t_2} \qquad \text{(C.111)} \\ &= \frac{8}{M}\int dx_2 \int dy_2 \ G_{3D}(-x_2, y, \mathrm{H}_0(y,t); x_2, y_2, \mathrm{H}_0(y_2,t))\dot{\mathrm{H}}_0(y_2,t) \qquad \text{(C.112)} \\ &= \frac{4}{M}\int dx_2 \int dy_2 \ G_{3D}(x, y, \mathrm{H}_0(y,t); x_2, y_2, \mathrm{H}_0(y_2,t))\dot{\mathrm{H}}_0(y_2,t) \ . \qquad \text{(C.113)}\end{aligned}$$

To obtain the Eq. (C.112) we have used the symmetry of the Green's function. The last equality is obtained by noticing that the single and double wall geometries are such that $G_{3D}(x_1, y_1, z_1; x_2, y_2, z_2)$ is only dependent on the difference $x_1 - x_2$. In the last line we have first made a change of variables $(x_2)_{new} = 2(x_2)_{old}$ and substituted x as a dummy entry for x_1, which can always be transformed away. On the right hand side of the zeroeth order equation of motion we have

$$\begin{aligned}F^p_{2D}[\mathrm{H}_0] &\equiv \int dy_1 \int dt_1 \int dy_2 \int dt_2 \ \frac{1}{2}\mathrm{H}_0(y_1,t_1)\left(-\sigma\partial^2_{y_1}\delta_{y_1|y_2}\delta_{t_1|t_2}\right)\mathrm{H}_0(y_2,t_2) \ . \qquad \text{(C.114)} \\ &= \int dy_1 \int dt_1 \ \frac{\sigma}{2}\left(\partial_{y_1}\mathrm{H}_0(y_1,t_1)\right)^2 + \mathit{boundary\ terms} \ . \qquad \text{(C.115)}\end{aligned}$$

The boundary terms arise if the y-integrals have finite bounds. For example, for double wall case they will be functions of $\mathrm{H}_0(y=0) = \mathrm{C}_0$ and $\mathrm{H}_0(y=L) = \mathrm{C}_0$, and thus they do not contribute to the variations with respect to $\mathrm{H}_0(y,t)$. Taking variation of $F^p_{2D}[\mathrm{H}_0]$ with respect to $\mathrm{H}_0(y,t)$ and setting it equal to $\delta R^p_{2D}/\delta\dot{\mathrm{H}}_0$ given in Eq. (C.113), we get the following result:

$$\int dx_1 \int dy_1 \ G_{3D}(x, y, \mathrm{H}_0(y,t); x_1, y_1, \mathrm{H}_0(y_1,t))\,\partial_t \mathrm{H}_0(y_1,t) = \frac{M\sigma}{4}\,\partial^2_y \mathrm{H}_0(y,t) \ . \tag{C.116}$$

We have thus reached our goal and been able to derive Eq. (C.100) using the variational technique.

For future purposes, we also consider another possibility for the choice of dissipation and free energy functionals, which in some sense requires less adjusting than the ones introduced above. Namely, the new dissipation functional $R^{p2}_{2D}[\dot{\mathrm{H}}_0]$ is readily produced by dropping the coupling terms from the functional $R_{2D}[\dot{\mathrm{H}}_0, \dot{h}]$ given in Eq. (C.94):

$$R^{p2}_{2D}[\dot{\mathrm{H}}_0] \equiv \frac{2}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2 \ \dot{\mathrm{H}}_0(1,t_1) G^{\mathrm{H}_0}_{3D}(1;2)\delta_{t_1|t_2}\dot{\mathrm{H}}_0(2,t_2) \ . \tag{C.117}$$

Similarly, by leaving out the coupling terms from $F_{2D}[\mathrm{H}_0, h]$ given in Eq. (C.99), we straightforwardly obtain the following expression for the new free energy functional $F_{2D}^{p2}[\mathrm{H}_0]$:

$$F_{2D}^{p2}[\mathrm{H}_0] \equiv \int dA_1 \int dt_1 \int dA_2 \int dt_2 \; \frac{1}{2}\mathrm{H}_0(1,t_1)\left(-\sigma\nabla^2\,\delta_{x_1|x_2}\delta_{y_1|y_2}\delta_{t_1|t_2}\right)\mathrm{H}_0(2,t_2) \quad \text{(C.118)}$$

$$= \int dx_1 \int dy_1 \int dt_1 \; \frac{\sigma}{2}\left(\partial_{y_1}\mathrm{H}_0(y_1,t_1)\right)^2 \; . \quad \text{(C.119)}$$

In the first line, $\nabla^2 \equiv \partial_{x_1}^2 + \partial_{y_1}^2$. Since H_0 does not depend on the coordinate in the direction of the solid wall, the x-integration just gives a trivial constant factor. It cancels against the corresponding factor coming from the variational derivative of the dissipation functional when forming the equation of motion. When taking the variations of these functionals according to Eq. (C.108) we obtain the following equation of motion for the zeroeth order meniscus solution:

$$\int dx_1 \int dy_1 \int dx_2 \int dy_2 \; G_{3D}(x_1, y_1, \mathrm{H}_0(y_1,t); x_2, y_2, \mathrm{H}_0(y_2,t))\,\partial_t \mathrm{H}_0(y_1,t)$$

$$= \frac{M\sigma}{4} \int dx_1 \int dy_1 \; \partial_{y_1}^2 \mathrm{H}_0(y_1,t) \; . \quad \text{(C.120)}$$

Due to the smaller number of delta function constraints there will be two extra integrals remaining on both sides of the final equation of motion as compared to Eq. (C.116). It is easy to see that the solution of Eq. (C.116) is automatically the solution of Eq. (C.120) as well, but not necessarily vice versa unless uniqueness can be proven by some means. Moreover, when deriving the contact line profile of pure system using R_{2D}^{p2} (Eq. (C.117)) and F_{2D}^{p2} (Eq. (C.118)) it will be shown in Sect. C.12 that the solutions do not differ significantly from the contact line profile derived using R_{2D}^{p} (Eq. (C.110)) and F_{2D}^{p} (Eq. (C.114)) in the limit of large wall separation where, roughly speaking, the effect of integration over x_1 and y_1 is just to produce the same constant on both sides of Eq. (C.120). Some further applications of Eq. (C.120) can be found in droplet spreading problems, for example.

C.5.4 Random system

We will follow exactly the same procedure as we did in the previous section with the pure system except that the coupling terms will not be dropped in the present case since they are needed to reproduce Eq. (C.101). Actually, we could define $R_{2D}^{r}[\dot{h}] \equiv R_{2D}[\dot{\mathrm{H}}_0, \dot{h}]$ and $F_{2D}^{r}[h] \equiv F_{2D}[\mathrm{H}_0, h]$, but since it is futile to drag along the part of the functionals which doesn't contain any dependence on $\dot{\mathrm{H}}_0$ or h, we redefine

$$R_{2D}^{r}[\dot{h}] \equiv \frac{2}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2 \; \delta_{t_1|t_2}\Big\{\dot{h}(1,t_1)\,G_{3D}^{\mathrm{H}_0}(1;2)\,\dot{h}(2,t_2)$$

$$+ 2\dot{h}(1,t_1)\left[\partial_{z_1}G_{3D}^{\mathrm{H}_0}(1;2)h(1,t_1) + \partial_{z_2}G_{3D}^{\mathrm{H}_0}(1;2)h(2,t_2)\right]\dot{\mathrm{H}}_0(2,t_2)\Big\} \; . \quad \text{(C.121)}$$

In addition to dropping terms depending only on the zeroeth order solution $\dot{\mathrm{H}}_0$, we have linearized the Green's function G_{3D} to first order in h. Analogously to previous sections, we have defined new two short-hand symbols for the derivatives of the Green's function:

$$\partial_{z_1}G_{3D}^{\mathrm{H}_0}(1;2) \;\equiv\; \partial_{z_1}G_{3D}(x_1, y_1, z_1; x_2, y_2, \mathrm{H}_0(y_2,t_2))|_{\mathrm{H}_0(y_1,t_1)} \; ; \quad \text{(C.122)}$$

$$\partial_{z_2}G_{3D}^{\mathrm{H}_0}(1;2) \;\equiv\; \partial_{z_2}G_{3D}(x_1, y_1, \mathrm{H}_0(y_1,t_1); x_2, y_2, z_2)|_{\mathrm{H}_0(y_2,t_2)} \; . \quad \text{(C.123)}$$

The variation with respect to $\dot{h}$ is easily calculated:

$$\begin{aligned} &\delta R^r_{2D}[\dot{h}]/\delta\dot{h}(x,y,t) = \\ &\frac{4}{M}\int dx_2 \int dy_2 \Big\{ G_{3D}(x,y,\mathrm{H}_0(y,t);x_2,y_2,\mathrm{H}_0(y_2,t))\dot{h}(x_2,y_2,t) \\ &\quad + \partial_z G_{3D}(x,y,z;x_2,y_2,\mathrm{H}_0(y_2,t))|_{\mathrm{H}_0}\, h(x,y,t)\dot{\mathrm{H}}_0(y_2,t) \\ &+ \partial_{z_2} G_{3D}(x,y,\mathrm{H}_0(y,t);x_2,y_2,z_2)|_{\mathrm{H}_0}\, h(x_2,y_2,t)\dot{\mathrm{H}}_0(y_2,t) \Big\} \ . \end{aligned} \tag{C.124}$$

On the third line the substitution $|_{\mathrm{H}_0} \equiv |_{\mathrm{H}_0(y,t)}$ and on the last line $|_{\mathrm{H}_0} \equiv |_{\mathrm{H}_0(y_2,t)}$. The free energy is constructed analogously. Contrary to construction of$R^r_{2D}[\dot{h}]$, we can not use the full functional given in Eq. (C.99) (with coupling term to H_0) if we wish to reproduce the linearized equation of motion (C.101). This shows that for fluctuations h it does matter whether one linearizes after taking variation $\delta\mathrm{H}$, or linearizes first the argument of the functional and then takes variation δh. These operations are not commutative. To obtain the equation (C.101), which we regard fundamental, we define

$$F^r_{2D}[h] \equiv \frac{1}{2}\int dA_1 \int dt_1 \int dA_2 \int dt_2\ h(1,t_1)\left(-\sigma\nabla^2\,\delta_{x_1|x_2}\delta_{y_1|y_2}\delta_{t_1|t_2}\right)h(2,t_2)\ , \tag{C.125}$$

where we have dropped the terms with no explicit dependence on h. Taking the functional derivative yields

$$-\frac{\delta F^r_{2D}[h]}{\delta h(x,y,t)} = \sigma\nabla^2 h(x,y,t)\ . \tag{C.126}$$

As required by Eq. (C.109), setting Eq. (C.126) equal to Eq. (C.124) gives Eq. (C.101), which describes the dynamics of the fluctuations h.

C.6 3D Green's function for two walls

Some representations of the 3D Green function arising from the inversion of the Laplacian in the restricted domain between two vertical walls will be derived in this section. We should satisfy

$$-\nabla^2 G^{2W}_{3D}(\mathbf{r};\mathbf{r}_1) = \delta(\mathbf{r}-\mathbf{r}_1) \tag{C.127}$$

with the homogeneous boundary data ($\mathbf{r} = (x,y,z)$)

$$\left\{ \begin{array}{l} \partial_y G^{2W}_{3D}(\mathbf{r};\mathbf{r}_1)|_0 = \partial_y G^{2W}_{3D}(\mathbf{r};\mathbf{r}_1)|_L = 0\ . \\ G^{2W}_{3D}(x,y,0;x_1,y_1,z_1) = 0\ . \end{array} \right. \tag{C.128}$$

The first condition guarantees that there will be no mass flux across the solid-fluid interfaces situated at $y = 0$ and $y = L$. The second establishes the coupling to the reservoir at $z = 0$. In the numerical simulation there is actually a little bit of leakage through the walls especially in the neighbourhood of the contact line, but all in all the no-flux condition is satisfied rather well even though it hasn't been imposed as a strict condition in the simulation. One should also keep in mind that using von Neumann boundary condition at the vertical walls doesn't restrict in any way the choice of boundary conditions for the meniscus H. This point is discussed more thoroughly in Sect. C.10.

Using the cosine decomposition in the y-direction to satisfy the no-flux condition of Eq. (C.128) we can write the Green function in the following form:

$$G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1) = \frac{1}{L}\sum_{n=-\infty}^{\infty} \cos(n\pi y/L)\cos(n\pi y_1/L)\, f_n(x,z;x_1,z_1) \ . \tag{C.129}$$

Separation of the zero component of the series turns out to be useful in making a connection with the 2D imbibition results.

$$G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1) = f_0(x,z;x_1,z_1) + \frac{2}{L}\sum_{n=1}^{\infty} \cos(n\pi y/L)\cos(n\pi y_1/L)\, f_n(x,z;x_1,z_1) \ . \tag{C.130}$$

It will be shown later (Eq. (C.135)) that $f_n = f_{-n}$ which allows us to change the summation limit as compared to Eq. (C.129). The coefficient functions f_0 and f_n $(n \geq 1)$ satisfy

$$-\left(\partial_x^2 + \partial_z^2\right) f_0(x,z;x_1,z_1) = \frac{1}{L}\,\delta(x-x_1)\delta(z-z_1) \ ; \tag{C.131}$$

$$\left[-\left(\partial_x^2 + \partial_z^2\right) + (n\pi/L)^2\right] f_n(x,z;x_1,z_1) = \delta(x-x_1)\delta(z-z_1) \ . \tag{C.132}$$

Note the chosen normalization factors in front of the delta functions for f_0. Using the definitions of f_n and the representation of the delta function,

$$\sum_{n=1}^{\infty} \cos(n\pi y/L)\cos(n\pi y_1/L) = (L/2)\,\delta(y-y_1) - 1/2 \ , \tag{C.133}$$

it is easy to check by direct differentiation that G_{3D}^{2W} indeed is a solution of Eq. (C.127). Solution to Eq. (C.131) which respects the condition $f_0 = 0$ at the plane $z = 0$ is simply related to the Green function appearing in 2D imbibition problem [4]:

$$f_0 = \frac{1}{L}\,\frac{1}{4\pi}\ln\left[\frac{(x-x_1)^2 + (z-z_1)^2}{(x-x_1)^2 + (z+z_1)^2}\right] = \frac{1}{L}\,G_{2D}^{I}(x,z;x_1,z_1) \ . \tag{C.134}$$

Eq. (C.132) is also simple to solve by going over to the Fourier space. For $n \geq 1$ we define first,

$$\tilde{f}_n(x,z) \equiv \frac{1}{(2\pi)^2}\int dk_x \int dk_z\, \frac{e^{-\imath k_x x} e^{-\imath k_z z}}{k_x^2 + (\pi n/L)^2 + k_z^2} \ . \tag{C.135}$$

This function does not respect the boundary condition $f_n = 0$ at $z = 0$ whereas

$$f_n(x,z;x_1,z_1) = \tilde{f}_n(x-x_1, z-z_1) - \tilde{f}_n(x-x_1, z+z_1) \ , \tag{C.136}$$

does fulfil it. Other representations can be obtained by working out the integrals. In terms of the modified Bessel function of zeroeth order K_0, $\tilde{f}_n = K_0((\pi n/L)\Delta r)$, where $\Delta r \equiv \sqrt{x^2+z^2}$. To see the limiting values of G_{3D}^{2W} for large wall separation L it is more convenient to stick to the integral representation of $\tilde{f}_n$. The same applies to the summation over n, which can be performed by changing the integration path to run over the imaginary axis in Eq. (C.135). However, the integration over both k_x and k_z cannot be done anymore in closed form in this case.

Next, we will study the limiting behaviour ($L \to \infty$) of the Green's function, which for convenience is divided into two parts based on the results derived above.

$$G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1) = \frac{1}{L}\, G_{2D}^{I}(x,z;x_1,z_1) + G_{3D}^{S}(\mathbf{r};\mathbf{r}_1)\ , \tag{C.137}$$

where G_{2D}^{I} has been defined in Eq. (C.134), and G_{3D}^{S} represents the series contribution to the full Green function:

$$G_{3D}^{S}(\mathbf{r};\mathbf{r}_1) \equiv \frac{2}{L}\sum_{n=1}^{\infty}\cos(n\pi y/L)\cos(n\pi y_1/L)\, f_n(x,z;x_1,z_1)\ . \tag{C.138}$$

In the limit $L \to \infty$ the first term of Eq. (C.137) vanishes and the only the series part contributes. The product of the cosine terms is represented as a sum of two terms,

$$\cos(n\pi y/L)\cos(n\pi y_1/L) = \frac{1}{2}\left[\cos(n\pi(y+y_1)/L) + \cos(n\pi(y-y_1)/L)\right]\ . \tag{C.139}$$

The full series is split accordingly: $G_{3D}^{S} = G_{3D}^{S+} + G_{3D}^{S-}$, where

$$\begin{aligned} G_{3D}^{S\pm} \ \equiv\ & \frac{1}{(2\pi)^2}\,\frac{1}{L}\sum_{n=1}^{\infty}\cos(n\pi(y\pm y_1)/L)\left(\int dk_x\int dk_z\,\frac{e^{-\imath k_x(x-x_1)}e^{-\imath k_z(z-z_1)}}{k_x^2+(\pi n/L)^2+k_z^2}\right.\\ & \left.-\int dk_x\int dk_z\,\frac{e^{-\imath k_x(x-x_1)}e^{-\imath k_z(z+z_1)}}{k_x^2+(\pi n/L)^2+k_z^2}\right)\ . \end{aligned} \tag{C.140}$$

The standard limiting procedure to convert sums to integrals will be used. Let L be the number of grid points and a is the length of the integration interval: $\Delta x \equiv a/L$. Then,

$$\lim_{L\to\infty}\sum_{n=0}^{a/\Delta x}\Delta x\, g(n\,\Delta x) \to \int_0^a dx\, g(x)\ . \tag{C.141}$$

Using the parameters of G_{3D}^{S} we identify $\Delta k_y = \pi/L$. The upper limit of integration will be infinity. Going to the limit gives

$$\begin{aligned} \lim_{L\to\infty} G_{3D}^{S\pm} \ \to\ & \frac{1}{(2\pi)^2}\,\frac{1}{\pi}\int_0^{\infty}dk_y\ \cos(k_y(y\pm y_1))\left(\int dk_x\int dk_z\,\frac{e^{-\imath k_x(x-x_1)}e^{-\imath k_z(z-z_1)}}{k_x^2+k_y^2+k_z^2}\right.\\ & \left.-\int dk_x\int dk_z\,\frac{e^{-\imath k_x(x-x_1)}e^{-\imath k_z(z+z_1)}}{k_x^2+k_y^2+k_z^2}\right)\ . \end{aligned} \tag{C.142}$$

The cosine function in the previous equation is traded for an exponential with lower integration limit switched from 0 to $-\infty$:

$$\int_0^{\infty}dk_y\ \cos(k_y y)\, g(k_y^2) = \frac{1}{2}\int_{-\infty}^{\infty}dk_y\, e^{\imath k_y y}\, g(k_y^2)\ . \tag{C.143}$$

Substituting Eq. (C.143) into Eq. (C.142) shows that $\lim_{L\to\infty} G_{3D}^{S\pm} \to G_{3D}^{\pm}$, where the functions $G_{3D}^{\pm}$ have been defined in real space through Eq. (C.210). Specifically,

$$\begin{aligned} \lim_{L\to\infty} G_{3D}^{S\pm} \ \to\ & \frac{1}{(2\pi)^3}\int dk_x\int dk_y\int dk_z\left(\frac{e^{-\imath k_x(x-x_1)}e^{-\imath k_y(y\pm y_1)}e^{-\imath k_z(z-z_1)}}{k_x^2+k_y^2+k_z^2}\right.\\ & \left.-\frac{e^{-\imath k_x(x-x_1)}e^{-\imath k_y(y\pm y_1)}e^{-\imath k_z(z+z_1)}}{k_x^2+k_y^2+k_z^2}\right) \end{aligned} \tag{C.144}$$

Indeed, the equivalence to the real space result is immediately seen by performing the integrations in spherical coordinate system. The result is

$$\frac{1}{(2\pi)^3}\int d\mathbf{k}\, e^{-\imath\mathbf{k}\cdot\mathbf{r}}\frac{1}{k^2} = \frac{1}{4\pi r} \ , \tag{C.145}$$

where $r \equiv \sqrt{x^2+y^2+z^2}$. There are altogether four similar terms in the expression of $\lim_{L\to\infty} G^S_{3D}$ due to distinct combinations of $(y \pm y_1)$ with $(z \pm z_1)$. These correspond to the four point charges of the Green's function for one wall:

$$\lim_{L\to\infty} G^S_{3D} \to G^-_{3D} + G^+_{3D} = G^{1W}_{3D} \ . \tag{C.146}$$

Thus, for infinite plate distance L the Green's function of two walls reduces to that of the one wall case.

C.7 Boundary conditions of μ and H

As pointed out in Sect. C.6, the boundary value problem for G^{2W}_{3D} obeys either von Neumann or Dirichlet boundary conditions at the solid walls (the boundary condition at reservoir plane $z = 0$ is of Dirichlet form in all our calculations). Which one we are going to choose is determined by the boundary conditions of the chemical potential μ, because G^{2W}_{3D} results from the inversion of the Laplacian operating on μ. Setting the boundary condition of the meniscus H is does not depend on what kind of boundary condition the chemical potential satisfies. These two issues are unrelated as far as we can think of the project equation of motion of the meniscus to be independent, though consistent, of the bulk equation of motion containing μ. Of course, there is a preferred choice for the boundary condition of the meniscus given that of the chemical potential. These choices are discussed in the subsequent sections. First, in Sect. C.7.1 we show how utilize the total mass (or volume $V(t)$, which is easily determined either from experiment or simulation) of fluid flown into the system at time t to fix the dynamic contact angle $\theta(t)$. The dynamic contact angle then acts as von Neumann boundary condition for the zeroeth order meniscus profile H_0 producing a non-zero curvature for the fluid front.

In Sect. C.7.2 the boundary condition of the chemical potential is chosen to be the non-homogeneous Dirichlet condition instead of the homogeneous von Neumann condition. Both of these conditions have to be compatible with each other such that they give rise to the same chemical potential distribution within the restricted domain of the fluid phase. It is important to note that we are not overdetermining the boundary value problem $\partial_t\phi = M\nabla^2\mu$ for μ by requiring that μ should satisfy both von Neumann and Dirichlet conditions at the solid walls confining the restricted domain of the fluid with *given* boundary data. The boundary data is not given at the edges of the restricted domain (it is only given at the outermost boundary of the simulation box including the solid walls) but it has to be found self-consistently. We propose only some *approximations* for self-consistent boundary data in Sect. C.7.1 ($\partial_y\mu|_0 = \partial_y\mu|_L = 0$) and in Sect. C.7.2 ($\mu|_0 = \mu|_L = \sigma/R$). Finally, in Sect. C.7.3 we discuss the boundary conditions of the fluctuation correction h.

C.7.1 Experimentally fixed boundary condition

The physical requirement of no mass flux through the solid walls gives rise to homogeneous von Neumann boundary conditions for the chemical potential:

$$\nabla_n \mu|_0 = \nabla_n \mu|_L = 0 \ . \tag{C.147}$$

The Green's function, which is going to be used in Green's boundary term Λ, satisfies *homogeneous* boundary conditions by construction:

$$-\nabla^2 G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1) = \delta(\mathbf{r}-\mathbf{r}_1) \ \ ; \ \ \begin{cases} \partial_y G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1)|_{y=0} = \partial_y G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1)|_{y=L} = 0 \ . \\ G_{3D}^{2W}(\mathbf{r};\mathbf{r}_1)|_{z=0} = 0 \ . \end{cases} \tag{C.148}$$

When projecting the meniscus equation of motion no Green's surface term Λ (Eq. (C.51)) will appear due to the homogeneity of the boundary conditions of the chemical potential. In other words, Eq. (C.63) reads now

$$I_A = \frac{M\sigma}{4}\partial_y^2 \mathrm{H}_0 \ . \tag{C.149}$$

We notice immediately that with Dirichlet boundary condition for H_0, that is, by fixing the height of the contact line $\mathrm{H}_0(y=0) = \mathrm{H}_0(y=L) = \mathrm{C}_0$, the meniscus will become planer ($\mathrm{H}_0(y) = \mathrm{C}_0$) after the mean position H_0 has equilibrated in a non-driven system (no chemical potential gradient at the reservoir boundary). This is easy to see from Eq. (C.149): $I_A \propto \partial_t \mathrm{H}_0 = 0$, and therefore $\partial_y^2 \mathrm{H}_0 = 0$ if H_0 satisfies the Dirichlet boundary conditions. If we want to generate a contact angle, which is different from $\theta = \pi/2$, for *both* moving *and* stopped meniscus position H_0, we have to put in the (dynamic) contact angle by hand and impose the following von Neumann boundary condition: $\partial_y \mathrm{H}_0|_0 = -\partial_y \mathrm{H}_0|_L = \tan(\theta(t))$. Obviously this condition makes the meniscus H_0 curved even in equilibrium where $\theta(t) = \theta_{eq}$, where the equilibrium contact angle θ_{eq} is set by the surface tensions [262]. Under non-equilibrium conditions one possible way of fixing the dynamic contact angle $\theta(t)$ is to experimentally measure the volumetric intake of liquid V(t) and the time dependent position of the contact line C_0. Supposing the real meniscus shape is parametrized by the contact line height $\mathrm{C}_0(t)$ and curvature $K(t)$, $\mathrm{H}_0 \approx \mathrm{C}_0(t) - K(t)Ly + K(t)y^2$, we can relate the experimental parameters to our boundary condition via

$$V(t) = L_x \int_0^{L_y} dy \, \mathrm{H}_0(y,t) \ , \tag{C.150}$$

where L_x is the spatial extent in x-direction and L_y is the separation of the plates in y-direction (usually denoted just as L). It follows from Eq. (C.150) that $K(t) = 6[L_x L_y \mathrm{C}_0(t) - V(t)]/(L_x L_y^3)$. On the other hand, it is easy to find the relation between the curvature $K(t)$ and $\theta(t)$.

C.7.2 Self-consistently fixed boundary condition

Choosing to use *nonhomogeneous* Dirichlet boundary condition for the chemical potential saves us from putting in by hand the curvature by fixing the derivatives of H_0 at $y = 0, L$. Instead of Eq. (C.147) we now set:

$$\mu(x,0,z) = f_1(x,z) \ \ ; \ \ \mu(x,L,z) = f_2(x,z) \ , \tag{C.151}$$

where f_1 and f_2 are values of the chemical potential at the wall which should be found self-consistently. They will give rise to non-zero Green's boundary term $\tilde{\Lambda}$ in the meniscus equation of motion. The Green function $\tilde{G}_{3D}^{2W}$ is determined by homogeneous boundary conditions as before. Thus, the problem is to find $\tilde{G}_{3D}^{2W}$ such that

$$-\nabla^2 \tilde{G}_{3D}^{2W}(\mathbf{r};\mathbf{r}_1) = \delta(\mathbf{r}-\mathbf{r}_1) \quad ; \quad \left\{ \begin{array}{l} \tilde{G}_{3D}^{2W}(\mathbf{r};\mathbf{r}_1)|_{y=0} = \tilde{G}_{3D}^{2W}(\mathbf{r};\mathbf{r}_1)|_{y=L} = 0 \ . \\ \tilde{G}_{3D}^{2W}(\mathbf{r};\mathbf{r}_1)|_{z=0} = 0 \ . \end{array} \right. \tag{C.152}$$

There will be a non-zero curvature created for the meniscus H_0 even when it doesn't move. In the previous case with von Neumann boundary conditions for the chemical potential and Dirichlet boundary conditions for the meniscus H_0, the meniscus will be straight $\mathrm{H}_0 = \mathrm{C}_0$ in equilibrium since $I_A \propto \partial_t \mathrm{H}_0 = 0$ and Eq. (C.149) tells us that $\partial_y^2 \mathrm{H}_0 = 0 \Rightarrow \mathrm{H}_0 =$ *constant*. However, if we choose nonhomogeneous Dirichlet boundary conditions for the chemical potential at the walls, the Green's boundary term will be non-zero. Even when $\partial_t \mathrm{H}_0 = 0$ ($I_A = 0$) we get from Eq. (8.64) that

$$\frac{\sigma}{4}\partial_y^2 \mathrm{H}_0 + \tilde{\Lambda}_{\mathrm{H}_0} = 0 \ . \tag{C.153}$$

Clearly, the term $\tilde{\Lambda}_{\mathrm{H}_0}$ acts as (time dependent) curvature. It should be remembered thought that the price we pay for automatic generation of curvature through $\tilde{\Lambda}_{\mathrm{H}_0}$ is the self-consistent determination of the boundary data f_1 and f_2 (if both walls have identical wetting properties, then $f_1 = f_2$). As a first approximation we can just assume that $\mu|_0 = \mu|_L = \sigma/R$ where R is related to the separation of the walls and equilibrium contact angle through Young's law.

C.7.3 Boundary conditions for fluctuations

Choosing boundary conditions for the chemical potential (G_{3D}^{2W}) and for the zeroeth order meniscus position H_0 is one thing, choosing them for the *fluctuations* h of the meniscus is another. Assume that we know now the 3D Green function and the zeroeth order meniscus configuration H_0 which is a solution of either Eq. (C.149) or Eq. (C.153) depending on the choice of the boundary conditions for μ. Leaving aside the extra complications arising from expanding $\tilde{\Lambda}$ to first order in the fluctuations h around H_0, we can proceed to study the dynamics of the fluctuations in a unified manner irrespective of whether we want to use Dirichlet or von Neumann boundary data for h. Choosing the latter means that we have to provide the local contact angles $\alpha(x,t)$ as the boundary data. The former choice means that we have to feed in the contact line profile $c(x,t)$ as the boundary data. In both cases the boundary condition is unknown to begin with, and has to be derived self-consistently. Notice, that in both cases the boundary data is time dependent which excludes, strictly speaking, the use of local equilibrium values as boundary conditions. The starting point will be the projected equation of motion for fluctuations (Eq. (C.101)):

$$I_B[h] + I_C[h] + I_D[h] = -\frac{M}{4}\frac{\delta F_{2D}[h]}{\delta h} \ . \tag{C.154}$$

In case we want to derive the von Neumann boundary data self consistently for the fluctuations, we should substitute in Eq. (C.154) h as functional of the local contact angles $h = h[\alpha]$ as given by Eq. (8.71). To derive the Dirichlet boundary data self consistently one substitutes into Eq. (C.154) $h = h[c]$ given by Eq. (8.72). The latter method is studied in more detail in Sect. C.13.

C.8 Small curvature expansion

Let us define what is meant by the small curvature approximation. When deriving explicit representation of the terms I_B, I_C and I_D below, we make use of the following approximations:

$$\begin{cases} \mathrm{c}_0(t) \gg K(t)\,(y-L/2)^2\ ,\ \text{for all } y\in[-L/2,L/2] \quad \Rightarrow \quad K \ll 4\,\mathrm{c}_0/L^2\ ; \\ \partial_t \mathrm{c}_0(t) \gg \partial_t K(t)\,(y-L/2)^2\ ,\ \text{for all } y\in[-L/2,L/2] \quad \Rightarrow \quad \partial_t K \ll 4\,\partial_t \mathrm{c}_0/L^2\ . \end{cases} \tag{C.155}$$

The same conditions for the curvature and its time derivative arise if we require y to lie inside the interval $[0,L]$ instead of $[-L/2,L/2]$. It will be shown below that satisfying these criteria naturally leads to the definition of the dimensionless expansion parameter which characterizes the deviation from the flat meniscus configuration:

$$\epsilon \equiv KL^2/\mathrm{c}_0\ . \tag{C.156}$$

In other words, small curvature K implies small ϵ. It should be also be noted that the magnitude of ϵ becomes smaller and smaller in the course of time since the meniscus is rising up and thus $\mathrm{c}_0(t)$ becomes larger. In the non-driven case macroscopic movement of the meniscus necessitates finite (small) curvature. Most of the formulae to be derived below make use of the local limit $\mathrm{c}_0|k| \ll 1$ which gives us an upper limit for curvature

$$K \ll 1/\mathrm{c}_0\ . \tag{C.157}$$

The derivation of this condition is given in Sect. C.11.4. Basically, it derives from the requirement that $I_D \gg I_B + I_C$. When this inequality is satisfied, the diffusive meniscus solution, to be introduced later, is valid.

To obtain finite curvature corrections to the equations of motion of the meniscus and the contact line, we need to consider two kinds of expansions in ϵ. First, in Sect. C.11.2 we will show that the fluctuations of the meniscus are expandable using a so-called memory expansion which gives rise to an nth order approximation $h^{(n)}$ of the full solution h:

$$h = \sum_{n=0}^{\infty} \epsilon^n h_n \tag{C.158}$$

where the nth correction term h_n is expressible in terms of the correction terms h_m with index $m < n$. The series representation does always have at least asymptotic relevance. Second, the Green's functions appearing in the expressions I_B, I_C and I_D must be expanded, too. Their dependence on ϵ derives from the the fact that the zeroeth order profile H_0 is a function of ϵ.

In Sect. C.8.3 we demonstrate that there are some fundamental problems in trying to develop a consistent approximation scheme which allows a unified perturbative treatment of *both* meniscus and contact line equations. Moreover, a second small parameter has to be introduced if the initial height of the meniscus is non-zero and we wish to use the quasi-stationary approximation to be introduced in Sect. C.11.1. This complicates things further as discussed below. To avoid these problems we present another approach in Sect. C.8.3, which allows explicit computation of relevant quantities.

C.8.1 Scaling

In order to use perturbation theory, we need to know how the zeroeth order meniscus and contact line solutions along with the curvature scale in terms of the expansion parameter ϵ. First we consider the case of zero initial height of the contact line, $c_i = 0$. Later on we generalize some of the results for $c_i > 0$.

Zero initial height

Let us assume that the initial height of the contact line $c_i = 0$ and that the Washburn's growth law is obeyed at all times. The equation of motion (C.100) for the contact line height in a pure system reads

$$I_A \approx u\,\partial_t \textsc{h}_0\,\textsc{h}_0 = (M\sigma/4)\,\partial_y^2 \textsc{h}_0 \Rightarrow u\,\partial_t \textsc{c}_0\,\textsc{c}_0 = M\sigma K/2 \ , \tag{C.159}$$

where the precise value of the constant u depends on the way we approximate the term term I_A. More details can be found in App. C.12. In the derivation of Eq. (C.159) we have utilized the ansatz, $\textsc{h}_0 = \textsc{c}_0 - KLy + Ky^2$, which fixes the meniscus to parabolic shape with $\textsc{h}_0(0,t) = \textsc{h}_0(L,t) = \textsc{c}_0(t)$. The numerical constant u derives from the term I_A. Dropping the time derivative of the curvature will be justified based on scaling arguments below. Solution of Eq. (C.159) is the Washburn's law for $\textsc{c}_0$:

$$\textsc{c}_0(t) = \sqrt{M\sigma K t/u} \ . \tag{C.160}$$

Since $\epsilon = KL^2/\textsc{c}_0 \Rightarrow \epsilon^2 = K^2L^4/\textsc{c}_0^2 = KL^4u/(M\sigma t)$ by Eq. (C.160). Solving for K, we get $K = M\sigma t\epsilon^2/(uL^4)$. Substitution of $K(\epsilon)$ into Eq. (C.160) yields $\textsc{c}_0 = M\sigma t\epsilon/(uL^2)$. Thus, we see that until the cross over time

$$t_* \equiv \frac{uL^2}{M\sigma} \ , \tag{C.161}$$

the contact line height $\textsc{c}_0 = \mathcal{O}(\epsilon)$ and $K = \mathcal{O}(\epsilon^2)$. The definition of t_* given above guarantees that when ever $t \le t_*$ the prefactor multiplying ϵ in the expression of $\textsc{c}_0$ is always less than or equal to unity: $M\sigma t/(uL^2) \le 1$. Without this restriction, for times as large as $t \sim 1/\epsilon$ the contact line height $\textsc{c}_0$ would not be a small number any more. As what comes to the smallness of the curvature, the value of K saturates pretty fast to a value which is rather close to its equilibrium value fixed by the surface tensions. By choosing the surface tensions properly, K can be made arbitrarily small and the time restriction $t \le t_*$ is really not needed to keep it that way.

Let us now express the rest of the quantities in terms of ϵ. Substitution of $\textsc{c}_0(\epsilon)$ and $K(\epsilon)$ into the expression of $\textsc{h}_0$ gives

$$\textsc{h}_0 = \textsc{c}_0 + K(y^2 - Ly) = \textsc{c}_0\left(1 + \frac{KL^2}{\textsc{c}_0}\left[\frac{y^2}{L^2} - \frac{y}{L}\right]\right) = \frac{M\sigma t}{uL^2}\,\epsilon\left(1 + \epsilon\left[\frac{y^2}{L^2} - \frac{y}{L}\right]\right) \ . \tag{C.162}$$

The average velocity of the contact line is $\partial_t \textsc{c}_0 = (1/2)(M\sigma K/u)^{1/2} t^{-1/2}$. Multiplication and division by $(M\sigma K/u)^{1/2}$ yields $\partial_t \textsc{c}_0 = (1/2)(M\sigma K/u)\,\textsc{c}_0^{-1}$. Finally, multiplying and dividing by KL^2 we get $\partial_t \textsc{c}_0 = M\sigma\epsilon/(2uL^2)$. Thus, the velocity is of first order in ϵ. Treating the curvature constant we get the following dependence on ϵ

$$\begin{cases} \textsc{h}_0 = \dfrac{M\sigma t}{uL^2}\,\epsilon\left(1 + \epsilon\left[\dfrac{y^2}{L^2} - \dfrac{y}{L}\right]\right) . \\ \textsc{c}_0 = \dfrac{M\sigma t}{uL^2}\,\epsilon \ . \\ K = \dfrac{M\sigma t}{uL^4}\,\epsilon^2 \ . \end{cases} \qquad \begin{cases} \partial_t \textsc{h}_0 = \partial_t \textsc{c}_0 \ . \\ \partial_t \textsc{c}_0 = \dfrac{M\sigma}{2uL^2}\,\epsilon \ . \\ \partial_t K = 0 \ . \end{cases} \tag{C.163}$$

It should be noted that in the constant curvature approximation K, as given by the relation on the bottom left, is truly independent of time.

Next, we show that even if we include the time dependence of the curvature only higher order corrections will be generated. If $K = K(t)$ the solution of Eq. (C.159) becomes $\mathrm{C}_0 = ((M\sigma/u)\int_0^t dsK(s))^{1/2}$. By carrying out differentiation of this expression with respect to time it is easy to show that the velocity of the contact line is still of first order in ϵ: $\partial_t \mathrm{C}_0 = M\sigma\epsilon/(2uL^2)$. Assume now that $K(t)$ is a monotonously growing function of t, which is always less than t^ζ with $\zeta < 1$. Then $\partial_t K \to 0$ for $t \to \infty$. We get

$$\mathrm{C}_0 \partial_t \mathrm{C}_0 = \frac{M\sigma}{2u}\int_0^t ds\, \partial_s K(s) \geq \frac{M\sigma}{2u}\, t\, \partial_t K(t) \;\Rightarrow\; \partial_t K(t) \leq \frac{2u}{M\sigma t}\mathrm{C}_0\, \partial_t \mathrm{C}_0 \ . \tag{C.164}$$

It is easy to convince oneself of the first inequality by comparing the area bounded by the curve t^ζ (that is, $\int_0^t ds\, s^\zeta$) with the area $t\,\partial_t K(t)$ of a rectangular box whose side lengths are t and $\partial_t K(t)$. Since the final inequality in Eq. (C.164) contains C_0, which on the other hand is defined thorough the integral over $K(s)$, it is not directly usable. Let us make use of the upper limit of C_0:

$$\mathrm{C}_0 = \sqrt{\left(\frac{M\sigma}{4}\int_0^t ds\, K(s)\right)} \;\leq\; \sqrt{\left(\frac{M\sigma}{4} t\, K(t)\right)} \;\Rightarrow\; \partial_t K(t) \;\leq\; \frac{2u}{M\sigma t}\sqrt{\left(\frac{M\sigma t}{u}K(t)\right)}\partial_t \mathrm{C}_0 \ . \tag{C.165}$$

The first inequality can be seen to hold by comparing the area $\int_0^t ds\, K(s)$ with the area of the rectangular box, $t\, K(t)$: the latter is always larger. Substitution of the upper limit of C_0 into to Eq. (C.164) yields the final inequality in Eq. (C.165). The remaining task is to find an upper limit for $K(t)$. This is readily found in terms of the upper limit of C_0:

$$K(t) = \frac{\epsilon \mathrm{C}_0}{L^2} \;\Rightarrow\; K(t)^2 = \frac{\epsilon^2 \mathrm{C}_0^2}{L^4} \;\leq\; \frac{\epsilon^2 M\sigma t K(t)}{uL^4} \;\Rightarrow\; K(t) \;\leq\; \frac{\epsilon^2 M\sigma t}{uL^4} \ . \tag{C.166}$$

Finally, substitution the upper limit for $K(t)$ defined in the previous equation into Eq. (C.165) gives the upper limit of the $\partial_t K(t)$:

$$\partial_t K(t) \;\leq\; \frac{2u}{M\sigma t}\sqrt{\left(\frac{M\sigma t}{u}\frac{\epsilon^2 M\sigma t}{uL^4}\right)}\partial_t \mathrm{C}_0 = \frac{2\epsilon}{L^2}\partial_t \mathrm{C}_0 = \frac{M\sigma}{uL^4}\epsilon^2 \ . \tag{C.167}$$

Thus, we conclude that when the curvature is time dependent, its time rate of change will be at least of order ϵ^2. Therefore, even for $K = K(t)$, we can approximate $\partial_t \mathrm{H}_0 = \partial_t \mathrm{C}_0 + \mathcal{O}(\epsilon^2)$. For $K = K(t)$ Eq. (C.163) becomes

$$\begin{cases} \partial_t \mathrm{H}_0 = \partial_t \mathrm{C}_0 + \mathcal{O}(\epsilon^2) \ . \\[2ex] \partial_t \mathrm{C}_0 = \dfrac{M\sigma}{2uL^2}\,\epsilon \ . \\[2ex] \partial_t K = \mathcal{O}(\epsilon^2) \ . \end{cases} \tag{C.168}$$

In addition it is easy to show that $K(t) = \mathcal{O}(\epsilon^2)$. Use the definition of ϵ to write $\epsilon^2 = K(t)^2 L^4/\mathrm{C}_0(t)^2$ and replace $\mathrm{C}_0(t) = ((M\sigma/u)\int_0^t ds\, K(s))^{1/2}$. Since the integral is bounded by $\int_0^t ds\, K(s) \leq K(t)t$ we obtain immediately that $K(t) \leq \epsilon^2 M\sigma t/(uL^4)$.

Non-zero initial height

The initial height of the contact line $c_i > 0$. Washburn's diffusive behaviour becomes visible clearly only for times sufficiently large, which is evident from the solution of the contact line equation

$$\mathrm{c}_0 = \sqrt{\frac{M\sigma K t}{u} + c_i^2} \ . \tag{C.169}$$

We only consider a constant curvature in this section. We could actually define c_i to be the height of the contact line at which the curvature can be said to have reached a constant value. As before, we can solve the dependence of the curvature on the expansion parameter from the definition $\epsilon = KL^2/\mathrm{c}_0(K)$. Squaring both sides gives $\epsilon^2(M\sigma Kt/u + c_i^2) = K^2L^4$. Thus,

$$K = \frac{\epsilon^2 M\sigma t}{2uL^4} + \frac{\epsilon}{L^2}\sqrt{c_i^2 + \left(\frac{\epsilon M\sigma t}{2uL^2}\right)^2} \ . \tag{C.170}$$

Only the root of with positive root can be accepted because convex meniscus remains convex, similarly for concave meniscus. To lowest order in ϵ,

$$K \longrightarrow \begin{cases} \dfrac{M\sigma t}{uL^4}\epsilon^2 \quad , \quad c_i = 0. \\ \dfrac{c_i}{L^2}\epsilon + \mathcal{O}(\epsilon^2) \quad , \quad c_i > 0 \ . \end{cases} \tag{C.171}$$

The latter results sets a lower bound for ϵ: $c_i^2 \gg (\epsilon M\sigma t/(2uL^2))^2$. It should be noted that if any truncated expansion is used to define the curvature, K will become dependent on t although we initially assumed K to be a constant. The assumption of constancy only holds if the exact form given in Eq. (C.170) is used. Substitution of the expression of K back into Eq. (C.169) allows us to obtain the ϵ-dependence of c_0:

$$\mathrm{c}_0 = \sqrt{\frac{M\sigma t}{u}\left(\frac{c_i\epsilon}{L^2} + \mathcal{O}(\epsilon^2)\right) + c_i^2} = c_i + \frac{M\sigma t}{2uL^2}\epsilon + \mathcal{O}(\epsilon^2) \ . \tag{C.172}$$

In other words, when $c_i = 0$ and $t < t_*$, $\mathrm{c}_0 = \mathcal{O}(\epsilon)$ and $K = \mathcal{O}(\epsilon^2)$. When $c_i > 0$, $\mathrm{c}_0 = \mathcal{O}(1)$ and $K = \mathcal{O}(\epsilon)$. Hence, curvature terms are always of higher order in the expansion parameter.

C.8.2 Perturbative approach

The linearized meniscus equation is solved order by order matching the powers of ϵ emerging from the expansion of the zeroeth order solution H_0 contained in the Green's functions, and the fluctuation correction h. We can write

$$I_B = \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \left[\sum_{n=0}^{\infty} \frac{\epsilon^n}{n!}(\partial_\epsilon^n G_B)|_0\right]\left[\sum_{m=0}^{\infty}\epsilon^m h_m\right]\frac{M\sigma}{2uL^2}\epsilon \ ; \tag{C.173}$$

$$I_C = \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \left[\sum_{n=0}^{\infty} \frac{\epsilon^n}{n!}(\partial_\epsilon^n G_C)|_0\right]\left[\sum_{m=0}^{\infty}\epsilon^m h_m\right]\frac{M\sigma}{2uL^2}\epsilon \ ; \tag{C.174}$$

$$I_D = \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \left[\sum_{n=0}^{\infty} \frac{\epsilon^n}{n!}(\partial_\epsilon^n G_D)|_0\right]\left[\sum_{m=0}^{\infty}\epsilon^m \partial_t h_m\right] . \tag{C.175}$$

The factor $M\sigma\epsilon/(2uL^2)$ in I_B and I_C comes from the approximation $\partial_t \mathrm{H}_0 \approx \partial_t \mathrm{C}_0$, as we assume a constant curvature for simplicity. The short-hand notation

$$\begin{aligned} G_B(\epsilon) &\equiv \partial_z G_{3D}^{2W}(x, y, z; x_1, y_1, \mathrm{H}_0(\epsilon))|_{\mathrm{H}_0(\epsilon)} \; ; && \text{(C.176)} \\ G_C(\epsilon) &\equiv \partial_{z_1} G_{3D}^{2W}(x, y, \mathrm{H}_0(\epsilon); x_1, y_1, z_1)|_{\mathrm{H}_0(\epsilon)} \; ; && \text{(C.177)} \\ G_D(\epsilon) &\equiv G_{3D}^{2W}(x, y, \mathrm{H}_0(\epsilon); x_1, y_1, \mathrm{H}_0(\epsilon)) \; . && \text{(C.178)} \end{aligned}$$

Based on the previous sections, we know that when the initial height $c_i = 0$ and $\epsilon = 0$ (corresponding to zero curvature for a finite system at finite time), the meniscus does not move. Equivalently, $\mathrm{H}_0 = \mathrm{C}_0 = 0$, $\partial_t \mathrm{H}_0 = \partial_t \mathrm{C}_0 = 0$. Yet, there will be motion associated with the relaxation of the fluctuations h. Therefore some non-zero contribution to the left hand side of the equation of motion of the fluctuations of the meniscus is generated by terms I_B, I_C and I_D.

Hierarchy of perturbative solutions with $c_i = 0$

We will now evaluate some of the lowest order derivatives of the Green's functions defined in Eq. (C.176) - Eq. (C.178) at $\epsilon = 0$ *assuming that this is permissible to differentiate the Fourier series representation of G_A, G_B and G_C with respect to ϵ* before carrying out the integrals over x_1 and y_1. Moreover, we set $c_i = 0$ and require that there is no driving chemical potential gradient at the reservoir boundary. The evaluation of the perturbation expansion begins with the term $(G_B)|_0 = \partial_z G_{2D}^I|_0 + \partial_z G_{3D}^S|_0$, where $G_{3D}^S = G_{3D}^{S+} + G_{3D}^{S-}$, as shown in Eq. (C.140). Since G_{2D}^I is $n = 0$ term appearing in the expression of G_{3D}^S, it suffices to study the latter. We have

$$\begin{aligned} \partial_z G_{3D}^{S\pm} = \frac{1}{(2\pi)^2} \frac{1}{L} \sum_{n=1}^{\infty} \cos(n\pi(y \pm y_1)/L) \Bigg(\int dk_x \int dk_z \, \frac{e^{-\imath k_x (x - x_1)} e^{-\imath k_z (z - z_1)} (-\imath k_z)}{k_x^2 + (\pi n/L)^2 + k_z^2} \\ - \int dk_x \int dk_z \, \frac{e^{-\imath k_x (x - x_1)} e^{-\imath k_z (z + z_1)} (-\imath k_z)}{k_x^2 + (\pi n/L)^2 + k_z^2} \Bigg) \; . \end{aligned} \tag{C.179}$$

Setting $z = z_1 = \mathrm{H}_0(\epsilon = 0) = 0$ the integrals vanish since an odd function is integrated over an even interval. Thus, $\partial_z G_{3D}^{S\pm}|_0 = 0$, $\partial_z G_{2D}^I|_0 = 0$ and $(G_B)|_0 = 0$. The only difference between $(G_B)|_0$ and $(G_C)|_0$ is that the differentiation is with respect to z_1 for the latter. Using expression on the right hand side of Eq. (C.179) it is easy to see that for the same reason (oddness of integrand) $(G_C)|_0 = 0$. Obviously, $(G_D)|_0 = 0$ as can be seen right away from Eq. (C.179) by leaving out the differentiation with respect to z.

Next order in derivatives of ϵ requires some more computation. Using the chain rule we obtain $(\partial_\epsilon G_B)|_0 = \partial_z G_B|_0 \, \partial_\epsilon z|_0 + \partial_{z_1} G_B|_0 \, \partial_\epsilon z_1|_0$. It is understood that $z = \mathrm{H}_0(y, t)$ and $z_1 = \mathrm{H}_0(y_1, t)$. Explicitly,

$$\left.\frac{\partial z}{\partial \epsilon}\right|_0 = \left.\frac{\partial \mathrm{H}_0(y,t)}{\partial \epsilon}\right|_0 = \left.\frac{\partial}{\partial \epsilon} \Big[\mathrm{C}_0(\epsilon) + K(\epsilon)(y^2 - yL) \Big]\right|_0 = \left.\frac{\partial \mathrm{C}_0}{\partial \epsilon}\right|_0 = \frac{M\sigma t}{uL^2} \; . \tag{C.180}$$

Hence, we get $\partial_\epsilon z|_0 = \partial_\epsilon z_1|_0 = M\sigma t/(uL^2)$. Expressing G_B in terms of the derivatives of G_{3D}^{2W}, we get

$$(\partial_\epsilon G_B)|_0 = \Big(\partial_z G_B|_0 + \partial_{z_1} G_B|_0 \Big) \frac{M\sigma t}{uL^2} = \Big(\partial_z^2 G_{3D}^{2W}|_0 + \partial_{zz_1}^2 G_{3D}^{2W}|_0 \Big) \frac{M\sigma t}{uL^2} \tag{C.181}$$

The first term on the right hand side of the previous equation can be split as $\partial_z^2 G_{3D}^{2W}|_0 = \partial_z^2 G_{2D}^I|_0 + \partial_z^2 G_{3D}^S|_0$. By a straightforward calculation, $\partial_z^2 G_{2D}^I|_0 = 0$. The constituents of the second term behave as

$$\partial_z^2 G_{3D}^{S\pm}\Big|_0 = \frac{1}{(2\pi)^2}\frac{1}{L}\sum_{n=1}^{\infty}\cos(n\pi(y\pm y_1)/L)\left(\int dk_x \int dk_z\, \frac{e^{-\imath k_x(x-x_1)}(-\imath k_z)^2}{k_x^2+(\pi n/L)^2+k_z^2}\right.$$
$$\left. - \int dk_x \int dk_z\, \frac{e^{-\imath k_x(x-x_1)}(-\imath k_z)^2}{k_x^2+(\pi n/L)^2+k_z^2}\right) = 0\ . \tag{C.182}$$

Thus, $\partial_z^2 G_{3D}^{2W}|_0 = 0$. We should be careful, though, as differentiation of the Fourier series representation of $G_{3D}^{S\pm}$ termwise becomes more and more divergent as can be seen by the increasing power of factors $(\imath k_z)$ in the numerator of the integral expression in Eq. (C.182). Keeping this in mind, what about the second term $\partial_{zz_1}^2 G_{3D}^{2W}|_0$? It turns out to be non-zero, which can be easily confirmed by noticing that since the derivatives are taken with respect to z and z_1, in the numerator of the first fraction of the previous equation we will have $(-\imath k_z)(+\imath k_z)$ instead of $(-\imath k_z^2)$. Similarly, in the numerator of the second fraction there will be a factor $(-\imath k_z)^2$ as in Eq. (C.182). Therefore, when the two fractions are subtracted we get a non-zero result:

$$\partial_{zz_1}^2 G_{3D}^{S\pm}\Big|_0 = \frac{2}{(2\pi)^2}\frac{1}{L}\sum_{n=1}^{\infty}\cos(n\pi(y\pm y_1)/L)\int dk_x \int dk_z\, \frac{e^{-\imath k_x(x-x_1)}k_z^2}{k_x^2+(\pi n/L)^2+k_z^2} \tag{C.183}$$

Therefore, $(\partial_\epsilon G_B)|_0 \neq 0$. Using similar arguments, it is easy to convince oneself that $(\partial_\epsilon G_C)|_0$ will also be something non-zero. Because $(\partial_\epsilon G_D)|_0 = (G_B)|_0\, \partial_\epsilon z|_0 + (G_C)|_0\, \partial_\epsilon z_1|_0$, and $(G_B)|_0 = (G_C)|_0 = 0$, it also follows that $(\partial_\epsilon G_D)|_0 = 0$. The first non-zero contribution in the expansion of G_D comes from the term $(\partial_\epsilon^2 G_D)|_0$. The non-zero contribution comes from terms like $\partial_{zz_1}^2 G_{3D}^{2W}$ which we have already shown to be non-zero. To summarize, termwise evaluation of the Taylor series leads to the vanishing of the lowest order contributions in ϵ assuming that it is allowed to differentiate the series representation of $G_{3D}^{S\pm}$ with respect to ϵ:

$$\left\{\begin{array}{l}(G_B)|_0 = (G_C)|_0 = (G_D)|_0 = (\partial_\epsilon G_D)|_0 = 0\ ;\\ (\partial_\epsilon G_B)|_0\, ,\, (\partial_\epsilon G_C)|_0\, ,\, (\partial_\epsilon^2 G_D)|_0 \neq 0\ .\end{array}\right. \tag{C.184}$$

As will be shown below the assumption of non-zero initial height will make all of these terms non-zero. Lower order non-zero contributions will also result if one changes the boundary condition of the chemical potential from $\mu = 0$ to $\partial_n \mu = \mathcal{F}$, where $\mathcal{F}$ is the mass flux driven into the system.

It is now time to sum up the contributions of equal order in ϵ coming from terms I_B, I_C and I_D and match them with the corresponding power on the right hand side of the equation of motion of the fluctuations of the meniscus, which contains the term $(M\sigma/4)\nabla^2 h = (M\sigma/4)\nabla^2 \sum_{n=0}^{\infty} \epsilon^n h_n$. The equation of motion can be rewritten as

$$I_B + I_C = \frac{M\sigma}{4}\nabla^2 h - I_D\ . \tag{C.185}$$

We moved the term I_D to the right since it is not proportional to $\partial_t c_0 \propto \epsilon$ in the current expansion scheme. As we will see, even though the summation over powers of ϵ goes from 0 to ∞ on the left and from 1 to ∞ on the right, the possibility of some of the derivatives of the Green's functions being zero, makes the matching of powers of ϵ a bit more challenging. We have

$$I_B + I_C =$$

$$\sum_{n=0}^{\infty} \epsilon^{n+1} \left\{ \frac{M\sigma}{2uL^2} \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \sum_{k=0}^{n} \left[G_B^{(k)} h_{n-k}(x,y,t) + G_C^{(k)} h_{n-k}(x_1,y_1,t) \right] \right\} ; \tag{C.186}$$

$$(M\sigma/4)\nabla^2 h - I_D =$$

$$\sum_{n=0}^{\infty} \epsilon^{n} \left\{ \frac{M\sigma}{4} \nabla^2 h_n - \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \sum_{k=0}^{n} G_D^{(k)} \partial_t h_{n-k}(x_1,y_1,t) \right\} , \tag{C.187}$$

where $G_{B,C}^{(k)} \equiv (1/k!)\,\partial_\epsilon^k G_{B,C}(x,y,\mathrm{H}_0(y,t);x_1,y_1,\mathrm{H}_0(y_1,t))|_0$. Dimensionless position and time arguments do not generate any powers of ϵ in the equation above, so we continue to use dimensionfull arguments. At zeroeth order in ϵ we get just

$$\frac{M\sigma}{4} \nabla^2 h_0 - \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_D^{(0)} \partial_t h_0(x_1,y_1,t) = 0 \ . \tag{C.188}$$

Since $G_D^{(0)} = 0$, this equation reduces to $\nabla^2 h_0 = 0$ corresponding to the quasi-stationary approximation discussed in Sect. C.11.1. If the result of termwise differentiation leading to Eq. (C.184) is to be trusted, the next nontrivial contribution will be of $\mathcal{O}(\epsilon^2)$ given that we fix the boundary condition as $h_0(x,0,t) = c(x,t)$, and $h_n(x,0,t) = 0$ for $n \geq 1$. The choice of the boundary conditions will be discussed more thoroughly in Sect. C.8.3.

Hierarchy of perturbative solutions with $c_i > 0$

Let us see now, how the perturbation expansion is modified, if the initial height of the contact line is taken to be positive: $c_i > 0$. Again, we assume that the curvature has reached its steady state value so we can neglect the time derivative $\partial_t K$. As before, $\partial_t \mathrm{H}_0 \approx \partial_t \mathrm{C}_0 \propto \epsilon$. Eq. (C.180) has to be modified since now there will be extra contribution to $\partial_t \mathrm{H}_0$ due to c_i: $\partial_\epsilon z|_0 = \partial_\epsilon z_1|_0 = M\sigma t/(uL^2) + c_i/L^2(y^2 - yL)$. Also, the lowest order derivatives of the Green's functions with respect to ϵ will not be zero anymore. At order $n = 0$, Eq. (C.186) and Eq. (C.187) reduce to

$$\frac{M\sigma}{4} \nabla^2 h_0 - \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_D^{(0)}(c_i) \, \partial_t h_0(x_1,y_1,t) = 0 \ , \tag{C.189}$$

where $G_D^{(0)}(c_i) \equiv G_{3D}^{2W}(x,y,c_i;x_1,y_1,c_i) \neq 0$. As will be shown in Sect. C.10.5, the Fourier transformation of the previous equation gives $\partial_t h(k,t) = \tilde{\sigma} k^2 h(k,t)$ for $c_i|k| \ll 1$. The renormalized surface tension $\tilde{\sigma} \equiv M\sigma/(4c_i)$. Thus, for long wave-lengths the first equation of the perturbation series behaves like a diffusion equation, and it is possible to write the solution of Eq. (C.189) in the form $h_0 \approx \hat{L}_0^{-1} c$, where we have defined

$$\hat{L}_0 \equiv \frac{M\sigma}{4} \nabla^2 - \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_D^{(0)}(c_i) \, \partial_t \approx \frac{M\sigma}{4} \nabla^2 - c_i \partial_t \tag{C.190}$$

The boundary condition $h(x,0,t) = c(x,t)$ has been chosen. At the next level of hierarchy we can utilize the operator $\hat{L}_0$ again:

$$\begin{aligned} &\frac{M\sigma}{2uL^2}\int_{-\infty}^{\infty}dx_1\int_0^L dy_1 \left[G_B^{(0)}(c_i)\, h_0(x,y,t) + G_C^{(0)}(c_i)\, h_0(x_1,y_1,t)\right] \\ &= \frac{M\sigma}{4}\nabla^2 h_1 - \int_{-\infty}^{\infty}dx_1\int_0^L dy_1 \left[G_D^{(0)}(c_i)\, \partial_t h_1(x_1,y_1,t) + G_D^{(1)}(c_i)\, \partial_t h_0(x_1,y_1,t)\right] . \end{aligned} \tag{C.191}$$

This we can rewrite as $\hat{L}_0 h_1 = S_1$, where S_1 is acts as the source term of the diffusion equation. The source contains only terms which contain h_0, which has been already solved. Explicitly,

$$\begin{aligned} S_1(x,y,t) \;\equiv\; &\frac{M\sigma}{2uL^2}\int_{-\infty}^{\infty}dx_1\int_0^L dy_1 \Bigg[G_B^{(0)}(c_i)\, h_0(x,y,t) + G_C^{(0)}(c_i)\, h_0(x_1,y_1,t) \\ &+ \frac{2uL^2}{M\sigma} G_D^{(1)}(c_i)\, \partial_t h_0(x_1,y_1,t)\Bigg] . \end{aligned} \tag{C.192}$$

The diffusion equation with a source term is easily solved: $h \approx h_0 + \epsilon h_1$. Choosing a zero boundary condition for higher order corrections, $h_1(x,0,t) = 0$ we get

$$h_1(x,y,t) = \int_0^t dt_1 \int_{-\infty}^{\infty}dx_1 \int_0^L dy_1\, L_0^{-1}(x,y,t;x_1,y_1,t_1) S_1(x_1,y_1,t_1) \ , \tag{C.193}$$

where L_0^{-1} is the kernel of the inverse operator $\hat{L}_0$ given in Eq. (C.190). It is easy to see that the same structure remains at all orders of perturbation theory. There is always a diffusion like equation with a source term which is expressible in terms of lower order known solutions. However, the choice of the boundary conditions is not quite unambiguous. This is the topic of the next section.

C.8.3 Gross-order approach

In this section we will show that the whole idea of expanding the meniscus fluctuation h as power series in ϵ is a bad idea, because it is not easy to fix the boundary conditions of the terms h_n at the contact line level. Taking $\epsilon = 0$ limit can be done, but it only gives a trivial flat solution for the meniscus. To keep the lowest order ϵ dependence of the theory sensible and yet make it computable is a difficult goal. Below we will argue that the goal can be achieved by approximating

$$\textsc{h}_0(\epsilon) = \textsc{c}_0(\epsilon) + K(\epsilon)(y^2 - Ly) \approx \textsc{c}_0(\epsilon) \ , \tag{C.194}$$

and leaving out the y-dependent part of $\textsc{h}_0$ from the Green's functions because its prefactor is of order $K(\epsilon) = \mathcal{O}(\epsilon^2)$ when $c_i = 0$. Thus, if we neglect the curvature contribution as indicated by Eq. (C.194) we only make an error which is of the order of $\mathcal{O}(\epsilon^2)$ when computing the expressions I_B, I_C and I_D:

$$I_B(\textsc{h}_0(\epsilon)) \approx I_B(\textsc{c}_0(\epsilon)) + \mathcal{O}(\epsilon^2) \ , \tag{C.195}$$

and similarly for I_C and I_D. We will also show that all the terms I_B, I_C and I_D are of $\mathcal{O}(\epsilon)$ in the regime where $|k|\textsc{c}_0 \ll 1$ and $t \le t_*$. These boundaries are not strict, but if the theory is used outside of its domain of validity, the results can only be trusted at order $\mathcal{O}(\epsilon)$. An important difference with Sect. C.8.2 is that we do not take the limit $\epsilon \to 0$ prior to integration over x_1 and y_1. For example, even though the *kernel* of the I_B integral vanishes for $\epsilon = 0$ as shown in the previous section, the integrated expression $I_B(\mathrm{c}_0(\epsilon))$ is independent of c_0 and gives a non-zero result even if we set $\epsilon = 0$. These results are discussed in more detail below.

Let us first recall the advantages and disadvantages of the perturbative method we have described in Sect. C.8.2. Whether we choose to use the zero or non-zero initial condition of the contact line height, a solvable perturbation series results given that there remains some ambiguity in fixing the boundary conditions. For $c_i = 0$ at each level of the hierarchy a simple Laplacian operator ∇^2 has to be inverted as seen from the first equation of the hierarchy $\nabla^2 h_0 = 0$. Thus, using this method we are unable to see the memory effects connecting the meniscus and the contact line motions because inversion of ∇^2 does not give rise to any dependence on the past. Perturbation theory is simple, though, owing to the fact that there is just a single expansion parameter in the theory. It is $\epsilon \equiv KL^2/\mathrm{c}_0$, which is needed for the expansion of the Green's functions. Given that the lowest order terms of the Green's function expansion vanish as in Eq. (C.184) the perturbative solution of the meniscus fluctuation goes like $h \approx h_0 + \epsilon^2 h_2$. Thus, taking into account the first non-zero correction term h_2 means that we also have to take into account the time dependence of the curvature, which is also $\mathcal{O}(\epsilon^2)$. This is clearly awkward.

For $c_i > 0$, one has to invert a diffusion like operator $c_i\partial_t - (M\sigma/4)\nabla^2$ for long wave length fluctuations. The advantage is that the lowest order terms of the Green's function expansion in powers of ϵ are not zero. Therefore, we can write $h \approx h_0 + \epsilon h_1$. Because for long wave lengths the operator to be inverted at each level of hierarchy is of diffusion type, this method gives rise to memory effects as explained in Sect. C.16. In other words the history of the contact line affects the motion of the meniscus. This is easily seen when solving for h_0 from

$$\left(c_i\partial_t - (M\sigma/4)\nabla^2\right) h_0 = 0 \tag{C.196}$$

with the time dependent boundary condition $h_0(x, 0, t) = c(x, t)$. We have done this (for moving contact line) in Sect. C.11.2. The disadvantage is that due to the presence of a new length scale c_i, the memory expansion parameter will be different than the expansion parameter $\epsilon \equiv KL^2/\mathrm{c}_0$. The memory expansion parameter ϵ_m can be read off from the (non-dimensionalized) first equation of the hierarchy, Eq. (C.196): $\epsilon_m^{-1} \equiv M\sigma t/(L^2 c_i)$. This is the dimensionless combination that appears in the argument of the exponential solution of Eq. (C.196). For $\epsilon_m \to 0$ the solution h_0 reduces to the quasi-stationary solution h_{qs} to be derived in Sect. C.11.1. The second expansion parameter of the theory is that of the Green's function expansion, $\epsilon \equiv KL^2/\mathrm{c}_0$. Since ϵ depends on t through $\mathrm{c}_0(t)$ it is possible that of ϵ_m is smaller or bigger than ϵ at different moments of time.

The fundamental problem with the perturbative approach, which appears in both cases $c_i = 0$ and $c_i > 0$, has to do with the boundary conditions of the meniscus. What we would like to do is to obtain $h = h(c)$, where the contact line position is unknown. Once this solution is used to convert the dissipation and free energy functionals of the meniscus into those of the contact line (Sect. C.13), after taking proper variations the contact line equation of motion results. Writing $h \approx h_0 + \epsilon h_1 + \epsilon^2 h_2 + \ldots$ the first issue we have to settle is whether we can treat all of these corrections as independent of (orthogonal to) each other from the point of view of the variational technique which we are using to produce the contact line equation. If the answer is yes (given that some suitable definition of 'orthogonality' can be found), taking variations with respect to $c_n(x,t)$, $n = 0, 1, 2, \ldots$ generates a *separate* equation of motion for each of the boundary conditions $c_n(x,t)$, which can not be taken zero anymore. This is due to two things. Firstly, the free energy functional is quadratic in collective coordinates $c_n(x,t)$ which induces mixing. Secondly, the noise term is highly nonlinear as well, which basically makes it extremely hard to develop any kind of sensible, systematic perturbation scheme for individual coordinates $c_n(x,t)$. To circumvent these problems, suppose that we choose to satisfy the boundary conditions by setting $h_0(x,0,t) = c(x,t)$ and $h_n(x,0,t) = 0$, $n = 1, 2, \ldots$. Then, we only have to deal with one collective coordinate $c(x,t)$ instead of many $c_n(x,t)$. Since $h_0(c)$ does not have any dependence on ϵ by definition, we immediately discover that the choice of this boundary condition leads to an inconsistency if we require that the full solution $h = \sum_n \epsilon^n h_n$ satisfies the same boundary condition: $h(x,0,t) = \sum_n \epsilon^n h_n(x,0,t) = c(x,t) \Rightarrow c = c(\epsilon)$, which can not be true since $h_0 = h_0(c)$ was supposed to be independent of ϵ. To summarize, choosing a separate boundary condition for all correction terms h_n of the meniscus fluctuations is impractical. On the other hand, the choice of a single non-zero boundary condition only for the first term of the expansion, h_0 leads to an inconsistency.

To make progress we device a third option, which allows for non-zero values for the curvature (non-zero ϵ). Instead of developing the Green's functions and the fluctuation h of the meniscus systematically into power series and matching powers, we expand the terms I_B, I_C and I_D in powers of ϵ by evaluating the gross-order of them *without* expanding h. The more terms we take into account from the Green's function expansion, the better h approximates the actual solution. Since we do not expand h itself, we avoid the problems associated with the choice of the boundary conditions. In this case there is just one possibility: $h(x,0,t) = c(x,t)$. To illustrate why this method is different form the two failures above, we first write down the equation of motion for the meniscus fluctuations: $I_B + I_C + I_D = (M\sigma/4)\nabla^2 h$, or

$$\begin{aligned} &\partial_t \mathrm{C}_0\, h(x,y,t) \int dx_1 \int dy_1\, G_B(c_i) + \partial_t \mathrm{C}_0 \int dx_1 \int dy_1\, G_C(c_i) h(x_1,y_1,t) \\ &+ \int dx_1 \int dy_1\, G_D(c_i)\, \partial_t h(x_1,y_1,t) + \int dx_1 \int dy_1\, G_D^{(1)}(c_i)\, \partial_t h(x_1,y_1,t) \\ &= (M\sigma/4)\nabla^2 h\ , \end{aligned} \tag{C.197}$$

where we have assumed that $c_i > 0$. We notice that different orders of ϵ appear on the left hand side: the first and second terms on the left are obviously of order ϵ since $\partial_t \mathrm{C}_0 \propto \epsilon$. The third is $\mathcal{O}(1)$ and the fourth one is again proportional to ϵ because $G_D^{(1)}(c_i) = \partial_z G_{3D}^{1W}|_{c_i} \partial_\epsilon \mathrm{H}_0(y,t)|_0\, \epsilon + \partial_{z_1} G_{3D}^{1W}|_{c_i} \partial_\epsilon \mathrm{H}_0(y_1,t)|_0\, \epsilon$. Fourier transforming the fourth term is not easy because of the the quantities $\partial_\epsilon \mathrm{H}_0(y,t)|_0$ ($\partial_\epsilon \mathrm{H}_0(y_1,t)|_0$) depends on y (y_1). To be more specific, take for example the term $\partial_{z_1} G_{3D}^{1W}|_{c_i} \partial_\epsilon \mathrm{H}_0(y_1,t)|_0\, \epsilon$ and use $\partial_{z_1} G_{3D}^{1W} = \partial_{z_1} G_{3D}^{+} + \partial_{z_1} G_{3D}^{-}$ (Eq. (C.211)). Let us concentrate on the behaviour of the term having $\partial_{z_1} G_{3D}^{-}$ as one of its factors. Specifically,

$$\begin{aligned} &4\pi\, \partial_{z_1} G_{3D}^{-}(x,y,\mathrm{H}_0(y,t);x_1,y_1,z_1)|_{\mathrm{H}_0(y_1,t)} = \qquad \text{(C.198)} \\ &\frac{A_-}{[(x-x_1)^2 + (y-y_1)^2 + A_-^2]^{3/2}} + \frac{A_+}{[(x-x_1)^2 + (y-y_1)^2 + A_+^2]^{3/2}}\ , \end{aligned}$$

where $A_\pm \equiv \mathrm{H}_0(y_1,t) \pm \mathrm{H}_0(y,t)$. Using the ansatz $\mathrm{H}_0(y,t) = \mathrm{C}_0 + K(y^2 - Ly)$ we see that $A_-|_{\epsilon=0} = 0$ and $A_+|_{\epsilon=0} = 2c_i$. Therefore, $G_D^{(1)}(c_i)$ will contain a term like

$$\partial_{z_1} G_{3D}^{-}|_{c_i} \partial_\epsilon \mathrm{H}_0(y_1,t)|_0\, \epsilon = \frac{2c_i\, (\partial_\epsilon \mathrm{C}_0|_0 + \partial_\epsilon K|_0 (y_1^2 - Ly_1))\, \epsilon}{[(x-x_1)^2 + (y-y_1)^2 + 4c_i^2]^{3/2}} \tag{C.199}$$

When this is multiplied with $\partial_t h(x_1, y_1, t)$ the resulting expression is not of convolution form in variable y_1 and non-local term in Fourier space will result if cosine transformation is attempted. More elaborate methods have to be used on linear integral equations containing terms like the one given above.

Let us now consider $c_i = 0$. We show below that if we use the approximation $\mathrm{H}_0 \approx \mathrm{C}_0$ by neglecting the y-dependent part of H_0, each of the terms I_B, I_C and I_D will actually have the same order in ϵ in the local regime $|k|\mathrm{C}_0 \ll 1$. This is to accompany the approximation of the velocity, $\partial_t \mathrm{H}_0 \approx \partial_t \mathrm{C}_0$ which we have already justified in Sect. C.8.1. Hence,

$$I_B \approx \partial_t \mathrm{C}_0 \, h(x, y, t) \int dx_1 \int dy_1 \, \partial_z G_{3D}(x, y, z; x_1, y_1, \mathrm{C}_0)|_{\mathrm{C}_0} \; . \tag{C.200}$$

It should be noted that the Green's function and its lowest order derivatives do not vanish here even though they vanished when the condition $c_i = 0$ was used together with systematic expansion of G_{3D} prior to integration over x_1 and y_1. The reason is that here we keep the ϵ-dependence of $c(\epsilon)$ and do not set it equal to zero. In other words, even though

$$\partial_z G_{3D}(x, y, z; x_1, y_1, \mathrm{C}_0)|_{\mathrm{C}_0} = \frac{2\mathrm{C}_0}{4\pi[(x - x_1)^2 + (y - y_1)^2 + 4\mathrm{C}_0^2]} = 0 \tag{C.201}$$

for $\mathrm{C}_0 = \mathrm{C}_0(\epsilon = 0) = 0$, the term I_B as a whole is independent of C_0 due to the integration. The simplest way of seeing this is to set the integration limits in Eq. (C.200) to correspond to those of single-wall set-up (for simplicity) whose Green's function is given above, and performing a change of variables $(x_1)_{old} = \mathrm{C}_0 (x_1)_{new}$, $(y_1)_{old} = \mathrm{C}_0 (y_1)_{new}$. Alternatively, one can just Fourier transform I_B with the single wall result

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_B\} = \frac{1}{2} \, \partial_t \mathrm{C}_0(t) \, h_{\mathbf{k}}(t) \; , \tag{C.202}$$

as shown in Sect. C.9. Clearly, $\mathcal{O}(I_B) = \mathcal{O}(\epsilon)$. In a similar manner one easily shows that the Fourier transformation of the approximation

$$I_C \approx \partial_t \mathrm{C}_0 h(x, y, t) \int dx_1 \int dy_1 \, \partial_{z_1} G_{3D}(x, y, \mathrm{C}_0; x_1, y_1, z_1)|_{\mathrm{C}_0} h(x_1, y_1, t) \; . \tag{C.203}$$

gives the result

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_C\} = \frac{1}{2} \partial_t \mathrm{C}_0(t) \, e^{-2\mathrm{C}_0|k|} \, h_{\mathbf{k}}(t) \; , \tag{C.204}$$

which goes like $\frac{1}{2}\partial_t \mathrm{C}_0(t) \, h_{\mathbf{k}}(t)$ for $|k|\mathrm{C}_0 \ll 1$. Thus, the order of the prefactor function of $h_{\mathbf{k}}$ is again $\mathcal{O}(\epsilon)$ since $\partial_t \mathrm{C}_0 \propto \epsilon$. Finally,

$$I_D \approx \int dx_1 \int dy_1 \, G_{3D}(x, y, \mathrm{C}_0; x_1, y_1, \mathrm{C}_0) \, \partial_t h(x_1, y_1, t) \; . \tag{C.205}$$

For $|k|\mathrm{C}_0 \ll 1$ the prefactor of $\partial_t h_{\mathbf{k}}$ goes like $\mathrm{C}_0 \propto \epsilon$ for times $t < t_*$. Hence, the gross order of I_D as well, is $\mathcal{O}(\epsilon)$:

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_D\} = \frac{1}{2|k|} \left(1 - e^{-2\mathrm{C}_0|k|}\right) \partial_t h_{\mathbf{k}}(t) \; . \tag{C.206}$$

As what comes to the ϵ-dependence of the terms, the same results are valid also for the double wall set-up. This can be easily confirmed by looking up the corresponding expressions of the

Fourier transforms of I_B, I_C and I_D given in Sect. C.10. One only has to change the norm of $\mathbf{k}$ from $(k_x^2 + k_y^2)^{1/2}$ to $(k_x^2 + (\pi m/L)^2)^{1/2}$, where the discrete modes are induced by the finite wall separation L.

The same approximation, $\textsc{h}_0 \approx \textsc{c}_0$, will also be used in Sect. C.16. where we discuss the memory effects. However, it should be remembered that the epsilonistics of the equation of motion of the contact line becomes much more difficult to control especially if we are using the full, history dependent solution $h(c)$ derived in C.11.4, which contains all powers of ϵ. Due to this reason the results presented in C.16 are merely suggestive, no attempt has been made at this point to systematize the power series expansion of the contact line profile. This is to say that even though we only keep in the evolution equation of the meniscus the term which are at most $\mathcal{O}(\epsilon)$, the solution $h(c,\epsilon)$ may contain higher powers of ϵ. Consequently, the equation of motion of the contact line can also contain higher powers of ϵ since we make use of $h(c,\epsilon)$ when deriving the equation of motion via the variational method.

C.9 Meniscus dynamics: one wall

Last section dealt predominantly with the contact line profile of a pure system. We assumed a parabolic profile for the meniscus, with two fitting parameters: $\textsc{c}_0$ the height of the contact line and K, the curvature of the meniscus. These can be solved from Eq. (C.116). To gain information about the dynamics of the fluctuations $c(x,t)$ we first need to find out how does the meniscus depend on the unknown contact line profile. Once we know $h(c)$ we substitute it back in the 2D functionals R^r_{2D} and F^r_{2D} and integrate out the dependence on y-direction. Thus, we are left with effective 1D functionals $R^r_{1D}[\dot{c}]$ and $F^r_{1D}[c]$, which generate the equation of motion according to the recipe (C.341).

To find out $h(c)$ we have to simplify the equations of motion of the meniscus. Ultimately, we want to derive equations for the double wall set-up, but for simplicity we will start with single wall case. Matching the zeroeth and first powers in fluctuation h we obtain the following set of equations ((C.63) and (C.64)) which governs the time evolution of the liquid-gas interface:

$$I_A = \frac{M\sigma}{4}\nabla^2 \textsc{h}_0 \; ; \qquad \text{(C.207)}$$

$$I_B + I_C + I_D = -\frac{M}{4}\frac{\delta F_{2D}[h]}{\delta h} \; . \qquad \text{(C.208)}$$

Before going on to the actual calculations, we point out that the single wall set-up (a semi-infinite system) without gravity is a bit artificial. This can be seen by studying the zeroeth order meniscus equation (C.207). Term I_A serves to fix the equation of motion of the zeroeth order solution $\textsc{h}_0$. If there is no gravity, the meniscus tries to assume the shape of a straight plane to minimize free energy. The contact angle at which the plane meets the solid wall is set by the wall potential A in the free energy functional. Consequently, if the curvature $K = 0$, then $\textsc{h}_0 = \textsc{c}_0 - \alpha y$. The only linearly y-dependent that interface profile that Eq. (C.207) admits is the trivial solution $\textsc{h}_0 = \textsc{c}_0 = const$ corresponding to $\alpha = 0$. Thus, the interface does not move since the contact line height is a time independent constant. If we have gravity, we can in principle allow for contact angle values other than ninety degrees. However, since the resulting equation of motion for $\textsc{h}_0(y,t)$ is non-linear it turns out to be easier to solve for $\textsc{c}_0(t)$ by assuming that $\textsc{h}_0$ obeys some reasonably simple form such as parabola for double well set-up. This will be discussed in more detail in Sect. C.10.1. The rest of this section is devoted to the the calculation of the terms I_B, I_C and I_D. Any y-dependence in the profile H_0 will be neglected assuming $\mathrm{H}_0 \approx \mathrm{C}_0(t)$. This allows comparison with the double wall results for small enough curvatures.

First, we need to construct the Green's function G_{3D}. It should satisfy the same boundary conditions as the chemical potential. Assuming no flux through the solid wall at $y = 0$ and contact with reservoir at $z = 0$ we have

$$\mu(x, 0, z) = 0 \;\; ; \;\; \partial_y \mu(x, y, z)|_0 = 0 \; . \tag{C.209}$$

The solution is easily constructed with the aid of the method of images. To satisfy the first condition we set a positive charge at (x_1, y_1, z_1) and a negative charge at $(x_1, y_1, -z_1)$. The contribution to the full Green's function G_{3D}^{1W} from this pair of charges is denoted by G_{3D}^{-}. To fulfil the second condition in Eq. (C.209) we set another pair of charges on the opposite side of the y-axis: a positive charge will be placed at $(x_1, -y_1, z_1)$ and a negative charge at $(x_1, -y_1, -z_1)$. The contribution from this pair is denoted by G_{3D}^{+}:

$$\begin{aligned} 4\pi\, G_{3D}^{\pm}(\mathbf{r}, \mathbf{r}_1) = & \frac{1}{\sqrt{(x - x_1)^2 + (y \pm y_1)^2 + (z - z_1)^2}} \\ & - \frac{1}{\sqrt{(x - x_1)^2 + (y \pm y_1)^2 + (z + z_1)^2}} \; . \end{aligned} \tag{C.210}$$

Thus, the only difference between G_{3D}^{-} and G_{3D}^{+} is that the former has $(y - y_1)^2$ as its argument whereas the latter has $(y + y_1)^2$. The full Green's function is the sum of the two contributions:

$$G_{3D}^{1W} = G_{3D}^{-} + G_{3D}^{+} \; . \tag{C.211}$$

The following calculations are essentially the same for both G_{3D}^{-} and G_{3D}^{+}, which is why we concentrate to display explicitly the behaviour of G_{3D}^{-} only.

We now proceed to evaluation of I_B, I_C and I_D. To compute the term I_B requires the derivative of the Green's function with respect to coordinate z evaluated at the linearization point ($z = \mathrm{H}_0(y, t) = \mathrm{C}_0(t)$, $z_1 = \mathrm{H}_0(y_1, t) = \mathrm{C}_0(t)$). We obtain

$$4\pi\, \partial_z G_{3D}^{-}(x, y, z; x_1, y_1, \mathrm{C}_0(t))|_{\mathrm{C}_0} = \frac{2\mathrm{C}_0(t)}{\left((x - x_1)^2 + (y - y_1)^2 + 4\mathrm{C}_0^2(t)\right)^{3/2}} \; . \tag{C.212}$$

To compactify the forthcoming calculations, we introduce a kernel function i_B related to $\partial_z G_{3D}^{-}|_{\mathrm{C}_0}$ given in the previous equation:

$$i_B(x, y, t) \equiv \frac{2\mathrm{C}_0(t)}{\left(x^2 + y^2 + 4\mathrm{C}_0^2(t)\right)^{3/2}} \; . \tag{C.213}$$

To evaluate the term I_C, we should calculate the derivative of the Green's function with respect to z_1. In terms of a kernel function i_C we can express the derivative at the linearization point as

$$4\pi\, \partial_{z_1} G_{3D}^{-}(x, y, \mathrm{C}_0(t); x_1, y_1, z_1)|_{\mathrm{C}_0} = i_C(x - x_1, y - y_1, t) = i_B(x - x_1, y - y_1, t) \; , \tag{C.214}$$

where the last relation holds only in the approximation $\mathrm{H}_0(y, t) \approx \mathrm{C}_0(t)$. Next, we evaluate the Green function at the linearization point which is needed for the evaluation of the term I_D.

$$4\pi\, G_{3D}^{-}(x, y, \mathrm{C}_0(t); x_1, y_1, \mathrm{C}_0(t)) = i_{D1}(x - x_1, y - y_1, t) - i_{D2}(x - x_1, y - y_1, t) \; . \tag{C.215}$$

In the usual manner, we have introduced two new kernel functions on the right hand side of the previous equation. They are given by

$$i_{D1}(x,y) \equiv \left(x^2+y^2\right)^{-\frac{1}{2}} \quad ; \quad i_{D2}(x,y,t) \equiv \left(x^2+y^2+4\textsc{c}_0^2(t)\right)^{-\frac{1}{2}} \ . \tag{C.216}$$

We are now ready to compute the explicit representation of the terms I_B^-, I_C^- and I_D^-. Substitution of Eq. (C.212) and Eq. (C.214) into Eq. (C.60) and Eq. (C.61) respectively, gives

$$I_B^- \approx \partial_t \textsc{c}_0 \, h(x,y,t) \, \frac{1}{4\pi} \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{2\textsc{c}_0(t)}{((x-x_1)^2+(y-y_1)^2+4\textsc{c}_0{}^2(t))^{3/2}} \ . \tag{C.217}$$

$$I_C^- \approx \partial_t \textsc{c}_0 \, \frac{1}{4\pi} \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{2\textsc{c}_0(t)}{((x-x_1)^2+(y-y_1)^2+4\textsc{c}_0{}^2(t))^{3/2}} \, h(x_1,y_1,t) \ . \tag{C.218}$$

The term I_D^- is split into two pieces based on the form of the Green function at the linearization point as given by Eq. (C.215). We write, $I_D^- = I_{D1}^- - I_{D2}^-$, where I_D^- corresponds to the first term on the fight hand side and I_D^+ to the second. Substitution of these two terms into Eq. (C.62) yields,

$$I_{D1}^- \approx \frac{1}{4\pi} \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \frac{1}{((x-x_1)^2+(y-y_1)^2)^{1/2}} \, \partial_t h(x_1,y_1,t) \ . \tag{C.219}$$

$$I_{D2}^- \approx \frac{1}{4\pi} \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \frac{1}{((x-x_1)^2+(y-y_1)^2+4\textsc{c}_0{}^2(t))^{1/2}} \, \partial_t h(x_1,y_1,t) \ . \tag{C.220}$$

As explained in the beginning of this section, we need to sum up the contributions of two pairs of mirror charges to get the full Green function of the one-wall set-up. Consequently, the terms I_s with $s = B, C, D1, D2$ consist of two contributions due to the structure of the full Green function G_{3D}^{1W}: we write $I_s \equiv I_s^- + I_s^+$. The form of the terms I_s containing the full Green function G_{3D}^{1W} is expressible in terms of the integral kernels i_B, i_C, i_{D1} and i_{D2} defined above,

$$I_B = \partial_t \textsc{c}_0 \, h(x,y,t) \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{1}{4\pi} \left[i_B(\Delta, y-y_1, t) + i_B(\Delta, y+y_1, t) \right] \ ; \tag{C.221}$$

$$I_C = \partial_t \textsc{c}_0 \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{1}{4\pi} \left[i_C(\Delta, y-y_1, t) + i_C(\Delta, y+y_1, t) \right] h(x_1,y_1,t) \ ; \tag{C.222}$$

$$I_{D1} = \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{1}{4\pi} \left[i_{D1}(\Delta, y-y_1, t) + i_{D1}(\Delta, y+y_1, t) \right] \partial_t h(x_1,y_1,t) \ ; \tag{C.223}$$

$$I_{D2} = \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{1}{4\pi} \left[i_{D2}(\Delta, y-y_1, t) + i_{D2}(\Delta, y+y_1, t) \right] \partial_t h(x_1,y_1,t) \ . \tag{C.224}$$

We have used the short-hand notation $\Delta \equiv x - x_1$ above. To get rid of the convolution integrals appearing in the previous expressions we would like to perform an integral transformation of some sort. Remembering that our integration domain is the half plane $y \geq 0$ we can use the Fourier cosine transformation ($\mathcal{F}^{\cos}_{y/k_y}$) to go from real space (y) to Fourier space (k_y). The definition of the cosine transformation of convolution is [356]

$$\mathcal{F}^{\cos}_{y/k_y} \left\{ \frac{1}{2} \int_0^{\infty} dy_1 \, g(y_1)[f(|y-y_1|) + f(y+y_1)] \right\} = \mathcal{F}^{\cos}_{y/k_y} \left\{ f(y) \right\} \mathcal{F}^{\cos}_{y/k_y} \left\{ g(y) \right\} \ . \tag{C.225}$$

It is clear that the sum of the contributions of G^-_{3D} and G^+_{3D} giving rise to $I^-_s + I^+_s$ ($s = B, C, D1, D2$) is exactly of the convolution form in y-coordinate presented in Eq. (C.225). For the x-coordinate we can use the ordinary Fourier transform ($\mathcal{F}_{x/k_x}$).

It turns out that all the other kernels can be conveniently expressed in terms of the single kernel i_{D2} defined above. We obtain immediately that

$$i_B = i_C = -\frac{1}{2}\frac{\partial i_{D2}}{\partial \mathrm{C}_0} \quad ; \quad i_{D1} = \lim_{\mathrm{C}_0 \to 0} i_{D2}(\mathrm{C}_0) \ . \tag{C.226}$$

Since the other kernels can be related to i_{D2}, let us first consider the cosine transform of the kernel i_{D2}. It is readily obtained using the evenness of the kernel in y-coordinate:

$$\mathcal{F}_{x/k_x}\mathcal{F}^{\cos}_{y/k_y}\{i_{D2}\} \equiv \int_{-\infty}^{\infty} dx\, e^{\imath k_x x} \int_0^{\infty} dy\, \cos(k_y y)\, i_{D2}(x, y, t) \tag{C.227}$$

$$= \frac{1}{4}\int_{-\infty}^{\infty} dx\, e^{\imath k_x x} \int_{-\infty}^{\infty} dy\, e^{\imath k_y y}\, i_{D2} + \frac{1}{4}\int_{-\infty}^{\infty} dx\, e^{\imath k_x x} \int_{-\infty}^{\infty} dy\, e^{-\imath k_y y}\, i_{D2} \ . \tag{C.228}$$

On the second line we have extended the integration over the y-coordinate to cover the negative values as well after which the cosine has been written in terms of the exponential functions. Since the end result will be even in k_x and k_y, both terms of Eq. (C.228) will give the same contribution. Computing the first one we get,

$$\int_{-\infty}^{\infty} dx\, e^{\imath k_x x} \int_{-\infty}^{\infty} dy\, e^{\imath k_y y}\, i_{D2} = \int_{-\infty}^{\infty} dx\, e^{\imath k_x x} \int_{-\infty}^{\infty} dy\, e^{\imath k_y y}\, \frac{1}{\sqrt{x^2 + y^2 + 4\mathrm{C}_0{}^2}} \tag{C.229}$$

$$= \int_0^{\infty} dr\, r \int_0^{2\pi} d\theta\ e^{\imath k r \cos\theta}\, \frac{1}{\sqrt{r^2 + 4\mathrm{C}_0{}^2}} = \int_0^{\infty} dr\, \frac{2\pi r J_0(kr)}{\sqrt{r^2 + 4\mathrm{C}_0{}^2}} \tag{C.230}$$

$$= \frac{1}{k}\int_0^{\infty} dr\, \frac{2\pi r J_0(r)}{\sqrt{r^2 + 4(\mathrm{C}_0 k)^2}} \equiv \frac{2\pi}{k}\, e^{-2\mathrm{C}_0 k} \ . \tag{C.231}$$

The norm $k \equiv \sqrt{k_x^2 + k_y^2}$ and J_0 is the zeroeth order Bessel function. In the last line we performed a change of integration variables, $kr_{old} = r_{new}$. To compactify notation, we define a new function

$$b(\mathrm{C}_0 k) \equiv \pi e^{-2\mathrm{C}_0 k} \ . \tag{C.232}$$

Taking into account the factors of 1/4 in Eq. (C.228), we can express the Fourier transform of i_{D2} in terms of b:

$$\mathcal{F}_{x/k_x}\mathcal{F}^{\cos}_{y/k_y}\{i_{D2}\} = \int_{-\infty}^{\infty} dx\, e^{\imath k_x x} \int_0^{\infty} dy\, \cos(k_y y)\, \frac{1}{\sqrt{x^2 + y^2 + 4(\mathrm{C}_0 k)^2}} = \frac{1}{k} b(\mathrm{C}_0 k) \ . \tag{C.233}$$

It is easy to obtain the other kernels with the aid of Eq. (C.226) and the fact that $i_{D2} = k^{-1} b(\mathrm{C}_0 k)$. We get

$$i_B(k_x, k_y, t) = i_C(k_x, k_y, t) = b(\mathrm{C}_0 k) \quad ; \quad i_{D1}(k_x, k_y) = \pi / k \ . \tag{C.234}$$

Knowing the form of the integral kernels, we will now proceed to calculate the transformations of the terms I_B, I_C, I_{D1} and I_{D2}. Let us begin with I_B. Although I^-_B or I^+_B alone are functions of y, their sum is not:

$$I_B = I^-_B + I^+_B = \partial_t \mathrm{C}_0\, h(x, y, t) \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dy_1\, \frac{1}{4\pi} i_B(x - x_1, y - y_1, t) \ . \tag{C.235}$$

Notice the change of the lower integration limit for y. Performing the change of variables $x_{old} - x_1 \equiv x_{new}$, $y_{old} - y_1 \equiv y_{new}$ allows us to get rid of the superficial dependence on x and y. We obtain

$$\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \, \frac{1}{4\pi} i_B(x_1, y_1, t) = \frac{1}{4\pi} \lim_{k\to 0} b(\mathrm{C}_0 k) = \frac{1}{4} \; . \tag{C.236}$$

as can be confirmed from Eq. (C.232). All in all, the transformation of I_B gives a simple expression:

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_B\} = 2 \partial_t \mathrm{C}_0(t)\, h_{\mathbf{k}}(t) \frac{1}{4\pi} \lim_{k\to 0} \mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{i_B\} = \frac{1}{2}\, \partial_t \mathrm{C}_0(t)\, h_{\mathbf{k}}(t) \; . \tag{C.237}$$

The factor of two on the right hand side of the first equality comes from the definition of the Fourier cosine transformation of the convolution (the other convoluted function above was a constant function as indicated by the limit $k \to 0$).

Transformation of I_C is performed next. In contrast to I_B, neither of the functions convoluted is a constant. Using Eq. (C.218) we straightforwardly obtain

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_C\} = 2 \partial_t \mathrm{C}_0(t)\, h_{\mathbf{k}}(t) \frac{1}{4\pi} \mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{i_C\} = \frac{1}{2\pi} \partial_t \mathrm{C}_0(t)\, b(\mathrm{C}_0 k)\, h_{\mathbf{k}}(t) \; . \tag{C.238}$$

Again, the factor of two on the far right of the first equality has to be there to respect Eq. (C.222) where one has to take into account the factor 1/2.

Term I_{D1} (Eq. (C.219)) is transformed next. For the same reason as above, we have to insert a factor of two. We also make use of Eq. (C.234):

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_{D1}\} = 2\, \partial_t h_{\mathbf{k}}(t) \frac{1}{4\pi} \mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{i_{D1}\} = \frac{1}{2k}\, \partial_t h_{\mathbf{k}}(t) \; . \tag{C.239}$$

Finally, transformation of I_{D2} (Eq. (C.220)) has essentially been done already, since everything was expressed with the aid of the kernel i_{D2}. Thus,

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_{D2}\} = 2\, \partial_t h_{\mathbf{k}}(t) \frac{1}{4\pi} \mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{i_{D2}\} = \frac{1}{2\pi k} b(\mathrm{C}_0 k)\, \partial_t h_{\mathbf{k}}(t) \; , \tag{C.240}$$

where the last equality follows from the definition of the function b in Eq. (C.233). Remembering that we defined $I_D \equiv I_{D1} - I_{D2}$, the right hand side of the Fourier transformed meniscus equation of motion for h reads

$$\mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_B + I_C + I_D\} = \mathcal{F}_{x/k_x} \mathcal{F}^{\cos}_{y/k_y} \{I_B + I_C + I_{D1} - I_{D2}\} \tag{C.241}$$

$$= g_1(k,t)\, \partial_t h_{\mathbf{k}}(t) + g_2(k,t)\, h_{\mathbf{k}}(t) \; , \tag{C.242}$$

where we have grouped terms of similar kind and defined two new functions g_1 and g_2.

$$g_1(k,t) \equiv \frac{1}{2k} \left(1 - b(\mathrm{C}_0 k)/\pi\right) = \frac{1}{2k} \left(1 - e^{-2\mathrm{C}_0(t) k}\right) \; ; \tag{C.243}$$

$$g_2(k,t) \equiv \frac{1}{2}\, \partial_t \mathrm{C}_0 \left(1 + b(\mathrm{C}_0 k)/\pi\right) = \frac{1}{2}\, \partial_t \mathrm{C}_0 \left(1 + e^{-2\mathrm{C}_0(t) k}\right) \; . \tag{C.244}$$

The evolution equation for the fluctuating modes of the meniscus becomes (Eq. (C.208))

$$g_1(k,t)\, \partial_t h_{\mathbf{k}}(t) + g_2(k,t)\, h_{\mathbf{k}}(t) = -\frac{M}{4} \frac{\delta F_{2D}[h]}{\delta h_{\mathbf{k}}} = -\frac{M\sigma}{4} k^2\, h_{\mathbf{k}}(t) \; , \tag{C.245}$$

where have substituted the drumhead free energy for F_{2D} and taken the functional derivative with respect to the Fourier modes $h_{\mathbf{k}}$ instead of $\textsc{h}$. To obtain a simplified equation of motion in the local regime $\textsc{c}_0 k \ll 1$ we Taylor expand the function $b(\textsc{c}_0 k)$. The lowest order approximations for g_1 and g_2 then read

$$g_1(k,t) \approx \textsc{c}_0(t) \;\; ; \;\; g_2(k,t) \approx \partial_t \textsc{c}_0(t) \; . \tag{C.246}$$

Assuming that we are interested in phenomena taking place close to pinning of the average contact line position, *i.e.* when $\partial_t \textsc{c}_0 \approx 0$ the simplified equation of motion for the meniscus in the local regime will take the form

$$\tilde{g}_1 \partial_t h_{\mathbf{k}}(t) = -\frac{M\sigma}{4} k^2 \, h_{\mathbf{k}}(t) \; , \tag{C.247}$$

where we have defined the stationary value $\tilde{g}_1 \equiv \textsc{c}_0$.

C.10 Meniscus dynamics: two walls

The goal of this section is to show that the linearized equation of motion for the *fluctuations* h around the zeroeth order meniscus profile $\textsc{h}_0$ follows a diffusion equation on certain time and length scales when $\partial_t \textsc{c}_0$ can be neglected. The velocity of the contact line is exactly zero when the meniscus is flat, *i.e.* when $K = 0$. Setting $K = 0$ (equivalently, $\epsilon = 0$) leads to certain problems, however, as discussed in Sect. C.8. Therefore we allow for non-zero contact line profile in the calculations below, but set neglect the spatial dependence of the zeroeth order meniscus solution via approximation $\textsc{h}_0(y,t) \approx \textsc{c}_0(t)$ as if the curvature would be zero. This approximation does render the order of the terms I_B, I_C and I_D the same to first order in expansion parameter ϵ, as explained in Sect. C.8.3. The velocity is approximated as $\partial_t \textsc{h}_0 \approx \partial_t \textsc{c}_0$ as the time variation of the curvature is argued to be negligible at least after a relatively rapid initial period.

It is easy to see that if $\epsilon = 0$ ($K = 0$) exactly, all terms I_A, I_B, I_C and I_D vanish. Therefore, without any driving chemical potential gradients imposed at the reservoir boundary, the interface does not move. However, if there is a chemical potential gradient $\mathcal{F}$ imposed at the reservoir boundary, even a flat meniscus can propagate ($K = 0$, $\partial_t \textsc{h}_0 \neq 0$ and consequently I_B and I_C being proportional to $\partial_t \textsc{h}_0 \propto \mathcal{F}$, are non-zero and besides motion of the zeroeth order meniscus profile $\textsc{h}_0$ there can also be time evolution of the fluctuation correction h. Finally, we point out that even if the meniscus is moving at the beginning, driven by its curvature or imposed chemical potential gradient or both, it can become pinned by gravity or evaporation and thus stop moving. However, in this section we do not explictly consider a non-zero driving chemical potential gradient or pinning effects induced by gravity.

C.10.1 Term I_A

We will first look at the zeroeth order equation of motion which fixes the solution $\textsc{h}_0$. Owing to the von Neumann boundary conditions for the chemical potential on the solid walls, the Green boundary term $\tilde{\Lambda}$ will be zero. Thus, $I_A = (M\sigma/4)\, \partial_y^2 \textsc{h}_0$, or

$$\int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_{3D}^{2W}(x, y, \textsc{h}_0(y,t); x_1, y_1, \textsc{h}_0(y_1,t)) \, \partial_t \textsc{h}_0(y_1,t) = \frac{M\sigma}{4} \partial_y^2 \textsc{h}_0(y,t) \; . \tag{C.248}$$

We have used the fact that H_0 is just a function of y and t for pure walls. Being a non-linear integro-differential equation Eq. (C.248) is not easy to solve. Instead of trying any perturbative attack, let us postulate an ansatz for H_0. As most of the numerical work has been performed using a geometry where the solid walls are situated at $y = \pm L/2$, we set

$$\mathrm{H}_0(y,t) = \mathrm{C}_0(t) - K(t)L^2/4 + K(t)y^2 \ , \tag{C.249}$$

where the two parameters are the mean contact line height is C_0 and curvature $K(t)$. This form does indeed produce a good approximation to the solution H_0 of Eq. (C.248) as demonstrated by direct numerical integration in Ref. [262]. We can fix C_0 (or K) either from numerics, from the approximative analytic solution presented in Sect. C.12.2, or from experimental data as explained in Sect. C.7. For example, knowing C_0 we can substitute Eq. (C.249) into Eq. (C.248) which now becomes an ordinary (non-linear) differential equation for K which can be solved by quadratures. Alternatively, we can use the experimentally determined volume V to fix curvature K and solve for C_0 from Eq. (C.248). The plausibility of these considerations depends on the sensitivity of the result to the ansatz of Eq. (C.249). If we neglect the terms proportional to curvature in Eq. (C.249), it reduces to the following form, which is utilized to simplify the expressions of this section:

$$\mathrm{H}_0(y,t) = \mathrm{H}_0(y_1,t) = \mathrm{C}_0 \ . \tag{C.250}$$

The approximation above also leads to relation between the velocity of the meniscus and the contact line: $\partial_t \mathrm{H}_0 = \partial_t \mathrm{C}_0$, which continues to hold to lowest order in ϵ even if the time dependence of the curvature would be included.

C.10.2 Term I_B

Term I_B is obtained from Eq. (C.60). Using the approximation of Eq. (C.250) we can pull the velocity term out of the integral:

$$\begin{aligned} I_B &\equiv \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1\, \partial_z G_{3D}^{2W}(x,y,z;x_1,y_1,\mathrm{H}_0(y_1,t))|_{\mathrm{H}_0}\, h(x,y,t)\, \partial_t \mathrm{H}_0(y_1,t) \\ &= \partial_t \mathrm{C}_0\, h(x,y,t) \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1\, \partial_z G_{3D}^{2W}(x,y,z;x_1,y_1,\mathrm{C}_0)|_{\mathrm{C}_0} \ . \end{aligned} \tag{C.251}$$

The substitution in the defining equation above should be understood as $|_{\mathrm{H}_0} = |_{\mathrm{H}_0(y,t)}$. Using the representation of G_{3D}^{2W} given in Eq. (C.137) allows us to split the Green's function into two pieces: $G_{3D}^{2W} = (1/L)\, G_{2D}^{I} + G_{3D}^{S}$. Eq. (C.136) gives for the series part

$$G_{3D}^{S} = \frac{2}{L} \sum_{n=1}^{\infty} \cos(n\pi y/L) \cos(n\pi y_1/L) \left[\tilde{f}_n(x-x_1, z-z_1) - \tilde{f}_n(x-x_1, z+z_1) \right] \ . \tag{C.252}$$

Evaluation of the derivative $\partial_z G_{3D}^{2W}$ at the linearization point is computed next. It is easy to see from the definition of $\tilde{f}_n$ in Eq. (C.135) that the first term in the square bracket above vanishes when $z = z_1 = \mathrm{C}_0$. We obtain,

$$\begin{aligned} \partial_z G_{3D}^{2W}(x,y,z;x_1,y_1,\mathrm{C}_0)|_{\mathrm{C}_0} &= \frac{1}{L}\, \partial_z G_{2D}^{I}(x,z;x_1,\mathrm{C}_0)|_{\mathrm{C}_0} \\ &\quad -\frac{2}{L} \sum_{n=1}^{\infty} \cos(n\pi y/L) \cos(n\pi y_1/L)\, \partial_z \tilde{f}_n(x-x_1,z)|_{2\mathrm{C}_0} \ . \end{aligned} \tag{C.253}$$

The argument of the second surviving term in the square bracket in Eq. (C.252) at the linearization point is $z + z_1$ giving rise to substitution of $2\textsc{c}_0$ in the previous equation instead of just $\textsc{c}_0$. Substitution of the previous expression back into Eq. (C.251) yields

$$\begin{aligned} I_B &= \partial_t \textsc{c}_0\, h(x,y,t) \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1\, \frac{1}{L}\, \partial_z G^I_{2D}(x,z;x_1,\textsc{c}_0)|_{\textsc{c}_0} \\ &\quad - \partial_t \textsc{c}_0\, h(x,y,t)\, \frac{2}{L} \sum_{n=1}^{\infty} \cos(n\pi y/L) \int_{-\infty}^{\infty} dx_1\, \partial_z \tilde{f}_n(x-x_1,z)|_{2\textsc{c}_0} \int_0^L dy_1\, \cos(n\pi y_1/L)\ . \end{aligned} \tag{C.254}$$

The integration over y_1 of the first term just gives a trivial factor L because the integrand is independent of y_1. The latter term on the right hand side of the previous equation vanishes since the cosine term is integrated over the full period L. However, to keep the notation symmetric, we do not drop it quite yet but write I_B in the following form

$$\begin{aligned} I_B &= \partial_t \textsc{c}_0\, h(x,y,t) \int_{-\infty}^{\infty} dx_1\, J_{B1}(x-x_1,\textsc{c}_0) \\ &\quad + 2\partial_t \textsc{c}_0\, h(x,y,t) \sum_{n=1}^{\infty} \cos(n\pi y/L) \int_{-\infty}^{\infty} dx_1\, J_{B2}(x-x_1,n,\textsc{c}_0)\, \delta_{n,0}\ , \end{aligned} \tag{C.255}$$

where $\delta_{i,j}$ denotes the Kronecker delta. We have introduced two new functions, J_{B1} and J_{B2}. It is shown in the next section that their partner functions J_{B1} and J_{B2} appearing in the expression of I_C are identical to them when approximation $\textsc{h}_0(y,t) = \textsc{c}_0$ is used. Explicitly,

$$J_{B1}(x-x_1,\textsc{c}_0) \equiv \partial_z G^I_{2D}(x,z;x_1,\textsc{c}_0)|_{\textsc{c}_0}\ ;\ J_{B2}(x-x_1,n,\textsc{c}_0) \equiv -\partial_z \tilde{f}_n(x-x_1,z)|_{2\textsc{c}_0}\ . \tag{C.256}$$

Further simplification results since it is easy to perform the integration over x_1 in the expression for J_{B1}. The result is

$$\int_{-\infty}^{\infty} dx_1\, J_{B1}(x-x_1,\textsc{c}_0) = 1/2\ . \tag{C.257}$$

Fourier transformation with respect to x is readily performed since $h(x,y,t)$ is the only x-dependent quantity in the expression I_B. Remembering that the second term in Eq. (C.255) is zero, we get

$$\mathcal{F}_{x/k_x}\{I_B\} = \frac{1}{2}\partial_t \textsc{c}_0\, h(k_x,y,t)\ , \tag{C.258}$$

Since the domain is restricted between 0 and L in the y-direction, we are trying to simplify the representation in terms of Fourier series. Therefore, we multiply I_B with $\cos(m\pi y/L)$ and integrate from 0 to L:

$$\int_0^L dy\, \cos(m\pi y/L)\, \mathcal{F}_{x/k_x}\{I_B\} = \left\{ \begin{array}{l} \frac{1}{2}\partial_t \textsc{c}_0\, L\grave{h}(k_x,0,t)\ \ ,\ \text{for } m = 0. \\ \frac{1}{2}\partial_t \textsc{c}_0\, L\grave{h}(k_x,m,t)\ ,\ \text{for } m \geq 1. \end{array} \right. \tag{C.259}$$

The factor L above arises from the definition of the coefficients of the Fourier cosine series:

$$\grave{h}(k_x,m,t) \equiv \frac{1}{L} \int_0^L dy\, \cos(m\pi y/L)\, h(k_x,y,t)\ . \tag{C.260}$$

In order not to overload the notation with accents, when taking the ordinary Fourier transform with respect to a variable, such as x, which has been defined on the whole real axis, we denote the transformed function in k-space by the same symbol as in real space, only the argument changes. For example,

$$\grave{h}(x,m,t) \equiv \frac{1}{L}\int_0^L dy\, \cos(m\pi y/L)\, h(x,y,t)\ . \tag{C.261}$$

With the aid of the Fourier coefficients defined above we can simplify the expressions of I_C and I_D more than the appearances of I_B, will become clear below.

C.10.3 Term I_C

Using the approximation $\textsc{h}_0 = \textsc{c}_0$ in the expression of I_C given in Eq. (C.61) results in the following simplification:

$$\begin{aligned} I_C &\equiv \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1\, \partial_{z_1} G_{3D}^{2W}(x,y,\textsc{h}_0(y,t);x_1,y_1,z_1)|_{\textsc{h}_0}\, h(x_1,y_1,t)\, \partial_t \textsc{h}_0(y_1,t) \\ &= \partial_t \textsc{c}_0 \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1\, \partial_{z_1} G_{3D}^{2W}(x,y,\textsc{c}_0;x_1,y_1,z_1)|_{\textsc{c}_0}\, h(x_1,y_1,t)\ . \end{aligned} \tag{C.262}$$

The substitution symbol should be understood as $|_{\textsc{h}_0} = |_{\textsc{h}_0(y_1,t)}$. Evaluation of the derivative $\partial_{z_1} G_{3D}^{2W}$ at the linearization point is computed next.

$$\begin{aligned} \partial_{z_1} G_{3D}^{2W}(x,y,\textsc{c}_0;x_1,y_1,z_1)|_{\textsc{c}_0} &= \frac{1}{L}\,\partial_{z_1} G_{2D}^{I}(x,\textsc{c}_0;x_1,z_1)|_{\textsc{c}_0} \\ &\quad -\frac{2}{L}\sum_{n=1}^{\infty} \cos(n\pi y/L)\cos(n\pi y_1/L)\, \partial_{z_1}\tilde{f}_n(x-x_1,z_1)|_{2\textsc{c}_0}\ . \end{aligned} \tag{C.263}$$

Just like in the case of I_B, only the second term in the square bracket in Eq. (C.252) survives after differentiation and substitution of the values of z and z_1 at the linearization point. Plugging the Green's function into Eq. (C.262) yields

$$\begin{aligned} I_C = {} & \partial_t \textsc{c}_0 \int_{-\infty}^{\infty} dx_1\, \frac{1}{L}\,\partial_{z_1} G_{2D}^{I}(x,\textsc{c}_0;x_1,z_1)|_{\textsc{c}_0} \int_0^L dy_1\, h(x_1,y_1,t) \\ & - \partial_t \textsc{c}_0\, \frac{2}{L}\sum_{n=1}^{\infty} \cos(n\pi y/L) \int_{-\infty}^{\infty} dx_1\, \partial_{z_1}\tilde{f}_n(x-x_1,z_1)|_{2\textsc{c}_0} \int_0^L dy_1\, \cos(n\pi y_1/L)\, h(x_1,y_1,t)\ . \end{aligned} \tag{C.264}$$

Making use of the Fourier coefficients defined in Eq. (C.261) and introducing two new functions, J_{C1} and J_{C2}, we can simplify the previous result

$$\begin{aligned} I_C &= \partial_t \textsc{c}_0 \int_{-\infty}^{\infty} dx_1\, J_{C1}(x-x_1,\textsc{c}_0)\, \grave{h}(x_1,0,t) \\ &\quad + 2\partial_t \textsc{c}_0 \sum_{n=1}^{\infty} \cos(n\pi y/L) \int_{-\infty}^{\infty} dx_1\, J_{C2}(x-x_1,n,\textsc{c}_0)\, \grave{h}(x_1,n,t)\ . \end{aligned} \tag{C.265}$$

The only difference between functions J_{C1} and J_{B1}, as well as J_{C2} and J_{B2}, is that the functions associated with respect to the term I_B are differentiated with respect to z, whereas the functions associated with the term I_C are differentiated with respect to z_1:

$$J_{C1}(x-x_1,\textsc{c}_0) \equiv \partial_{z_1} G_{2D}^{I}(x,\textsc{c}_0;x_1,z_1)|_{\textsc{c}_0}\quad ;\quad J_{C2}(x-x_1,n,\textsc{c}_0) \equiv -\partial_{z_1}\tilde{f}_n(x-x_1,z_1)|_{2\textsc{c}_0}\ . \tag{C.266}$$

It is easy to show by direct computation that due to the approximation $\textsc{h}_0 = \textsc{c}_0$, $J_{C1} = J_{B1}$. The fact that $J_{C2} = J_{B2}$ is clear from Eq. (C.266): the dummy variable z has been replaced with the dummy variable z_1 as compared to Eq. (C.256). The explicit forms of these functions in real space are the following:

$$J_{B1}(\Delta, \textsc{c}_0) = J_{C1}(\Delta, \textsc{c}_0) = -\frac{1}{\pi} \frac{\textsc{c}_0}{\Delta^2 + 4\textsc{c}_0^2} \ . \tag{C.267}$$

$$J_{B2}(\Delta, n, \textsc{c}_0) = J_{C2}(\Delta, n, \textsc{c}_0) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_z \, \frac{e^{-\imath k_x \Delta} e^{-\imath k_z (2\textsc{c}_0)} (\imath k_z)}{k_x^2 + (\pi n/L)^2 + k_z^2} \ , \tag{C.268}$$

where $\Delta \equiv x - x_1$. Since the expression I_C has the convolution form in real variable x, it is straightforward to switch to Fourier space:

$$\mathcal{F}_{x/k_x}\{I_C\} = \partial_t \textsc{c}_0 \, J_{C1}(k_x, \textsc{c}_0) \, \grave{h}(k_x, 0, t) + 2\partial_t \textsc{c}_0 \sum_{n=1}^{\infty} \cos(n\pi y/L) J_{C2}(k_x, n, \textsc{c}_0) \, \grave{h}(k_x, n, t) \ . \tag{C.269}$$

As for I_B, we will find the Fourier components in the y-direction by projecting with the cosine term $\cos(m\pi y/L)$:

$$\int_0^L dy \, \cos(m\pi y/L) \, \mathcal{F}_{x/k_x}\{I_C\} = \begin{cases} \partial_t \textsc{c}_0 J_{C1}(k_x, \textsc{c}_0) \, L\grave{h}(k_x, 0, t) & , \text{ for } m = 0. \\ \partial_t \textsc{c}_0 J_{C2}(k_x, m, \textsc{c}_0) \, L\grave{h}(k_x, m, t) & , \text{ for } m \geq 1. \end{cases} \tag{C.270}$$

The zero mode ($m = 0$) projection of the sum term in Eq. (C.265) is zero by construction and the only contribution comes from the first term ($\propto J_{C1}$). When projecting with $\cos(m\pi y/L)$ with $m \geq 1$, the first term gives zero and in the second term ($\propto J_{C2}$) the emerging product of two cosine functions is simplified as follows:

$$\int_0^L dy \, \cos(m\pi y/L) \cos(n\pi y/L) \tag{C.271}$$

$$= \frac{1}{2} \int_0^L dy \, \left[\cos((m+n)\pi y/L) + \cos((m-n)\pi y/L)\right] = \frac{L}{2} \left(\delta_{m,-n} + \delta_{m,n}\right) \ .$$

Notice, that since only the terms with $n \geq 1$ are included in the summation in Eq. (C.269), we have effectively just a single Kronecker's delta remaining in the previous expression: $\delta_{m,n}$. The other one, $\delta_{m,-n}$ is always zero as we require $m \geq 1$.

C.10.4 Term I_D

The approximation $\textsc{h}_0 = \textsc{c}_0$ together with Eq. (C.250) leads to the following simplification of Eq. (C.62) defining I_D:

$$\begin{aligned} I_D &\equiv \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_{3D}^{2W}(x, y, \textsc{h}_0(y,t); x_1, y_1, \textsc{h}_0(y_1,t)) \, \partial_t h(x_1, y_1, t) \\ &= \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_{3D}^{2W}(x, y, \textsc{c}_0; x_1, y_1, \textsc{c}_0) \, \partial_t h(x_1, y_1, t) \ . \end{aligned} \tag{C.272}$$

Substituting of the Green function into the previous equation and effecting the integration over the y_1-coordinate on $\partial_t h(x_1, y_1, t)$ gives

$$I_D = \int_{-\infty}^{\infty} dx_1 \frac{1}{L} \, G_{2D}^{I}(x, \textsc{c}_0; x_1, \textsc{c}_0) \int_0^L dy_1 \, \partial_t h(x_1, y_1, t) \tag{C.273}$$

$$+ \frac{2}{L} \sum_{n=1}^{\infty} \cos(n\pi y/L) \int_{-\infty}^{\infty} dx_1 \, \left[\tilde{f}_n(\Delta, 0) - \tilde{f}_n(\Delta, 2\textsc{c}_0)\right] \int_0^L dy_1 \, \cos(n\pi y_1/L) \, \partial_t h(x_1, y_1, t) \ ,$$

where $\Delta \equiv x - x_1$. Making again use of the definition of the coefficients of the Fourier series (Eq. (C.261)) the previous equation is casted into

$$\begin{aligned} I_D &= \int_{-\infty}^{\infty} dx_1\, J_{D1}(x - x_1, \mathrm{c}_0)\, \partial_t \grave{h}(x_1, 0, t) \\ &\quad + 2 \sum_{n=1}^{\infty} \cos(n\pi y/L) \int_{-\infty}^{\infty} dx_1\, J_{D2}(x - x_1, n, \mathrm{c}_0)\, \partial_t \grave{h}(x_1, n, t)\ . \end{aligned} \tag{C.274}$$

The new functions J_{D1} and J_{D2} are short-hand notations for the following kernels:

$$J_{D1}(x - x_1, \mathrm{c}_0) \equiv G^I_{2D}(x, \mathrm{c}_0; x_1, \mathrm{c}_0)\ ; \tag{C.275}$$

$$J_{D2}(x - x_1, n, \mathrm{c}_0) \equiv \tilde{f}_n(x - x_1, 0) - \tilde{f}_n(x - x_1, 2\mathrm{c}_0)\ . \tag{C.276}$$

Fourier transformation of I_D with respect to variable x is readily performed with the result,

$$\mathcal{F}_{x/k_x}\{I_D\} = J_{D1}(k_x, \mathrm{c}_0)\, \partial_t \grave{h}(k_x, 0, t) + 2 \sum_{n=1}^{\infty} \cos(n\pi y/L) J_{D2}(k_x, n, \mathrm{c}_0)\, \partial_t \grave{h}(k_x, n, t) \tag{C.277}$$

Finally, projection of the previous equation with $\cos(m\pi y/L)$ yields

$$\int_0^L dy\ \cos(m\pi y/L)\, \mathcal{F}_{x/k_x}\{I_D\} = \begin{cases} J_{D1}(k_x, \mathrm{c}_0)\, L \partial_t \grave{h}(k_x, 0, t)\ \ , \text{ for } m = 0. \\ J_{D2}(k_x, m, \mathrm{c}_0)\, L \partial_t \grave{h}(k_x, m, t)\ , \text{ for } m \geq 1. \end{cases} \tag{C.278}$$

This result is similar to Eq. (C.270). The sum term doesn't contribute to the zero mode ($m = 0$) projection because it only contains modes with $n \geq 1$. Conversely, the first term on the right hand side of Eq. (C.277) doesn't contribute to projection with $\cos(m\pi y/L)$ with $m \geq 1$ as it contains only the zero mode ($n = 0$) of the Green function G^{2W}_{3D}.

C.10.5 Meniscus equations for zero and non-zero modes

Let us collect the results of the previous subsections. Both zero mode and non-zero mode equations can be combined to a single equation governing the dynamics of all modes $n = 0, 1, 2, \ldots$:

$$\begin{aligned} & J_{D2}(k_x, m, \mathrm{c}_0)\, \partial_t \grave{h}(k_x, m, t) + \partial_t \mathrm{c}_0 \left[1/2 + J_{C2}(k_x, m, \mathrm{c}_0)\right]\ \grave{h}(k_x, m, t) \\ & = -\frac{M\sigma}{4} \left(k^2 + (m\pi/L)^2\right) \grave{h}(k_x, m, t)\ . \end{aligned} \tag{C.279}$$

When Fourier cosine transforming, we have dropped the Green's boundary term, which arises when partial integrating with respect to y an expression $\int_{-\infty}^{\infty} dx \int_0^L dy\ \cos(m\pi y/L)\, e^{\imath k_x x} f(x, y)$. Eq. (C.279) is the equation for non-zero modes extended to cover the case with $m = 0$ as well. Indeed, it is true by construction that $J_{C2}(k_x, 0, \mathrm{c}_0) = J_{C1}(k_x, \mathrm{c}_0)$ and $J_{CD2}(k_x, 0, \mathrm{c}_0) = J_{D1}(k_x, \mathrm{c}_0)$. The easiest way to see this is to notice that the zero mode limit limit f_m (see Eq. (C.135)) is well defined and yielding the correct values of J_{B1}, J_{C1} and J_{D1}. Therefore, setting $m = 0$ in Eq. (C.279) produces the equation of motion of the zero mode fluctuations in y-direction:

$$\begin{aligned} & J_{D1}(k_x, \mathrm{c}_0)\, \partial_t \grave{h}(k_x, 0, t) + \partial_t \mathrm{c}_0 \left[1/2 + J_{C1}(k_x, \mathrm{c}_0)\right]\ \grave{h}(k_x, 0, t) \\ & = -\frac{M\sigma}{4} k^2\, \grave{h}(k_x, 0, t)\ . \end{aligned} \tag{C.280}$$

The common factor of L resulting from the definition of the Fourier coefficients has been cancelled on both sides of the equation.

Fourier representation of the coefficient functions

For future purposes we will now compute the Fourier representations of the various coefficient functions appearing in the equation of motion above. We will also use the results as a consistency check to confirm that we have not made errors in changing from one representation to the other. Let us start with the coefficient function J_{D1} which is familiar from the imbibition model [4]:

$$J_{D1}(k_x, \mathrm{c}_0) = \mathcal{F}_{x/k_x}\Big\{G^I_{2D}(x, \mathrm{c}_0; x_1, \mathrm{c}_0)\Big\} = \frac{1}{2|k_x|}\left(1 - e^{-2\mathrm{c}_0|k_x|}\right) \; . \tag{C.281}$$

Using Eq. (C.276) we can write the Fourier transform of J_{D2} as

$$J_{D2}(k_x, m, \mathrm{c}_0) = \tilde{f}_m(k_x, 0) - \tilde{f}_m(k_x, 2\mathrm{c}_0) \; . \tag{C.282}$$

We calculate $\tilde{f}_m(k_x, 2\mathrm{c}_0)$ first. Setting $\mathrm{c}_0 = 0$ in the result gives us $\tilde{f}_m(k_x, 0)$. From Eq. (C.135) we get

$$\tilde{f}_m(k_x, 2\mathrm{c}_0) = \frac{1}{2\pi}\int dk_z \, \frac{e^{-\imath k_z (2\mathrm{c}_0)}}{k_x^2 + (\pi m/L)^2 + k_z^2} \; . \tag{C.283}$$

Transformation to a dimensionless integration variable, $(k_z)_{new} \equiv 2\mathrm{c}_0 k_z$, gives

$$J_{D2}(k_x, m, \mathrm{c}_0) = \frac{1}{4\pi\mathrm{c}_0}\int dk_z \, \frac{1 - e^{-\imath k_z}}{k_x^2 + (\pi m/L)^2 + (k_z/(2\mathrm{c}_0))^2} \; . \tag{C.284}$$

By introducing a new variable $\tilde{k}_m \equiv \sqrt{k_x^2 + (m\pi/L)^2}$ we can rewrite the previous equation as

$$J_{D2}(k_x, m, \mathrm{c}_0) = \frac{\mathrm{c}_0}{\pi}\int dk_z \, \frac{1 - e^{-\imath k_z}}{(2\mathrm{c}_0\tilde{k}_m)^2 + k_z^2} = \frac{(1 - e^{-2\mathrm{c}_0\tilde{k}_m})}{2\tilde{k}_m} \; , \tag{C.285}$$

where the last equality results right away from the method of residues. Indeed, when $m = 0$ in the previous equation, or, when $\tilde{k}_m = |k_x|$, we get $J_{D2}(k_x, 0, \mathrm{c}_0) = J_{D1}(k_x, \mathrm{c}_0)$ as expected. A similar calculation can be performed for the pair J_{C2} and J_{C1}. Using the definition in Eq. (C.266) we get

$$J_{C2}(k_x, m, t) = -\frac{\partial}{\partial z_1}\left\{\frac{1}{2\pi}\int dk_z \, \frac{e^{-\imath k_z z_1}}{\tilde{k}_m^2 + k_z^2}\right\}\Bigg|_{2\mathrm{c}_0} = \frac{1}{2}e^{-2\mathrm{c}_0\tilde{k}_m} \; . \tag{C.286}$$

When $m = 0$ we see that indeed J_{C2} reduces to J_{C1} which can be confirmed by Fourier transforming the real space representation of $J_{C1}(x, \mathrm{c}_0)$ given in Eq. (C.267), or more directly by noticing that we can represent J_{C1} in the form

$$J_{C1}(k_x, \mathrm{c}_0) = \frac{\partial}{\partial z_1}\left\{\frac{1}{2\pi}\int dk_z \, \frac{e^{-\imath k_z(\mathrm{c}_0 - z_1)}}{k_x^2 + k_z^2} - \frac{1}{2\pi}\int dk_z \, \frac{e^{-\imath k_z(\mathrm{c}_0 + z_1)}}{k_x^2 + k_z^2}\right\}\Bigg|_{z_1 = \mathrm{c}_0} = J_{C2}(k_x, 0, \mathrm{c}_0) \; . \tag{C.287}$$

Naturally, since the reduction holds for J_{C2} and J_{C1}, it is also true that $J_{B2}(k_x, 0, \mathrm{c}_0) = J_{B1}(k_x, \mathrm{c}_0)$, although J_{B2} does not appear in the equation of motion.

Meniscus evolution equation

Two kinds of limits are need to be considered. First of all, we show that the double wall result for the evolution equation correctly reduces to single wall result in the limit of the wall separation $L \to \infty$. The second limit of small wave vectors helps us to reduce the equation of motion to the familiar diffusion equation for the Fourier modes of the fluctuations, which is easier to study than the original equation.

Starting with the double wall set-up we substitute the expressions derived above into Eq. (C.281). This yields the double wall result:

$$\frac{(1-e^{-2\mathrm{C}_0\tilde{k}_m})}{2\tilde{k}_m}\,\partial_t\grave{h}(k_x,m,t)+\frac{1}{2}\partial_t\mathrm{C}_0\,(1+e^{-2\mathrm{C}_0\tilde{k}_m})\,\grave{h}(k_x,m,t)=-\frac{M\sigma}{4}\tilde{k}_m^2\,\grave{h}(k_x,m,t)\ , \tag{C.288}$$

where $\tilde{k}_m \equiv \sqrt{k_x^2+(\pi m/L)^2}$. In the limit $L \to \infty$ starts approaching k_y. Thus, we can simply replace $\tilde{k}_m$ by $\tilde{k} \equiv \sqrt{k_x^2+k_y^2}$ and $\grave{h}(k_x,m,t)$ by $h(k_x,k_y,t)$ yielding us the single wall result

$$\frac{(1-e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}})}{2\sqrt{k_x^2+k_y^2}}\,\partial_t h(k_x,k_y,t)+\frac{1}{2}\partial_t\mathrm{C}_0\,(1+e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}})\,h(k_x,k_y,t)$$
$$=-\frac{M\sigma}{4}(k_x^2+k_y^2)\,h(k_x,k_y,t)\ , \tag{C.289}$$

These results are confirmed by the observation that we can produce the integral kernels of the single wall set-up by transforming Eq. (C.289) back into real space. Using the Hankel transform pair, $\int_0^\infty dk\,kJ_0(kx)e^{-ak} = a/(a^2+x^2)^{3/2}$, where J_0 is the zeroeth order Bessel function, we note that

$$\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}dk_x\int_{-\infty}^{\infty}dk_y\,e^{-\imath k_x x-\imath k_y y}\frac{1}{2}\,e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}}=\frac{1}{4\pi}\frac{2\mathrm{C}_0}{(x^2+y^2+4\mathrm{C}_0^2)}=\frac{1}{4\pi}i_B(x,y,t)\ . \tag{C.290}$$

The known relations between the integral kernels given in Eq. (C.226) together with the previous equation suffice to generate the terms I_B, I_C and I_D of the single wall problem whose real space form has been given in Eq. (C.221) - (C.224).

Next, we show under what circumstances Eq. (C.279) (equivalently, Eq. (C.288)) reduces to a diffusion equation. In the zero curvature case, $K=0$, both I_B and I_C vanish being proportional to $\partial_t\mathrm{C}_0 \propto \sqrt{K}$. Alternatively, we can consider a non-zero curvature with some pinning mechanism such as gravity to be present and study fluctuations around the pinned state where $\partial_t\mathrm{C}_0 = 0$. Thus,

$$J_{D2}(k_x,m,\mathrm{C}_0)\,\partial_t\grave{h}(k_x,m,t)=-\frac{M\sigma}{4}\left(k^2+(m\pi/L)^2\right)\grave{h}(k_x,m,t) \tag{C.291}$$

In the local limit, $\mathrm{C}_0\tilde{k}_m \ll 1$, the previous equation takes a simpler form

$$\mathrm{C}_0\,\partial_t\grave{h}(k_x,m,t)=-\frac{M\sigma}{4}\left(k_x^2+(m\pi/L)^2\right)\grave{h}(k_x,m,t)\ . \tag{C.292}$$

If C_0 is time dependent, Eq. C.292 can be considered as a diffusion equation in non-linear time. In pinned state C_0 is time independent constant and we can take it to the right hand side. In real space

$$\partial_t h(x,y,t)=\sigma_r\nabla^2 h(x,y,t)\ , \tag{C.293}$$

where $\sigma_r \equiv M\sigma/(4\mathrm{c}_0)$. Of course, one should remember that the inverse Fourier transform Eq. (C.293) applies strictly speaking only to those modes which satisfy $\mathrm{c}_0\tilde{k}_m \ll 1$. However, it is correct to say that on local scales the meniscus equation starts resembling an ordinary diffusion equation. The quick and dirty way of seeing this is just to ignore the Green function G_{3D} in Eq. (8.43). This, however doesn't reveal the renormalization of the surface tension σ_r.

C.11 Solution of meniscus fluctuations

Let us summarize the essential results of the meniscus dynamics which are needed for the determination of the equation of motion of the contact line. The dynamics of the meniscus fluctuations by Eq. (C.288). In the local limit, $\mathrm{c}_0\tilde{k}_m \ll 1$ it reduces to the following form:

$$\mathrm{c}_0(t)\partial_t\grave{h}(k_x,m,t)+\partial_t\mathrm{c}_0(t)\grave{h}(k_x,m,t)=-\frac{M\sigma}{4}\left(k_x^2+(m\pi/L)^2\right)\grave{h}(k_x,m,t)\ . \tag{C.294}$$

Inversion of this simplified equation back to real space using Fourier transform is strictly speaking not permitted because of the wave vector restriction $\mathrm{c}_0\tilde{k}_m \ll 1$, unless we regard the theory given by

$$\mathrm{c}_0(t)\partial_t h(x,y,t)+\partial_t\mathrm{c}_0(t)h(x,y,t)=-\frac{M\sigma}{4}\nabla^2 h(x,y,t)\ , \tag{C.295}$$

as an effective theory which is valid only on large enough scales $\xi \gg \mathrm{c}_0^{-1}$. Utilizing a nonlinear time coordinate τ, which satisfies $d\tau/dt = \mathrm{c}_0^{-1}$, and introducing new fluctuating meniscus and contact line fields through $\tilde{f}(\tau(t)) \equiv f(t)$, we obtain

$$\partial_\tau\tilde{h}(x,y,\tau)+\frac{1}{\tau}\tilde{h}(x,y,\tau)=-\frac{M\sigma}{4}\nabla^2\tilde{h}(x,y,\tau)\ , \tag{C.296}$$

where we have also made use of the fact that $\partial_\tau\tilde{\mathrm{c}}_0(\tau) = 1/\tau$. This result follows if one assumes Washburn's growth law to hold right from the start of the experiment and neglects the initial time dependence of the curvature: $\tau = \int_0^t ds(M\sigma Ks/u)^{-1/2}$. To solve the partial differential equation (C.296) we proceed in three steps. We start with the simplest case and ignore the left hand side of the previous equation altogether. This approximation corresponds to situation where the fluctuations have become stationary. In the next approximation we take into account the velocity term, $\partial_\tau\tilde{h}$ on the left hand side of Eq. (C.296) but ignore the term $(1/\tau)\,\tilde{h}$. Finally, we discuss the solution of the full equation with both terms on the left included.

C.11.1 Quasi-stationary solution

This section presents the solutions of the fluctuations of the meniscus in the the quasi stationary approximation where all the time dependence of the modes has vanished. We also assume that the velocity of the contact line has slowed down so much that we can take $\partial_t\mathrm{c}_0 \approx 0$. Let us first present the quasi stationary solution with finite plate separation L. We will allow for nontrivial contact line profile on both plates. The one on the wall at $y = 0$ will be denoted by $\tilde{c}^a$ and the one one the wall at $y = L$ will be denoted by $\tilde{c}^b$. So, mathematically we are looking for the solutions of the Poisson equation

$$\nabla^2\tilde{h} = 0 \tag{C.297}$$

with the boundary data $\tilde{h}(x,0,\tau) = \tilde{c}^a(x,\tau)$ and $\tilde{h}(x,L,\tau) = \tilde{c}^b(x,\tau)$. The solutions in real space are

$$\tilde{h}^a(x,y,\tau) = \frac{\sin(\pi y/L)}{2L}\int_{-\infty}^{\infty} dx' \, \frac{1}{\cosh(\pi(x'-x)/L) - \cos(\pi y/L)}\,\tilde{c}^a(x',\tau) \quad \text{(C.298)}$$

$$\tilde{h}^b(x,y,\tau) = \frac{\sin(\pi y/L)}{2L}\int_{-\infty}^{\infty} dx' \, \frac{1}{\cosh(\pi(x-x')/L) + \cos(\pi y/L)}\,\tilde{c}^b(x',\tau) \ . \quad \text{(C.299)}$$

Time in the equations above is just a parameter. In Fourier space these equations simplify a great deal. Using residue summation it is possible to show that

$$\int_{-\infty}^{\infty} dx \, e^{\imath kx} \frac{1}{\cosh(\pi x/L) - \cos(\pi y/L)} = \frac{2L}{\sin(\pi y/L)} \frac{\sinh(|k|(L-y))}{\sinh(|k|L)} \ . \quad \text{(C.300)}$$

Substituting this into the Fourier transforms of Eqs. (C.298) and (C.299) yields the result immediately. A more convenient way to arrive at the correct result is to use an exponential (hyperbolic) attempt kernel which satisfies the boundary conditions at $y = 0, L$. Thus, the fluctuations $\tilde{h} = \tilde{h}^a + \tilde{h}^b$ can be written as:

$$\tilde{h}_{qs}(x,y,\tau) = \int dk \, e^{\imath kx} \frac{\sinh(|k|(L-y))}{\sinh(|k|L)}\,\tilde{c}^a(k,\tau) + \int dk \, e^{\imath kx} \frac{\sinh(|k|y)}{\sinh(|k|L)}\,\tilde{c}^b(k,\tau) \quad \text{(C.301)}$$

Taking the limit $L \to \infty$ obviously recovers the kernel of Ref. [355] since the contribution from $\tilde{h}^b$ vanishes:

$$\lim_{L\to\infty} \tilde{h}_{qs} \to \int dk e^{\imath kx} e^{-|k|y}\,\tilde{c}^a(k) \ . \quad \text{(C.302)}$$

where the normalization factor of $1/(2\pi)$ has been dropped to make the notations consistent. It should also be noted that the quasi-stationary solution $\tilde{h}(x,\tau) \equiv h(x,t)$ by definition. So, the tildes above the function names can be dropped if τ is replaced with t.

C.11.2 Diffusive solution: memory expansion

In the following we will discuss the justification of making the boundary data time dependent in the quasi stationary approximation. Including time dependence of the fluctuations means that instead of Eq. (C.297) we should solve the diffusion type of problem, which is valid in the regime $k c_0 \ll 1$:

$$\left(\partial_\tau - \tilde{\sigma}\nabla^2\right)\tilde{h} = 0 \quad \text{(C.303)}$$

with the same boundary conditions as above: $\tilde{h}(x,0,\tau) = \tilde{c}^a(x,\tau)$ and $\tilde{h}(x,L,\tau) = \tilde{c}^b(x,\tau)$. With the aid of Green function G_d of the time dependent diffusion problem we can write

$$\tilde{h}^a(x,y,\tau) = \tilde{\sigma}\int_0^\tau d\tau_1 \int_{-\infty}^{\infty} dx_1 \, \partial_{y_1} G_d(x,y,\tau;x_1,y_1,\tau_1)|_0 \, \tilde{c}^a(x_1,\tau_1) + \tilde{h}^a_i(\tau) \ , \quad \text{(C.304)}$$

with a similar result for $\tilde{h}^b$. The contribution from the non-zero initial profile $\tilde{h}^a_i(\tau)$ will be left out in the following. For finite wall separation the Green function which satisfies

$$(\partial_\tau - \tilde{\sigma}\nabla^2) G_d(x,y,\tau;x_1,y_1,\tau_1) = \delta(x-x_1)\delta(y-y_1)\delta(\tau-\tau_1) \ , \quad \text{(C.305)}$$

is expressible via the eigenfunction expansion of the form

$$G_d(x,y,\tau;x_1,y_1,\tau_1) = \tag{C.306}$$
$$\theta(\tau-\tau_1)\int_{-\infty}^{\infty}\! dk_x\,\frac{2}{L}\sum_{n=1}^{\infty} e^{-\tilde{\sigma}[k_x^2+(\pi n/L)^2](\tau-\tau_1)}\, e^{\imath k_x(x-x_1)}\,\sin(n\pi y/L)\sin(n\pi y_1/L)\ ,$$

where θ is the Heaviside step function. Substitution of the Green function G_d into Eq. (C.304) gives in the single wall case

$$\tilde{h}^a(x,y,\tau) = \tilde{\sigma}\int_0^{\tau}\! d\tau_1\int_{-\infty}^{\infty}\! dk_x\,\frac{2}{L}\sum_{n=1}^{\infty} e^{-\tilde{\sigma}[k_x^2+(n\pi/L)^2](\tau-\tau_1)}(n\pi/L)\sin(n\pi y/L)\,\tilde{c}^a(k_x,\tau_1)\,e^{\imath k_x x}\ , \tag{C.307}$$

where we performed the integration over x_1 resulting in the Fourier transform of $\tilde{c}(x_1,\tau_1)$. The memory expansion parameter will be made explicitly through introduction of dimensionless time coordinate s: $\tau_1 \equiv \tau s$. Eq. (C.307) takes the form

$$\begin{aligned}\tilde{h}^a(x,y,\tau) = \tilde{\sigma}\tau\int_0^1\! ds\int_{-\infty}^{\infty}\! dk_x &\left\{\frac{2}{L}\sum_{n=1}^{\infty} e^{-(\tilde{\sigma}\tau/L^2)[(k_xL)^2+(n\pi)^2](1-s)}\right.\\ &\left.\times\ (n\pi/L)\sin(n\pi y/L)\,\tilde{c}^a(k_x,\tau s)\,e^{\imath k_x x}\right\}\ .\end{aligned} \tag{C.308}$$

The prefactor of the argument of the exponential function is calculated by using the definitions of $\tilde{\sigma} = M\sigma/4$ and $\tau = \int_0^t ds\, 1/\mathrm{c}_0(s)$ with $\mathrm{c}_0(t)$ given in Eq. (C.160). Hence,

$$\tilde{\sigma}\tau/L^2 = M\sigma\tau/(4L^2) = u\mathrm{c}_0/(2KL^2) = u/(2\epsilon)\ , \tag{C.309}$$

where the small curvature expansion parameter $\epsilon \equiv KL^2/\mathrm{c}_0$. Thus, we can Taylor expand the solution as power series in ϵ. In order to do this, we shift the origin of the time integration through $1 - s_{old} = s_{new}$ and define $\tilde{u} \equiv u/2$. Eq. (C.308) becomes

$$\begin{aligned}\tilde{h}^a(x,y,\tau) = \tilde{\sigma}\tau\int_0^1\! ds\int_{-\infty}^{\infty}\! dk_x &\left\{\frac{2}{L}\sum_{n=1}^{\infty} e^{-(\tilde{u}/\epsilon)[(k_xL)^2+(n\pi)^2]s}\right.\\ &\left.\times\ (n\pi/L)\sin(n\pi y/L)\,\tilde{c}^a(k_x,\tau(1-s))\,e^{\imath k_x x}\right\}\ .\end{aligned} \tag{C.310}$$

We notice that because ϵ goes to zero, only the values of s around zero will contribute significantly to the integral because the larger values are exponentially damped. Therefore, it makes sense to expand $\tilde{c}^a$ around $s = 0$:

$$\tilde{c}^a(k_x,\tau(1-s)) = \tilde{c}^a(k_x,\tau) + \partial_s\tilde{c}^a(k_x,\tau(1-s))|_0\, s + \frac{1}{2}\partial_s^2\tilde{c}^a(k_x,\tau(1-s))|_0 + \ldots \tag{C.311}$$

$$= \sum_{n=0}^{\infty}\frac{1}{n!}\,\partial_\tau^n\tilde{c}^a(k_x,\tau)(-\tau s)^n\ . \tag{C.312}$$

At this point, we introduce a short-hand symbol $Y \equiv (\tilde{u}/\epsilon)[(k_xL)^2 + (n\pi)^2]$. Obviously $Y \to \infty$ when $\epsilon \to 0$ because $n \geq 1$. Substitution of the Taylor series into Eq. (C.310) and shifting the order of the time integration and summation yields

$$\begin{aligned}\tilde{h}^a(x,y,\tau) = \tilde{\sigma}\tau\int_{-\infty}^{\infty}\! dk_x\,\frac{2}{L}\sum_{n=1}^{\infty} &\left\{\int_0^1\! ds\ e^{-Ys}\,(n\pi/L)\sin(n\pi y/L)\right.\\ &\left.\times\ \sum_{m=0}^{\infty}\frac{1}{m!}\,\partial_\tau^m\tilde{c}^a(k_x,\tau)(-\tau s)^m\,e^{\imath k_x x}\right\}\ .\end{aligned} \tag{C.313}$$

Collecting the time dependent quantities in the previous expression leads us to study the properties of the integral $\int_0^1 ds \exp(-Ys)\, s^m$, which can be conveniently represented as

$$(-\partial_Y)^m \int_0^1 ds \exp(-Ys) = (-\partial_Y)^m \left[Y^{-1}(1-e^{-Y})\right] \approx (-1)^m m!\, Y^{-1-p} \ , \qquad \text{(C.314)}$$

where the last relation holds for Y sufficiently large. Thus, we could work out the derivatives and write down the full solution $\tilde{h}$ in terms of them. However, to simplify the result we will drop all the terms proportional to e^{-Y} from the expression of Eq. (C.314) and keep only the largest term, $(-1)^m m!\, Y^{-1-p}$:

$$\begin{aligned}\tilde{h}^a(x,y,\tau) \approx \tilde{\sigma}\tau \int_{-\infty}^{\infty} dk_x \, \frac{2}{L} \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \Big\{ & (-1)^m m!\, Y^{-1-m} (n\pi/L) \sin(n\pi y/L) \\ & \times \frac{1}{m!}\, \partial_\tau^m \tilde{c}^a(k_x,\tau)(-\tau)^m \, e^{\imath k_x x} \Big\} \ . \end{aligned} \qquad \text{(C.315)}$$

Next, we cancel out the factorials $m!$ and the powers of (-1). Extraction of a factor of Y^{-1} allows us to write:

$$\tilde{h}^a(x,y,\tau) \approx \int_{-\infty}^{\infty} dk_x \, \frac{2}{L} \sum_{n=1}^{\infty} \frac{\tilde{\sigma}\tau}{Y} \sum_{m=0}^{\infty} (\tau/Y)^m (n\pi/L) \sin(n\pi y/L)\, \partial_\tau^m \tilde{c}^a(k_x,\tau)\, e^{\imath k_x x} \ . \qquad \text{(C.316)}$$

Plugging in the definitions of Y and τ, we obtain $\tilde{\sigma}\tau/Y = L^2/[(k_x L)^2 + (n\pi)^2]$. The powers of the expansion parameter emerge from the factor $(\tau/Y)^m \propto \epsilon^m$:

$$\tilde{h}^a(x,y,\tau) \approx \sum_{m=0}^{\infty} \epsilon^m \int_{-\infty}^{\infty} dk_x \, \frac{2}{L} \sum_{n=1}^{\infty} \frac{(n\pi/L)\sin(n\pi y/L)}{(k_x)^2 + (n\pi/L)^2} \, \frac{\tau^m\, \partial_\tau^m \tilde{c}^a(k_x,\tau)}{[(k_x L)^2 + (n\pi)^2]^m} \, e^{\imath k_x x} \ . \qquad \text{(C.317)}$$

In the limit $\epsilon \to 0$ only the first term of the sum over m survives. We denote it $\tilde{h}_{qs}$ because it is exactly the same solution which we will find in Sect. C.11.3 to be the solution of the Laplace's equation $\nabla^2 \tilde{h} = 0$:

$$\tilde{h}^a_{qs}(x,y,\tau) = \int_{-\infty}^{\infty} dk_x \, e^{\imath k_x x} \, \frac{2}{L} \sum_{n=1}^{\infty} \frac{(n\pi/L)\sin(n\pi y/L)}{(k_x)^2 + (n\pi/L)^2} \, \tilde{c}^a(k_x,\tau) \ . \qquad \text{(C.318)}$$

For small enough ϵ we can approximate the full solution by the quasi-stationary solution and a first order correction term. Then, $\tilde{h}^a \approx \tilde{h}^a_{qs} + \epsilon \tilde{h}^a_1$, where

$$\tilde{h}^a_1(x,y,\tau) = \int_{-\infty}^{\infty} dx_1 \, g_1(x-x_1,y,\tau)\, \partial_\tau \tilde{c}^a(x_1,\tau) \ , \qquad \text{(C.319)}$$

where the kernel function g_1 does not depend on the history (times prior to τ) in any way. There is a factor τ multiplying the time derivative of the contact line position, though. In Fourier space the new kernel function is given by

$$g_1(k_x,y,\tau) \equiv \frac{2}{L} \sum_{n=1}^{\infty} \frac{(n\pi/L)\sin(n\pi y/L)}{(k_x)^2 + (n\pi/L)^2} \, \frac{\tau}{\tilde{u}[(k_x L)^2 + (n\pi)^2]} \ . \qquad \text{(C.320)}$$

Of course, an infinite series of time derivatives can give rise to history dependence. In this particular case an exact summation over all m would reproduce the history dependent solution given in Eq. (C.307). The particular representation given of Eq. (C.319) will be needed later on in Sect. C.16 when trying to justify the chosen variational scheme for producing the equation of motion of the contact line.

C.11.3 Diffusive solution: reduction to quasi-stationary solution

Next, we will rewrite the results of the quasi stationary approximation in similar form as above in order to see better, if the the time dependent problem reduces to the quasi stationary one in some limit. The Green function in the quasi-stationary approximation can be written as

$$g_{qs}(x,y;x_1,y_1) = \int_{-\infty}^{\infty} dk_x \, \frac{2}{L} \sum_{n=1}^{\infty} \frac{e^{\imath kx(x-x_1)} \sin(n\pi y/L) \sin(n\pi y_1/L)}{k_x^2 + (n\pi/L)^2} \; . \tag{C.321}$$

In terms of g^a_{qs}, the fluctuations of the meniscus are expressible as

$$\begin{aligned} \tilde{h}^a_{qs}(x,y,\tau) &= \int_{-\infty}^{\infty} dx_1 \partial_{y_i} g_{qs}(x,y;x_1,y_1)|_0 \, \tilde{c}^a(x_1,\tau) & \text{(C.322)} \\ &= \int_{-\infty}^{\infty} dk_x \, \frac{2}{L} \sum_{n=1}^{\infty} \frac{1}{k_x^2 + (n\pi/L)^2} \, (n\pi/L) \sin(n\pi y/L) \, \tilde{c}^a(k_x,\tau) e^{\imath k_x x} & \text{(C.323)} \end{aligned}$$

Comparing this with Eq. (C.307) suggests that we should check if it is possible to make the exponential term approach a delta function in time. We first note that if the contact line $\tilde{c}^a$ is not time dependent, we can integrate

$$\int_0^{\tau} d\tau_1 \, e^{-\tilde{\sigma}[k_x^2 + (n\pi/L)^2](\tau - \tau_1)} = \frac{1 - e^{-\tilde{\sigma}[k_x^2 + (n\pi/L)^2]\tau}}{\tilde{\sigma}[k_x^2 + (n\pi/L)^2]} \tag{C.324}$$

We notice that the denominator has the correct form appearing in the expression of the quasi stationary Green function g_{qs}. To get rid of the exponentially decaying time dependent term in the numerator in Eq. (C.324), we can set $t \to \infty$. Alternatively, in the limit $\epsilon \to 0$, or $\tilde{\sigma}\tau/L^2 \propto 1/\epsilon \to \infty$,

$$\begin{aligned} \tilde{\sigma} \int_0^{\tau} d\tau_1 \, e^{-\tilde{\sigma}[k_x^2 + (n\pi/L)^2](\tau - \tau_1)} &= \frac{\tilde{\sigma}\tau}{L^2} \int_0^1 ds_1 \, L^2 \, e^{-(\tilde{\sigma}\tau/L^2)[(Lk_x)^2 + (n\pi)^2](1 - s_1)} & \text{(C.325)} \\ &\to \frac{1}{k_x^2 + (n\pi/L)^2} \; . & \text{(C.326)} \end{aligned}$$

Based on this observation we construct the representation of the one-sided delta function. For $x \geq 0$,

$$\lim_{\tilde{\sigma} \to \infty} \tilde{\sigma} e^{-\tilde{\sigma} x} \to \delta(x) \; . \tag{C.327}$$

In case the argument of the exponential being more complicated, we will use the usual rules to simplify the argument of the delta function. In particular,

$$\lim_{\tilde{\sigma} \to \infty} \tilde{\sigma} e^{-\tilde{\sigma}[k_x^2 + (n\pi/L)^2](\tau - \tau_1)} \to \frac{1}{k_x^2 + (n\pi/L)^2} \, \delta(\tau - \tau_1) \; . \tag{C.328}$$

Thus, for large values of $\tilde{\sigma}$ the system looses its memory and we have the relation

$$\lim_{\tilde{\sigma} \to \infty} \tilde{h}^a(x,y,\tau) \to \tilde{h}^a_{qs}(x,y,\tau) \; . \tag{C.329}$$

In conclusion, we have given an intuitive explanation for the use of $\tilde{h}^a_{qs}(x,y,\tau)$ instead of $\tilde{h}^a(x,y,\tau)$ in the limit ϵ very small. As shown in the previous section, $\tilde{h}_{qs}$ is just the beginning of a systematic expansion in powers of ϵ.

C.11.4 Full solution

The full solution of this equation is expressible in terms of the kernel functions g^a and g^b when there are two walls present in the system. In other words,

$$\begin{aligned}\tilde{h}(x,y,\tau) &= \int_0^\tau d\tau_1 \int_{-\infty}^{\infty} dx_1\, g^a(x-x_1,y,\tau,\tau_1)\, \tilde{c}^a(x_1,\tau_1) \\ &+ \int_0^\tau d\tau_1 \int_{-\infty}^{\infty} dx_1\, g^b(x-x_1,y,\tau,\tau_1)\, \tilde{c}^b(x_1,\tau_1)\ , \qquad \text{(C.330)}\end{aligned}$$

where superscripts a and b refer to the two walls situated at $y = 0$ and $y = L$, respectively. A straightforward generalization of Eq. (C.307) yields

$$g^a(x,y,\tau,\tau_1) \equiv \frac{M\sigma}{4} \mathcal{F}^{-1}_{x/k_x} \left\{ \frac{2}{L} \sum_{m=1}^{\infty} e^{-(M\sigma/4)\,\tilde{k}_m^2(\tau-\tau_1)+\ln(\tau/\tau_1)} \left(\frac{m\pi}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \right\}, \qquad \text{(C.331)}$$

where $\tilde{k}_m = \sqrt{k_x^2 + (m\pi/L)^2}$. Next, we will derive the criterion that allows us to reduce the full solution to the diffusive one. The condition for ignoring the second term on the right hand side of Eq. (C.295) can be obtained by comparing it to the diffusive term on the right. The condition is $(M\sigma/4)k^2 \gg \partial_t \mathrm{c}_0$, which can be also expressed as

$$(M\sigma/4)\, k^2 \gg \partial_t \mathrm{c}_0 = M\sigma\epsilon/(2uL^2) \ \Rightarrow\ k \gg [2\epsilon/(uL^2)]^{1/2} = [2KL^2/(\mathrm{c}_0 uL^2)]^{1/2} \qquad \text{(C.332)}$$

$$\Rightarrow\ 1/\mathrm{c}_0 \gg k \gg (K/\mathrm{c}_0)^{1/2} \ \Rightarrow\ K \ll 1/\mathrm{c}_0\ . \qquad \text{(C.333)}$$

The first equality in Eq. (C.332) has been obtained by substituting the Washburn's growth law for c_0. The next equality is due to definition of $\epsilon \equiv KL^2/\mathrm{c}_0$. Finally, in Eq. (C.333) we have taken into account the wave number restriction $k\mathrm{c}_0 \ll 1$. Hence, when the second term in the equation of motion of the meniscus can be ignored, the kernel function g^a reduces to

$$g^a(x,y,\tau,\tau_1) \equiv \frac{M\sigma}{4} \mathcal{F}^{-1}_{x/k_x} \left\{ \frac{2}{L} \sum_{m=1}^{\infty} e^{-(M\sigma/4)\,\tilde{k}_m^2(\tau-\tau_1)} \left(\frac{m\pi}{L}\right) \sin\left(\frac{m\pi y}{L}\right) \right\}, \qquad \text{(C.334)}$$

This result can be immediately obtained by comparing it with the integral kernel presented in Eq. (C.304). For double wall set-up

$$\begin{aligned} g^a(x-x_1,y,\tau,\tau_1) &\equiv \partial_{y_1} G_d(x,y,\tau;x_1,y_1,\tau_1)|_0\ ; \qquad &\text{(C.335)} \\ g^b(x-x_1,y,\tau,\tau_1) &\equiv \partial_{y_1} G_d(x,y,\tau;x_1,y_1,\tau_1)|_L\ . \qquad &\text{(C.336)}\end{aligned}$$

Finally, in the limit of vanishing curvature we can reduce the diffusive solution to the quasi-stationary one. That is, when $\epsilon \ll 1$ we can replace the kernel functions of the previous equation with the corresponding ones of the quasi-stationary kernels:

$$\begin{aligned} g^a(x-x_1,y) &\equiv \partial_{y_1} G_0(x,y;x_1,y_1)|_0\ ; \qquad &\text{(C.337)} \\ g^b(x-x_1,y) &\equiv \partial_{y_1} G_0(x,y;x_1,y_1)|_L\ , \qquad &\text{(C.338)}\end{aligned}$$

where the homogeneous Green's function G_0 has been defined in Eq. (C.507). Naturally, the time integrals are not needed any more as in Eq. (C.330) and we simply have

$$\tilde{h}(x,y,\tau) = \int_{-\infty}^{\infty} dx_1\, g^a(x-x_1,y)\, \tilde{c}^a(x_1,\tau) + \int_{-\infty}^{\infty} dx_1\, g^b(x-x_1,y)\, \tilde{c}^b(x_1,\tau)\ . \qquad \text{(C.339)}$$

Thus, we have shown how the different approximations can be generated by the full solution of the meniscus fluctuations. When deriving the contact line equation we will first use the quasi-stationary solution, and later on, when discussing memory effects, the diffusive solution.

C.12 Contact line dynamics of pure system

In Sect. C.5 we separated the zeroeth order meniscus motion (H_0) of a system with pure walls from the fluctuating part (h) which accounts for the effect of random surface tensions of impure walls. Consequently, we constructed two variational equations, Eq. (C.108) and Eq. (C.109) which in this section will be further projected to produce the contact line equations of motion. Specifically, acting with projection operator $\mathcal{P}_\mathrm{C}$ on both sides of the meniscus equations of motion, we obtain

$$\frac{\delta R^p_{1D}[\dot{\mathrm{C}}_0]}{\delta \dot{\mathrm{C}}_0(t)} = -\frac{\delta F^p_{1D}[\mathrm{C}_0]}{\delta \mathrm{C}_0(t)} \; ; \tag{C.340}$$

$$\frac{\delta R^r_{1D}[\dot{c}]}{\delta \dot{c}(x,t)} = -\frac{\delta F^r_{1D}[c]}{\delta c(x,t)} \; , \tag{C.341}$$

where the new 1D functionals are obtained from the 2D meniscus functionals by substituting $\mathrm{H}_0(\mathrm{C}_0)$ and $h(c)$ into the 2D functionals and integrating out the y-coordinate. This will be demonstrated in Sect. C.12.2. In the following we will concentrate the pure part C_0 and discuss two different representations.

C.12.1 VarF derivation for pure system

As shown in Sect. C.5.3, there are two different constructions for the functionals (VarF1 given by Eq. (C.116) and VarF2 given by Eq. (C.120)) which produce almost the same equation of motion for the zeroeth order meniscus profile H_0; the only difference is that VarF2 contains two extra integrals on both sides of the equation of motion as compared to the other. This means that the exact solution $\mathrm{H}_0(\mathrm{C}_0)$ of Eq. (C.120)) will also be the exact solution of Eq. (C.116). Moreover, due to its construction, the equation of motion of H_0 as given by VarF1 is identical with the equation motion produced by the direct projection method DirP in Eq. (C.100).

We will now study if the same conclusion, equivalence of VarF1 and DirP that is, holds also at the contact line level C_0. At the meniscus level H_0 we were able to design our functionals in such a way that the variational formulation VarF1 reduced to the direct projection of the bulk equation of motion, which can be derived in various ways. At contact line level we do not know the correct answer in beforehand. However, since it is possible to use DirP to produce the equation of motion of C_0 owing to the ansatz $\mathrm{H}_0 = \mathrm{C}_0 + K(y^2 - Ly)$, as a consistency check we want to show that DirP and VarF applied to C_0 do give similar results. If they did not, we could not trust the variational formulation to give a sensible result for the contact line fluctuations c for which there is no DirP available due to the lack of the analogue of $\mathrm{H}_0 = \mathrm{C}_0 + K(y^2 - Ly)$ for h.

Our starting point is the assumption that the pure meniscus profile is a parabolic one (let us concentrate on double wall case for simplicity):

$$\mathrm{H}_0(\mathrm{C}_0) = \mathrm{C}_0(t) + K(t)(y^2 - Ly) \; , \tag{C.342}$$

where the contact line height $\mathrm{C}_0(t)$ and the curvature $K(t)$ are unknown functions of time to be determined from Eq. (C.340). In the following we assume that the curvature and the contact line can be independently varied. This assumption is not crucial for δR^p_{1D}, where we can additionally require that we are in a regime where the curvature has reached its stationary value and therefore $\dot{K}(t) \approx 0$. However, this requirement is not used in the following.

$$R^p_{1D}[\dot{\mathrm{C}}_0] \equiv \frac{4}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2 \left(\dot{\mathrm{C}}_0(t_1) + \dot{K}(t_1)(y_1^2 - Ly_1)\right)$$

$$\times \left(G_{3D}^{\mathrm{H}_0}(1;2)\delta_{t_1|t_2}\,\delta_{-x_1|x_2}\right)\left(\dot{\mathrm{C}}_0(t_2)+\dot{K}(t_2)(y_2^2-Ly_2)\right)\ . \tag{C.343}$$

The variation with respect to contact line velocity is obtained at once. Integrating out the time coordinates we obtain

$$\begin{aligned}
&\delta R_{1D}^{p}[\dot{\mathrm{C}}_0]/\delta\dot{\mathrm{C}}_0(t) = \\
&\frac{8}{M}\int dA_1\int dA_2\, G_{3D}(x_1,y_1,\mathrm{H}_0(y_1,t);x_2,y_2,\mathrm{H}_0(y_2,t))\delta_{-x_1|x_2}\left(\dot{\mathrm{C}}_0(t)+\dot{K}(t)(y_2^2-Ly_2)\right)\\
&=\frac{4}{M}\int dy_1\int dx_2\int dy_2\ G_{3D}(0,y_1,\mathrm{H}_0(y_1,t);x_2,y_2,\mathrm{H}_0(y_2,t))\left(\dot{\mathrm{C}}_0(t)+\dot{K}(t)(y_2^2-Ly_2)\right)\\
&=\frac{4}{M}\int dy\int dx_1\int dy_1\ G_{3D}(x,y,\mathrm{H}_0(y,t);x_1,y_1,\mathrm{H}_0(y_1,t))\left(\dot{\mathrm{C}}_0(t)+\dot{K}(t)(y_1^2-Ly_1)\right)
\end{aligned} \tag{C.344}$$

In the third line we made a change of variables, $(x_2)_{new}=2(x_2)_{old}$ and in the last line we renamed the arguments and added a dummy argument x. Adding a dummy argument is possible if $G_{3D}(1;2)$ depends on the difference x_1-x_2 only. In addition, the x_1 integration must run from $-\infty$ to ∞.

The right hand side of the equation of motion of the contact line is based on the functional $F_{2D}^{p}[\mathrm{H}_0]$ given in Eq. (C.114):

$$\begin{aligned}
F_{1D}^{p}[\mathrm{C}_0] \equiv \int dy_1\int dt_1\int dy_2\int dt_2\ \frac{1}{2}\Big\{&\left(\mathrm{C}_0(t_1)+K(t_1)(y_1^2-Ly_1)\right)\\
\times&\left(-\sigma\partial_{y_1}^2\delta_{y_1|y_2}\delta_{t_1|t_2}\right)\left(\mathrm{C}_0(t_2)+K(t_2)(y_2^2-Ly_2)\right)\Big\}\ .
\end{aligned} \tag{C.345}$$

It is noted that if one uses the other representation of $F_{2D}^{p}[\mathrm{H}_0]$ given in Eq. (C.115) to generate $F_{1D}^{p}[\mathrm{C}_0]$ one fails if the boundary terms are not taken into account: the derivatives with respect to y_1 destroy constant C_0. Variation yields

$$-\frac{\delta F_{1D}^{p}[\mathrm{C}_0]}{\delta\mathrm{C}_0(t)}=\int dy_1\int dy_2\left(\sigma\partial_{y_2}^2\delta_{y_1|y_2}\right)\left(\mathrm{C}_0(t)+K(t)(y_2^2-Ly_2)\right)=\int dy_1\, 2\sigma K=2\sigma KL\ . \tag{C.346}$$

The first equality is obtained by removing the delta functions of time coordinates. Next, we have integrated by parts twice with respect to variable y_2. Finally, the integral over y_1 goes from 0 to L in the double wall set-up.

Let us now collect the results and see what the equation of motion for the contact line profile, C_0, of the pure system looks like. Setting Eq. (C.344) equal to Eq. (C.346) gives the VarF equation of motion for C_0:

$$\begin{aligned}
\int dy\int dx_1\int dy_1\Big\{&G_{3D}\Big(x,y,\mathrm{C}_0(t)+K(t)(y^2-Ly)\,;\,x_1,y_1,\mathrm{C}_0(t)+K(t)(y_1^2-Ly_1)\Big)\\
&\times\left(\dot{\mathrm{C}}_0(t)+\dot{K}(t)(y_1^2-Ly_1)\right)\Big\}=\frac{1}{2}M\sigma KL\ .
\end{aligned} \tag{C.347}$$

The previous equation obtained through variational method (VarF) will be compared below with the equation of motion which can be obtained from directly projecting the zeroeth order meniscus equation.

C.12.2 Comparison of VarF and DirP: Washburn's law

In this section we show that both variational and direct projection methods yield a solution which goes like $\mathrm{C}_0\sim t^{1/2}$ consistent with Washburn's law, which states that the mean meniscus height (contact line height) should grow like $t^{1/2}$ for large times without pinning mechanisms. Direct projection of Eq. (C.100), which is the same as Eq. (C.116), onto the plane $y = 0$ gives the following DirP equation of motion for c_0:

$$\int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \left\{ G_{3D}^{2W}\Big(x, 0, \mathrm{c}_0(t); x_1, y_1, \mathrm{c}_0(t) + K(t)(y_1^2 - Ly_1)\Big) \right. \\ \left. \times \Big(\dot{\mathrm{c}}_0(t) + \dot{K}(t)(y_1^2 - Ly_1)\Big) \right\} = \frac{1}{2} M\sigma K \ , \tag{C.348}$$

where we have used the fact that $\mathrm{H}_0(0,t) = \mathrm{c}_0(t)$ and $\partial_y^2 \mathrm{H}_0(y,t)|_0 = 2K$. As compared to VarF equation (C.347), there is the factor L missing from the right hand side (due to integration over y_1) and likewise, there is an integral over y missing on the left hand side. In addition the argument z of the Green's function $G_{3D}^{2W}(x, y, z; x_1, y_1, z_1)$ is $\mathrm{H}_0(0,t)$ for DirP where as for VarF it is $\mathrm{H}_0(y,t)$. The question is, whether these two equations give the same physics for some parameter range or not.

Let us simplify the problem by requiring that the curvature of the meniscus is small. The small parameter of the theory is the dimensionless number $\epsilon \equiv KL^2/\mathrm{c}_0 \ll 1$. We will also assume that the rise of the meniscus follows Washburn's diffusive $t^{1/2}$ law from the beginning which allows us to ignore the time variation of the curvature: $\dot{K} = \mathcal{O}(\epsilon^2)$. Thus, Eq. (C.348) reduces to

$$\int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \ G_{3D}^{2W}(x, 0, \mathrm{c}_0(t); x_1, y_1, \mathrm{c}_0(t))\, \dot{\mathrm{c}}_0(t) \approx \frac{1}{2} M\sigma K \ , \tag{C.349}$$

Correspondingly, Eq. (C.347) yields to order $\mathcal{O}(\epsilon)$

$$\int_0^L dy \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \, G_{3D}^{2W}(x, y, \mathrm{c}_0(t); x_1, y_1, \mathrm{c}_0(t))\, \dot{\mathrm{c}}_0(t) \approx \frac{1}{2} M\sigma KL \ . \tag{C.350}$$

In the new coordinate frame it becomes easier to study the limit of the wall separation L becoming large. To further simplify the computational task, we make use of the fact that the larger the separation of the two walls, the more the Green's function G_{3D}^{2W} starts resembling the Green function G_{3D}^{1W}. This can be seen directly through mirror charge technique as shown in Sect. C.6. Thus, we replace G_{3D}^{2W} with G_{3D}^{1W} yet keeping the upper integration limit L finite. Let

$$w(x, y) \equiv \frac{1}{4\pi} \left(\frac{1}{\sqrt{x^2 + y^2}} - \frac{1}{\sqrt{x^2 + y^2 + 4\mathrm{c}_0^2}} \right) \ . \tag{C.351}$$

With G_{3D}^{1W} replaced by $G_{3D}^{1W}(x, y, \mathrm{c}_0; x_1, y_1, \mathrm{c}_0) = w(x - x_1, y - y_1) + w(x - x_1, y + y_1)$, the DirP equation. (C.349) reads

$$\int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \ w(x_1, y_1)\, \dot{\mathrm{c}}_0(t) + \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \ w(x_1, y_1)\, \dot{\mathrm{c}}_0(t) \approx \frac{1}{2} M\sigma K \ , \tag{C.352}$$

Expressing G_{3D}^{1W} in terms of the new function u and plugging it into Eq. (C.350) reveals the difference the y-argument of u as compared to DirP:

$$\int_0^L dy \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \ w(x_1, y - y_1)\, \dot{\mathrm{c}}_0(t) + \int_0^L dy \int_{-\infty}^{\infty} dx_1 \int_0^L dy_1 \ w(x_1, y + y_1)\, \dot{\mathrm{c}}_0(t) \approx \frac{1}{2} M\sigma KL \ , \tag{C.353}$$

The integrals can be explicitly computed for both cases and the final result is the VarF and Dirp equations of motion differ by terms of the order L^{-1}. Therefore, in the single wall limit they both reduce to the form

$$u\,\mathrm{c}_0\partial_t\mathrm{c}_0 = \frac{M\sigma K}{2}\ , \tag{C.354}$$

where $u = 4\pi$. In the bulk of the text we will use just the general coefficient u, as for finite L we should include also higher order correction terms of the Green's function given in a mirror charge series representation, not just the single wall contribution corresponding to summand $m = 0$ used in the calculation above. From Eq. (C.354) it follows that

$$\mathrm{c}_0(t) = \sqrt{\frac{M\sigma Kt}{u} + c_i^2}\ , \tag{C.355}$$

where $c_i = \mathrm{c}_0(0)$ is the initial height of the contact line at time $t = 0$. When c_i is zero, the Washburn's law is seen to hold for all times. The choice of a non-zero value for the initial height c_i is discussed in Sect. C.8. Yet another factor which can affect the dynamics of c_0 is a non-zero projected boundary term $\tilde{\Lambda}_{\mathrm{H}_0}$ which modifies the equation of motion to the following form

$$u\,\partial_t(\mathrm{c}_0^2/2) = M\sigma K/2 + \tilde{\Lambda}_{\mathrm{H}_0}\ , \tag{C.356}$$

where we have neglected possible spatial dependence of $\tilde{\Lambda}$ for simplicity. Even if $K = 0$ some nontrivial $\mathrm{c}_0(t)$ will be generated depending on the time dependence of $\tilde{\Lambda}_{\mathrm{H}_0}$. For $K \neq 0$, Washburn's behaviour can change. However, for present boundary conditions $\tilde{\Lambda}_{\mathrm{H}_0} = 0$ and it will be excluded from the analysis to follow.

C.13 Variational derivation of contact line fluctuations

Variational derivation of the fluctuations of the contact line dynamics is presented in this section. We derive the dynamics of the double wall set-up and show that the result reduce to those corresponding to single wall when the wall separation $L \to \infty$. Our approach is to project the meniscus functionals defined in a 2D space into one dimensional functionals containing the contact line as collective coordinate. The full meniscus solution $\mathrm{H} = \mathrm{H}_0 + h$, where the pure meniscus solution is assumed to be parabolic, $\mathrm{H}_0(y,t) = \mathrm{c}_0 - KLy + Ky^2$, and the fluctuation correction $h(x,y,t) = h^a(x,y,t) + h^b(x,y,t)$ describing the effect of nonhomogeneous surface tension of the walls a and b. In this section we will use the quasi-stationary solutions h^a_{qs} and h^b_{qs}. Inclusion of memory effects will be discussed in Sect. C.16. Specifically,

$$h^i_{qs}(x,y,t) = \int_{-\infty}^{\infty} dx_1\, g^i_{qs}(x - x_1, y)\, c^i(x_1,t)\ , \tag{C.357}$$

where $i = a, b$. We have made use of the fact that $\tilde{h}(x,y,\tau(t)) = h(x,y,t)$ and $\tilde{c}(x,\tau(t)) = c(x,t)$. In the memoryless case the Rayleigh dissipation functional can be written down immediately. We first use the definition of R^r_{2D} in Eq. (C.121), where we replace $\dot{h} = \dot{h}^a + \dot{h}^b$:

$$\begin{aligned} R^r_{1D}[\,\dot{c}^a, \dot{c}^b\,] \equiv \frac{2}{M}\int dA_1 \int dt_1 \int dA_2 \int dt_2\ \delta_{t_1|t_2} \Big\{ \\ \Big[\dot{h}^a_{\mathrm{C}}(1,t_1) + \dot{h}^b_{\mathrm{C}}(1,t_1)\Big]\ G^{\mathrm{H}_0}_{3D}(1;2)\ \Big[\dot{h}^a_{\mathrm{C}}(2,t_2) + \dot{h}^b_{\mathrm{C}}(2,t_2)\Big] \\ + 2\Big[\dot{h}^a_{\mathrm{C}}(1,t_1) + \dot{h}^b_{\mathrm{C}}(1,t_1)\Big]\Big[\partial_{z_1}G^{\mathrm{H}_0}_{3D}(1;2)h_{\mathrm{C}}(1,t_1) + \partial_{z_2}G^{\mathrm{H}_0}_{3D}(1;2)h_{\mathrm{C}}(2,t_2)\Big]\,\dot{\mathrm{H}}_0(2,t_2)\Big\}\ . \end{aligned} \tag{C.358}$$

The limit specification reads $\int dA_i = \int_{-\infty}^{\infty} dx_i \int_0^L dy_i$, $i = 1, 2$. The notation $\dot{h}^i_{\mathrm{C}}$ means that the actual variable is not $\dot{h}^i$ but velocity of the contact line at wall i. There is an obvious relation between these two in the quasi-stationary approximation where we take $h^i_{\mathrm{C}} = h^i_{qs}$. Thus,

$$\dot{h}^i_{\mathrm{C}}(x, y, t) \equiv \frac{\partial}{\partial t} \int_{-\infty}^{\infty} dx_1\, g^i(x - x_1, y)\, c^i(x_1, t) = \int_{-\infty}^{\infty} dx_1\, g^i(x - x_1, y)\, \dot{c}^i(x_1, t) \tag{C.359}$$

for $i = a, b$. It should also be noted that h is not taken to depend on the velocities $\dot{c}^i$. For this reason, and because it saves some space, we do not single out the contributions $h = h^a + h^b$ inside the square brackets of Eq. (C.359) until right at the end. This point will be further discussed later on in Sect. C.16. Next, we isolate terms depending on $\dot{c}^a$ into a functional of their own which we call:

$$\begin{aligned} R^a_{1D}[\,\dot{c}^a, \dot{c}^b\,] \equiv \frac{2}{M} \int dA_1 \int dt_1 \int dA_2 \int dt_2\ \delta_{t_1|t_2} \Big\{ & \\ \dot{h}^a_{\mathrm{C}}(1, t_1)\, G^{\mathrm{H}_0}_{3D}(1;2)\, \dot{h}^a_{\mathrm{C}}(2, t_2) + 2\dot{h}^a_{\mathrm{C}}(1, t_1)\, G^{\mathrm{H}_0}_{3D}(1;2)\, \dot{h}^b_{\mathrm{C}}(2, t_2) & \\ + 2\dot{h}^a_{\mathrm{C}}(1, t_1) \Big[\partial_{z_1} G^{\mathrm{H}_0}_{3D}(1;2) h_{\mathrm{C}}(1, t_1) + \partial_{z_2} G^{\mathrm{H}_0}_{3D}(1;2) h_{\mathrm{C}}(2, t_2)\Big]\, \dot{\mathrm{H}}_0(2, t_2) \Big\}. & \end{aligned} \tag{C.360}$$

Next, we substitute Eq. (C.359) into the previous equation and take functional differentials of the terms $\dot{h}^a$ with respect to $\dot{c}^a$ to produce the contact line equation for c^a:

$$\begin{aligned} \frac{\delta R^a_{1D}[\,\dot{c}^a, \dot{c}^b\,]}{\delta \dot{c}^a(x, t)} \equiv \frac{2}{M} \int dA_1 \int dt_1 \int dA_2 \int dt_2\ \delta_{t_1|t_2} \Big\{ & \\ \int dx_1'\, g^a(x_1 - x_1', y_1)\, \delta_{x|x_1'} \delta_{t|t_1}\, G^{\mathrm{H}_0}_{3D}(1;2) \int dx_2'\, g^a(x_2 - x_2', y_2)\, \dot{c}^a(x_2', t_2) & \\ + \int dx_1'\, g^a(x_1 - x_1', y_1)\, \dot{c}^a(x_1', t_1)\, G^{\mathrm{H}_0}_{3D}(1;2) \int dx_2'\, g^a(x_2 - x_2', y_2)\, \delta_{x|x_2'} \delta_{t|t_2} & \\ + 2 \int dx_1'\, g^a(x_1 - x_1', y_1)\, \delta_{x|x_1'} \delta_{t|t_1}\, G^{\mathrm{H}_0}_{3D}(1;2) \int dx_2'\, g^b(x_2 - x_2', y_2)\, \dot{c}^b(x_2', t_2) & \\ + 2 \int dx_1'\, g^a(x_1 - x_1', y_1)\, \delta_{x|x_1'} \delta_{t|t_1} \Big[\partial_{z_1} G^{\mathrm{H}_0}_{3D}\, h_{\mathrm{C}}(1, t_1) + \partial_{z_2} G^{\mathrm{H}_0}_{3D}\, h_{\mathrm{C}}(2, t_2)\Big]\, \dot{\mathrm{H}}_0(2, t_2) \Big\}. & \end{aligned} \tag{C.361}$$

The arguments of the Green's functions in brackets on the last line are $\partial_{z_i} G^{\mathrm{H}_0}_{3D} = \partial_{z_i} G^{\mathrm{H}_0}_{3D}(1;2)$, for $i = 1, 2$. Next, we perform the integrals associated with the delta functions. The symmetry of the Green's functions shows that the expressions in the first two terms are the same and can be combined. Eq. (C.361) reduces to

$$\begin{aligned} \frac{\delta R^a_{1D}[\,\dot{c}^a, \dot{c}^b\,]}{\delta \dot{c}^a(x, t)} \equiv \frac{4}{M} \int dx_1 \int dx_2 \int dy_1 \int dy_2 \Big\{ & \\ g^a(x_1 - x, y_1)\, G_{3D}(x_1, y_1, \mathrm{H}_0(y_1, t); x_2, y_2, \mathrm{H}_0(y_2, t)) \int dx_2'\, g^a(x_2 - x_2', y_2)\, \dot{c}^a(x_2', t) & \\ + g^a(x_1 - x, y_1)\, G_{3D}(x_1, y_1, \mathrm{H}_0(y_1, t); x_2, y_2, \mathrm{H}_0(y_2, t)) \int dx_2'\, g^b(x_2 - x_2', y_2)\, \dot{c}^b(x_2', t_2) & \\ + \ g^a(x_1 - x, y_1) \Big[\partial_{z_1} G_{3D}(x_1, y_1, z_1; x_2, y_2, \mathrm{H}_0(y_2, t))|_{\mathrm{H}_0}\, h_{\mathrm{C}}(x_1, y_1, t) & \\ + \ \partial_{z_2} G_{3D}(x_1, y_1, \mathrm{H}_0(y_1, t); x_2, y_2, z_2))|_{\mathrm{H}_0}\, h_{\mathrm{C}}(x_2, y_2, t)\Big]\, \dot{\mathrm{H}}_0(y_2, t_2) \Big\}. & \end{aligned} \tag{C.362}$$

The substitution symbols in the previous equation are to be interpreted as $\partial_{z_1} G_{3D}|_{\mathrm{H}_0} \equiv \partial_{z_1} G_{3D}|_{\mathrm{H}_0(y_1,t)}$ and $\partial_{z_2} G_{3D}|_{\mathrm{H}_0} \equiv \partial_{z_2} G_{3D}|_{\mathrm{H}_0(y_2,t)}$. This completes the derivation of the left hand side of the equation of motion of the contact line in real space.

Let us now move on to derive the right hand side, too. The free energy functional of the fluctuations, $F^r_{2D}[h^a, h^b]$, is given in Eq. (C.125). We first simplify the functional by removing some integrals:

$$
\begin{aligned}
F^r_{2D}[h] = \frac{1}{2} \int dA_1 \int dt_1 \int dA_2 \int dt_2 \; h(1,t_1) \Big[& -\sigma\, \delta_{t_1|t_2} (\partial^2_{x_1} \delta_{x_1|x_2}) \delta_{y_1|y_2} \\
& -\sigma\, \delta_{t_1|t_2} \delta_{x_1|x_2} (\partial^2_{y_1} \delta_{y_1|y_2}) \Big] h(2,t_2) \;, \qquad \text{(C.363)}
\end{aligned}
$$

Delta functions $\delta_{t_1|t_2}$ serve just to make the kernel symmetric, and they can be integrated out right away. Assuming that $h(x,y,t)$ dies off at $x = \pm\infty$, we can transfer the derivative of the delta function into derivative of the meniscus without any surface terms arising from partial integration. Since the domain is restricted in y-direction, we have to be more careful:

$$
\begin{aligned}
\int_0^L dy_1 \int_0^L dy_2 \, h(x_1,y_1) (\partial^2_{y_1} \delta_{y_1|y_2}) h(x_2,y_2) \;&=\; \int_0^L dy_1 \int_0^L dy_2 \, \partial_{y_1} h(x_1,y_1)\, \delta_{y_1|y_2} \partial_{y_2} h(x_2,y_2) \\
&+\; \textit{boundary terms} \qquad \text{(C.364)}
\end{aligned}
$$

Time arguments were dropped for simplicity. The boundary terms will be functions of c_0 and therefore irrelevant when taking variations with respect to the contact line fluctuations c^a or c^b. Therefore, we are left with

$$
\begin{aligned}
F^r_{2D}[h] \;&=\; \int dA_1 \int dA_2 \int dt_1 \Big[\partial_{x_1} h(x_1,y_1,t_1)\, \delta_{x_1|x_2} \delta_{y_1|y_2}\, \partial_{x_2} h(x_2,y_2,t_1) \qquad \text{(C.365)} \\
&+\; \partial_{y_1} h(x_1,y_1,t_1)\, \delta_{x_1|x_2} \delta_{y_1|y_2}\, \partial_{y_2} h(x_2,y_2,t_1) \Big] \\
&=\; \int dx_1 \int dy_1 \int dt \; \Big[(\partial_{x_1} h(x_1,y_1,t_1))^2 + (\partial_{y_1} h(x_1,y_1,t_1))^2 \Big] \qquad \text{(C.366)}
\end{aligned}
$$

Following the same recipe as for the Rayleigh dissipation functional, we substitute $h_{\mathrm{C}} = h^a_{\mathrm{C}} + h^b_{\mathrm{C}}$. Again, the subscript C refers to the fact that h is a function of the contact line profile, given by Eq. (C.357). Thus,

$$
F^r_{1D}[c^a, c^b] \equiv \int dx_1 \int dy_1 \int dt_1 \; \Big\{ (\partial_{x_1} [h^a_{\mathrm{C}}(1,t_1) + h^b_{\mathrm{C}}(1,t_1)])^2 + (\partial_{y_1} [h^a_{\mathrm{C}}(1,t_1) + h^b_{\mathrm{C}}(1,t_1)])^2 \Big\} \tag{C.367}
$$

When taking functional derivative with respect to c^a we can ignore those parts of the functional which depend solely on c^b. Therefore, we define a reduced free energy functional:

$$
F^a_{1D}[c^a, c^b] \equiv \int dx_1 \int dy_1 \int dt_1 \; \Big\{ |\nabla h^a_{\mathrm{C}}(1,t_1)|^2 + 2 \nabla h^a_{\mathrm{C}}(1,t_1) \nabla h^b_{\mathrm{C}}(1,t_1) \Big\} \;, \tag{C.368}
$$

where $\nabla \equiv \mathbf{e}_x \partial_x + \mathbf{e}_y \partial_y$ is the two dimensional gradient operator. After setting $h^i_{\mathrm{C}} = h^i_{qs}$ and expressing h_{qs} in terms of c^i according to Eq. (C.357), the variation with respect to c^a gives

$$
-\frac{\delta F^a_{1D}[c^a, c^b]}{\delta c^a(x,t)} = -\int dA_1 \int dt_1 \Big\{ \tag{C.369}
$$

$$
2 \int dx'_1 \, \partial_{x_1} g^a(x_1 - x'_1, y_1)\, \delta_{x|x'_1} \delta_{t|t_1} \int dx''_1 \, \partial_{x_1} g^a(x_1 - x''_1, y_1)\, c^a(x''_1, t_1)
$$

$$\begin{aligned}
&+2\int dx'_1\,\partial_{y_1}g^a(x_1-x'_1,y_1)\,\delta_{x|x'_1}\delta_{t|t_1}\int dx''_1\,\partial_{y_1}g^a(x_1-x''_1,y_1)\,c^a(x''_1,t_1)\\
&+2\int dx'_1\,\partial_{x_1}g^a(x_1-x'_1,y_1)\,\delta_{x|x'_1}\delta_{t|t_1}\int dx''_1\,\partial_{x_1}g^b(x_1-x''_1,y_1)\,c^b(x''_1,t_1)\\
&+2\int dx'_1\,\partial_{y_1}g^a(x_1-x'_1,y_1)\,\delta_{x|x'_1}\delta_{t|t_1}\int dx''_1\,\partial_{y_1}g^b(x_1-x''_1,y_1)\,c^b(x''_1,t_1)\Big\}
\end{aligned}$$

The factor of two on the first two lines is due to the fact that c^a appears twice in the expression $|\nabla h^a_{\mathrm{C}}|^2=(\partial_{x_1}h^a_{\mathrm{C}})^2+(\partial_{y_1}h^a_{\mathrm{C}})^2$. On the last two lines it derives from the expression $2\nabla h^a_{\mathrm{C}}\nabla h^b_{\mathrm{C}}$. Removal of delta functions and regrouping gives

$$\begin{aligned}
-\frac{\delta F^a_{1D}[c^a,c^b]}{\delta c^a(x,t)} = -2\int dy_1\Big\{&\int dx_1\,\partial_{x_1}g^a(x_1-x,y_1)\int dx''_1\,\partial_{x_1}g^a(x_1-x''_1,y_1)\,c^a(x''_1,t)\\
+&\int dx_1\,\partial_{y_1}g^a(x_1-x,y_1)\int dx''_1\,\partial_{y_1}g^a(x_1-x''_1,y_1)\,c^a(x''_1,t)\\
+&\int dx_1\,\partial_{x_1}g^a(x_1-x,y_1)\int dx''_1\,\partial_{x_1}g^b(x_1-x''_1,y_1)\,c^b(x''_1,t)\\
+&\int dx_1\,\partial_{y_1}g^a(x_1-x,y_1)\int dx''_1\,\partial_{y_1}g^b(x_1-x''_1,y_1)\,c^b(x''_1,t)\Big\}\,.
\end{aligned}\tag{C.370}$$

Together with Eq. (C.362) the previous equation constitutes the real space equation of motion of the contact line fluctuations.

C.14 Fourier components of contact line fluctuations

The equation of motion for the fluctuations derived in the previous section will be simplified below by performing a spatial Fourier transformation and by integrating out the dependence on the y-coordinate. Processing the left hand side of the equation,

$$\mathcal{F}_{x/k_x}\left\{\frac{\delta R^a_{1D}[\dot c^a,\dot c^b]}{\delta\dot c^a(x,t)}\right\}=\mathcal{F}_{x/k_x}\left\{-\frac{\delta F^a_{1D}[\,c^a,c^b\,]}{\delta c^a(x,t)}\right\},\tag{C.371}$$

with the Rayleigh dissipation functional will take considerably more effort than transforming the free energy. Thus, let us begin simplification of expression (C.362). We write

$$\mathcal{F}_{x/k_x}\left\{\frac{\delta R^a_{1D}[\dot c^a,\dot c^b]}{\delta\dot c^a(x,t)}\right\}=\mathcal{F}_{x/k_x}\{I'_B\}+\mathcal{F}_{x/k_x}\{I'_C\}+\mathcal{F}_{x/k_x}\{I'_D\}\ ,\tag{C.372}$$

where the different terms on the right hand side can be immediately read off from Eq. (C.362). The time derivative terms (which are dependent on $\dot c^a$ or $\dot c^b$) contribute to I'_D, the rest are grouped into I'_B and I'_C.

$$\begin{aligned}
\mathcal{F}_{x/k_x}\{I'_B\}&\equiv\mathcal{F}_{x/k_x}\Big\{\int dA_1\int dA_2\,g^a(x-x_1,y_1)\,h_{\mathrm{C}}(x_1,y_1,t)\,\partial_{z_1}G_{3D}(1;2;t)\,\partial_t\mathrm{H}_0(y_2,t)\Big\}\\
&=\int_0^L dy_1\int_0^L dy_2\Big\{\ g^a(k_x,y_1)\left(g^a(k_x,y_1)c^a(k_x,t)+g^b(k_x,y_1)c^b(k_x,t)\right)\\
&\qquad\times\int dx_2\,\partial_{z_1}G_{3D}(1;2;t)\,\partial_t\mathrm{H}_0(y_2,t)\Big\}
\end{aligned}\tag{C.373}$$

where $\partial_{z_1} G_{3D}(1;2;t) \equiv \partial_{z_1} G_{3D}(x_1, y_1, z_1; x_2, y_2, \mathrm{H}_0(y_2,t))|_{\mathrm{H}_0(y_1,t)}$. It should be noted that $\int dx_2\, \partial_{z_1} G_{3D}(1;2;t)$ is not a function of x_1 because G_{3D} is translationally invariant object in the x-direction.

$$\begin{aligned}
\mathcal{F}_{x/k_x}\{I'_C\} &\equiv \mathcal{F}_{x/k_x}\left\{\int dA_1 \int dA_2\, g^a(x-x_1,y_1)\, \partial_{z_2} G_{3D}(1;2;t)\, h_{\mathrm{C}}(x_2,y_2,t)\, \partial_t \mathrm{H}_0(y_2,t)\right\} \\
&= \int_0^L dy_1 \int_0^L dy_2 \Bigg\{\; g^a(k_x,y_1)\, \mathcal{F}_{x_1/k_x}\Big\{\partial_{z_2} G_{3D}(1;2;t)\Big\} \\
&\qquad \times \Big(g^a(k_x,y_2) c^a(k_x,t) + g^b(k_x,y_2) c^b(k_x,t)\Big)\, \partial_t \mathrm{H}_0(y_2,t) \;\Bigg\}. \qquad \text{(C.374)}
\end{aligned}$$

The short-hand notation $\partial_{z_2} G_{3D}(1;2;t) \partial_{z_2} G_{3D}(x_1, y_1, \mathrm{H}_0(y_1,t); x_2, y_2, z_2)|_{\mathrm{H}_0(y_2,t)}$. In contrast to I'_B, there is a true convolution between $h_{\mathrm{C}}(2,t)$ and the derivative of the Green's function $\partial_{z_2} G_{3D}(1;2;t)$.

$$\begin{aligned}
\mathcal{F}_{x/k_x}\{I'_D\} &\equiv \mathcal{F}_{x/k_x}\left\{\int dA_1 \int dA_2\, g^a(x-x_1,y_1)\, G_{3D}(1;2;t)\, \partial_t h_{\mathrm{C}}(x_2,y_2,t)\right\} \\
&= \int_0^L dy_1 \int_0^L dy_2 \Bigg\{\; g^a(k_x,y_1)\, \mathcal{F}_{x_1/k_x}\Big\{G_{3D}(1;2;t)\Big\} \\
&\qquad \times \Big(g^a(k_x,y_2) \partial_t c^a(k_x,t) + g^b(k_x,y_2) \partial_t c^b(k_x,t)\Big) \;\Bigg\}. \qquad \text{(C.375)}
\end{aligned}$$

We have denoted $G_{3D}(1;2;t) \equiv G_{3D}(x_1, y_1, \mathrm{H}_0(y_1,t); x_2, y_2, \mathrm{H}_0(y_2,t))$. Having now Fourier transformed the left hand side of the contact line equation of motion we proceed to perform the integrals over y_1 and y_2. For this purpose we present the Fourier transforms of the quasi-stationary kernels

$$g^a(k_x,y_1) = \frac{\sinh(|k_x|(L-y_1))}{\sinh(|k_x|L)} \quad ; \quad g^b(k_x,y_1) = \frac{\sinh(|k_x|y_1)}{\sinh(|k_x|L)}\,. \qquad \text{(C.376)}$$

It should be kept in mind that due to the fact that the contact line equation should be Fourier transformed only in variable x (y_1 and y_2 being integrated over), the contact line equation of motion can be obtained for *arbitrary* $\mathrm{H}_0(y,t)$: we do not need to use the approximation $\mathrm{H}_0(y,t) \approx \mathrm{C}_0(t)$ which was needed to make the left hand side of the meniscus equation of motion both Fourier transformable and all the terms (I_B, I_C and I_D) of the same order in expansion parameter ϵ. However, since the solution of the meniscus equation is needed to produce the equation of motion of the contact line, it is consistent to keep on using the same approximation $\mathrm{H}_0(y,t) \approx \mathrm{C}_0(t)$ also here.

The treatment of all the terms $\mathcal{F}_{x/k_x} I'_s$, $s = B, C, D$, will be similar to each other. For clarity we consider them in separate subsections below. To summarize before going into the actual calculations, the left hand side of the contact line equation of motion for double wall set-up takes the following form:

$$\begin{aligned}
\mathcal{F}_{x/k_x}\left\{\frac{\delta R^a_{1D}[\dot{c}^a,\dot{c}^b]}{\delta \dot{c}^a(x,t)}\right\} &= \mathcal{F}_{x/k_x}\{I'_B\} + \mathcal{F}_{x/k_x}\{I'_C\} + \mathcal{F}_{x/k_x}\{I'_D\} \\
&= \Big(p^a_B\, c^a + p^b_B\, c^b\Big) + \Big(p^a_C\, c^a + p^b_C\, c^b\Big) + \Big(p^a_D\, \partial_t c^a + p^b_D\, \partial_t c^b\Big)\,, \qquad \text{(C.377)}
\end{aligned}$$

where the explicit representations of the coefficient functions $p^{a,b}_s$ ($s = B, C, D$) will be derived in the following sections.

C.14.1 Term I'_B

To avoid overly lengthy expressions we will consider separately the two contributions coming from contact line profiles a and b:

$$\mathcal{F}_{x/k_x}\left\{I'_B\right\} = p^a_B(k_x,t)c^a(k_x,t) + p^b_B(k_x,t)c^b(k_x,t)\ , \tag{C.378}$$

where we have defined the coefficient functions

$$p^a_B(k_x,t) \equiv \int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)g^a(k_x,y_1) \int_{-\infty}^{\infty} dx_2\, \partial_{z_1} G_{3D}(1;2;t)\, \partial_t \mathrm{H}_0(y_2,t)\ ; \tag{C.379}$$

$$p^b_B(k_x,t) \equiv \int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)g^b(k_x,y_1) \int_{-\infty}^{\infty} dx_2\, \partial_{z_1} G_{3D}(1;2;t)\, \partial_t \mathrm{H}_0(y_2,t)\ . \tag{C.380}$$

Since the Green's function $G_{3D} = (1/L)G^I_{2D} + G^S_{3D}$ can be further split in two, corresponding to the zeroeth order Fourier mode and the sum over the nonzero modes due to the finite wall separation in the y-direction, we can further subdivide the coefficient functions p^a_B and p^b_B accordingly. The definition of the Green's function leads to

$$\begin{aligned}
\partial_{z_1} G^{2W}_{3D}(x_1,y_1,z_1;x_2,y_2,\mathrm{C}_0)|_{\mathrm{C}_0} &= \frac{1}{L}\partial_{z_1} G^I_{2D}(x_1,z_1;x_2,\mathrm{C}_0)|_{\mathrm{C}_0} && \text{(C.381)}\\
&\quad -\frac{2}{L}\sum_{n=1}^{\infty} \cos(n\pi y_1/L)\cos(n\pi y_2/L)\, \partial_{z_1}\tilde{f}_n(x_1-x_2,z_1)|_{2\mathrm{C}_0} \\
&= \frac{1}{L}J_{B1}(x_1-x_2,\mathrm{C}_0) + \frac{2}{L}\sum_{n=1}^{\infty}\cos(n\pi y_1/L)\cos(n\pi y_2/L)\, J_{B2}(x_1-x_2,n,\mathrm{C}_0)\ . && \text{(C.382)}
\end{aligned}$$

We have dropped out the y-dependence of H_0 and approximated $\mathrm{H}_0 \approx \mathrm{C}_0$. The definitions of J_{B1} and J_{B2} have been given in Eq. (C.256). Substitution of the previous equation into the definition of p^a_B (Eq. (C.379)) gives rise to the following terms:

$$p^a_B(k_x,t) = p^{aI}_B(k_x,t) + p^{aS}_B(k_x,t)\ , \tag{C.383}$$

where the superscripts I and S refer to the contribution of the $n=0$ term of the sum over Fourier components in y-direction and S contains the sum over all non-zero components. Specifically,

$$p^{aI}_B(k_x,t) \equiv \frac{1}{L}\int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)g^a(k_x,y_1) \int_{-\infty}^{\infty} dx_2\, J_{B1}(x_2,\mathrm{C}_0)\partial_t \mathrm{C}_0\ , \tag{C.384}$$

where we have removed the dummy argument x_1 from the integral over x_2 by shifting the origin.

$$\begin{aligned}
p^{aS}_B(k_x,t) \equiv \frac{2}{L}\int_0^L dy_1 \int_0^L dy_2 \Bigg\{ & g^a(k_x,y_1)g^a(k_x,y_1) && \text{(C.385)}\\
\times \int_{-\infty}^{\infty} dx_2 & \sum_{n=1}^{\infty}\cos\!\left(\frac{n\pi y_1}{L}\right)\cos\!\left(\frac{n\pi y_2}{L}\right) J_{B2}(x_2,n,\mathrm{C}_0)\,\partial_t \mathrm{C}_0 \Bigg\}\ .
\end{aligned}$$

Again, the dummy variable x_1 vanishes by shifting the origin of x_2. Because the integral $\int_0^L dy_2\, \cos(n\pi y_2/L) = 0$, we get that $p^{aS}_B(k_x,t) = 0$ in the current approximation. For p^{aI}_B we get

$$
\begin{aligned}
p_B^{aI}(k_x,t) &= \partial_t \mathrm{c}_0 \frac{1}{L}\int_0^L dy_1\, g^a(k_x,y_1) g^a(k_x,y_1) \int_0^L dy_2 \int_{-\infty}^{\infty} dx_2\, J_{B1}(x_2,\mathrm{c}_0) && \text{(C.386)}\\
&= \frac{1}{2}\partial_t \mathrm{c}_0 \int_0^L dy_1\, g^a(k_x,y_1) g^a(k_x,y_1)\ , && \text{(C.387)}
\end{aligned}
$$

The second equality above follows from the fact that $\int_{-\infty}^{\infty} dx_2 J_{B1}(x_2,\mathrm{c}_0) = 1/2$. Performing the integral over y_1 yields

$$
p_B^{aI}(k_x,t) = \frac{1}{2}\partial_t \mathrm{c}_0 \frac{\sinh(2|k_x|L) - 2|k_x|L}{4|k_x|\sinh^2(|k_x|L)}\ . \tag{C.388}
$$

In the limit $L \to \infty$ the expression simplifies, $p_B^{aI} \to \partial_t \mathrm{c}_0/(4|k_x|)$. There is also another limit which has physical relevance and yields an expression for p_B^{aI} which does not diverge for $k_x \to 0$. Keeping L finite but letting $|k_x|L$ approach zero, we get $p_B^{aI} \to L\partial_t \mathrm{c}_0/3$.

The results for the contact line profile c^b will be derived similarily. The main difference as can be seen by comparing Eq. (C.379) with Eq. (C.380) is that one of the two Green's function g^a present is replaced with g^b. Therefore, we can immediately write down the terms in the decomposition $p_B^b = p_B^{bI} + p_B^{bS}$, where

$$
p_B^{bI}(k_x,t) \equiv \frac{1}{L}\int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1) g^b(k_x,y_1) \int_{-\infty}^{\infty} dx_2\, J_{B1}(x_2,\mathrm{c}_0)\partial_t \mathrm{c}_0\ , \tag{C.389}
$$

where the dummy argument x_1 from the integral over x_2 has been removed. The second term of the decomposition,

$$
\begin{aligned}
p_B^{bS}(k_x,t) \equiv \frac{2}{L}\int_0^L dy_1 \int_0^L dy_2 \Big\{ & g^a(k_x,y_1) g^b(k_x,y_1) && \text{(C.390)}\\
\times \int_{-\infty}^{\infty} dx_2 \sum_{n=1}^{\infty} & \cos\Big(\frac{n\pi y_1}{L}\Big)\cos\Big(\frac{n\pi y_2}{L}\Big) J_{B2}(x_2,n,\mathrm{c}_0)\,\partial_t \mathrm{c}_0 \Big\} = 0\ ,
\end{aligned}
$$

For the same reason $p_B^{aS}(k_x,t) = 0$. The evaluation of p_B^{bI} is equally easy as it was for p_B^{aI}, the integrals of the hyperbolic argument functions are easy to perform. The result is

$$
p_B^{bI}(k_x,t) = \frac{1}{2}\partial_t \mathrm{c}_0 \int_0^L dy_1\, g^a(k_x,y_1) g^b(k_x,y_1) = \frac{1}{2}\partial_t \mathrm{c}_0 \frac{L|k_x|\cosh(|k_x|L) - \sinh(|k_x|L)}{2|k_x|\sinh^2(|k_x|L)}\ . \tag{C.391}
$$

In the limit $L \to \infty$ corresponding to single wall set-up, $p_B^{bI} \to 0$ exponentially fast. In the other limit $|k_x|L \to 0$, $p_B^{bI} \to L\partial_t \mathrm{c}_0/24$.

C.14.2 Term I'_C

The decomposition of the Fourier transform of I'_C follows the same lines as that of I'_B. Separation of the two contact line profiles yields

$$
\mathcal{F}_{x/k_x}\left\{I'_C\right\} = p_C^a(k_x,t)c^a(k_x,t) + p_C^b(k_x,t)c^b(k_x,t)\ , \tag{C.392}
$$

where we have defined the coefficient functions

$$p_C^a(k_x,t) \equiv \int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)\mathcal{F}_{x_1/k_x}\{\partial_{z_2}G_{3D}(1;2;t)\}\, g^a(k_x,y_2)\,\partial_t \mathrm{H}_0(y_2,t)\ ; \quad \text{(C.393)}$$

$$p_C^b(k_x,t) \equiv \int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)\mathcal{F}_{x_1/k_x}\{\partial_{z_2}G_{3D}(1;2;t)\}\, g^b(k_x,y_2)\,\partial_t \mathrm{H}_0(y_2,t)\ ; \quad \text{(C.394)}$$

The only difference in Eq. (C.393) and Eq. (C.394) is that in the former there are two Green's functions of type g^a whereas in the latter one of the Green's functions has changed to g^b.

In the approximation we are using, $\mathrm{H}_0 \approx \mathrm{C}_0$, the derivatives of G_{3D} evaluated at the linearization point are the same: $\partial_{z_1}G_{3D}(1;2;t) = \partial_{z_2}G_{3D}(1;2;t)$ where the short-hand symbols were defined in the beginning of Sect. C.14. Therefore, when writing

$$\partial_{z_2}G_{3D}^{2W}(x_1,y_1,\mathrm{C}_0;x_2,y_2,z_2)|_{\mathrm{C}_0} = \frac{1}{L}\partial_{z_2}G_{2D}^{I}(x_1,\mathrm{C}_0;x_2,z_2)|_{\mathrm{C}_0} \quad \text{(C.395)}$$

$$-\frac{2}{L}\sum_{n=1}^{\infty}\cos(n\pi y_1/L)\cos(n\pi y_2/L)\,\partial_{z_2}\tilde{f}_n(x_1-x_2,z_2)|_{2\mathrm{C}_0}$$

$$= \frac{1}{L}J_{C1}(x_1-x_2,\mathrm{C}_0) + \frac{2}{L}\sum_{n=1}^{\infty}\cos(n\pi y_1/L)\cos(n\pi y_2/L)\,J_{C2}(x_1-x_2,n,\mathrm{C}_0)\ , \quad \text{(C.396)}$$

analogously to Eq. (C.382), we have to keep in mind that $J_{B1} = J_{C1}$ and $J_{B2} = J_{C2}$ in this approximation (see Sect. C.10.3). We shall continue using different symbols for these coefficient functions to sustain certain degree of symmetry in the notation. Separation of $\partial_{z_2}G_{3D}$ into two parts gives rise to

$$p_C^a(k_x,t) = p_C^{aI}(k_x,t) + p_C^{aS}(k_x,t)\ . \quad \text{(C.397)}$$

The resulting expressions for p_C^{aI} and p_C^{aS} are a bit more complicated than their counterparts p_B^{aI} and p_B^{aS} because the integration over x_2 is part of the convolution integral.

$$p_C^{aI}(k_x,t) \equiv \frac{1}{L}\int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)g^a(k_x,y_2)\mathcal{F}_{x_1/k_x}\{J_{C1}(x_1,\mathrm{C}_0)\}\,\partial_t \mathrm{C}_0\ . \quad \text{(C.398)}$$

It should be noted that the arguments of the two Green's functions g^a are different from each other. For p_C^{aS} we obtain

$$p_C^{aS}(k_x,t) \equiv \frac{2}{L}\int_0^L dy_1 \int_0^L dy_2 \left\{ g^a(k_x,y_1)g^a(k_x,y_2) \right. \quad \text{(C.399)}$$

$$\left. \times\ \mathcal{F}_{x_1/k_x}\left\{\sum_{n=1}^{\infty}\cos\left(\frac{n\pi y_1}{L}\right)\cos\left(\frac{n\pi y_2}{L}\right)J_{C2}(x_1,n,\mathrm{C}_0)\right\}\partial_t \mathrm{C}_0 \right\}\ .$$

This time the contribution to the Fourier series from the sum over the non-zero modes does not vanish because of the term $g^a(k_x,y_2)$. Let us start simplifying the previous equations.

$$p_C^{aI}(k_x,t) = \partial_t \mathrm{C}_0 \frac{1}{L}J_{C1}(k_x,\mathrm{C}_0)\int_0^L dy_1\, g^a(k_x,y_1)\int_0^L dy_2\, g^a(k_x,y_2)\ . \quad \text{(C.400)}$$

The Fourier transform of J_{C1} is easily obtained from the defining Eq. (C.267):

$$J_{C1}(k_x,\mathrm{C}_0) = \exp(-2|k_x|\mathrm{C}_0)/2\ . \quad \text{(C.401)}$$

It is easy to check that $\int_0^L dy_1\, g^a(k_x, y_1) = (\cosh(|k_x|L) - 1)/(|k_x|\sinh(|k_x|L))$. Combining this result with Eq. (C.401) we obtain

$$p_C^{aI}(k_x,t) = \frac{1}{2L}\partial_t \mathrm{C}_0\, e^{-2|k_x|\mathrm{C}_0}\left[\frac{\cosh(|k_x|L)-1}{|k_x|\sinh(|k_x|L)}\right]^2 . \tag{C.402}$$

Both limits $L \to \infty$ and $|k_x| \to 0$ are well defined just as they were for p_B^{aI}. Assuming that the Fourier transform and the integrals over y_1 and y_2 commute, Eq. (C.399) yields

$$p_C^{aS}(k_x,t) = \partial_t \mathrm{C}_0 \frac{2}{L}\sum_{n=1}^{\infty} J_{C2}(k_x,n,\mathrm{C}_0)\int_0^L dy_1\, g^a(k_x,y_1)\cos\left(\frac{n\pi y_1}{L}\right) \tag{C.403}$$

$$\times \int_0^L dy_2\, g^a(k_x,y_2)\cos\left(\frac{n\pi y_2}{L}\right) . \tag{C.404}$$

The Fourier transform of J_{C2} is given by Eq. (C.286). It remains to compute the value of the integral

$$\int_0^L dy_1\, g^a(k_x,y_1)\cos\left(\frac{n\pi y_1}{L}\right) = \frac{\cosh(|k_x L|) - \cos(n\pi)}{\sinh(|k_x|L)}\frac{|k_x|}{(n\pi/L)^2 + k_x^2} \equiv U(k_x,n,L) \ , \tag{C.405}$$

where we have defined a new function U. The integral over y_1 was done by using the exponential representation of sinh-function in Eq. (C.376) and the cosine term. In terms of U we can express

$$p_C^{aS}(k_x,t) = \partial_t \mathrm{C}_0 \frac{1}{L}\sum_{n=1}^{\infty} e^{-2\mathrm{C}_0\sqrt{k_x^2+(n\pi/L)^2}}\, U^2(k_x,n,L) \ . \tag{C.406}$$

For L going to infinity, only the latter fraction in the expression defining U will be important: $U \to |k_x|/(k_x^2 + (n\pi/L)^2)$ for large L.

Below we determine the expressions for $p_C^b = p_C^{bI} + p_C^{bS}$, where the only difference as compared to calculation of p_C^{aI} and p_C^{aS} is that the Green's function $g^a(k_x, y_2)$ is replaced by $g^b(k_x, y_2)$ which is readily seen by comparing the definitions (C.393) and (C.394). Thus,

$$p_C^{bI}(k_x,t) = \partial_t \mathrm{C}_0\, J_{C1}(k_x,t)\int_0^L dy_1\, g^a(k_x,y_1)\cos\left(\frac{n\pi y_1}{L}\right)\int_0^L dy_2\, g^b(k_x,y_2)\cos\left(\frac{n\pi y_2}{L}\right) \tag{C.407}$$

$$= \frac{1}{2L}\partial_t \mathrm{C}_0\, e^{-2|k_x|\mathrm{C}_0}\left[\frac{\cosh(|k_x|L)-1}{|k_x|\sinh(|k_x|L)}\right]^2 . \tag{C.408}$$

The result is the same as for p_C^{aI} because $\int_0^L dy_2\, g^b(k_x,y_2) = \int_0^L dy_2\, g^a(k_x,y_2)$. Contribution from the non-zero modes is

$$p_C^{bS}(k_x,t) = \partial_t \mathrm{C}_0 \frac{2}{L}\sum_{n=1}^{\infty} J_{C2}(k_x,n,\mathrm{C}_0)\int_0^L dy_1\, g^a(k_x,y_1)\cos\left(\frac{n\pi y_1}{L}\right) \tag{C.409}$$

$$\times \int_0^L dy_2\, g^b(k_x,y_2)\cos\left(\frac{n\pi y_2}{L}\right) .$$

$$= \partial_t \mathrm{C}_0 \frac{1}{L}\sum_{n=1}^{\infty} e^{-2\mathrm{C}_0\sqrt{k_x^2+(n\pi/L)^2}}\cos(n\pi)\, U^2(k_x,n,L) \ , \tag{C.410}$$

where we used the fact that $\int_0^L dy_2\, g^b(k_x,y_2)\cos(n\pi y_2/L) = \cos(n\pi)U(k_x,n,L)$. When L approaches infinity, p_C^{bS} goes to zero. This is easily seen by noticing that

$$\sum_{n=1}^{\infty}(-1)^n f(n\Delta k_y)\,\Delta k_y = \sum_{n=0}^{\infty} f((2n+1)\Delta k_y)\,\Delta k_y - \sum_{n=1}^{\infty} f((2n)\Delta k_y)\,\Delta k_y \to 0 \qquad \text{(C.411)}$$

for $\Delta k_y \to 0$. In other words, in the continuum limit the sum of the alternating series presented in Eq. (C.410) approaches zero.

C.14.3 Term I'_D

The decomposition of the Fourier transform of I'_D is standard. Separation of the two contact line profiles yields

$$\mathcal{F}_{x/k_x}\left\{I'_D\right\} = p_D^a(k_x,t)\partial_t c^a(k_x,t) + p_D^b(k_x,t)\partial_t c^b(k_x,t)\ . \qquad \text{(C.412)}$$

Thanks to the similarity of the terms I'_D and I'_C, the coefficient functions are easily calculated based on the results of the previous section. We define

$$p_D^a(k_x,t) \equiv \int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)\mathcal{F}_{x_1/k_x}\{G_{3D}(1;2;t)\}\, g^a(k_x,y_2)\ ; \qquad \text{(C.413)}$$

$$p_D^b(k_x,t) \equiv \int_0^L dy_1 \int_0^L dy_2\, g^a(k_x,y_1)\mathcal{F}_{x_1/k_x}\{G_{3D}(1;2;t)\}\, g^b(k_x,y_2)\ ; \qquad \text{(C.414)}$$

The decomposition of the Green's function G_{3D} into the zero mode and non-zero mode contributions gives rise to the functions J_{D1} and J_{D2}, which in the current approximation $\mathrm{H}_0 \approx \mathrm{C}_0$ become

$$G_{3D}^{2W}(x_1,y_1,\mathrm{C}_0;x_2,y_2,\mathrm{C}_0) = \frac{1}{L}G_{2D}^{I}(x_1,\mathrm{C}_0;x_2,\mathrm{C}_0) \qquad \text{(C.415)}$$

$$-\frac{2}{L}\sum_{n=1}^{\infty}\cos(n\pi y_1/L)\cos(n\pi y_2/L)\left[\tilde{f}_n(x_1-x_2,0) - \tilde{f}_n(x_1-x_2,2\mathrm{C}_0)\right]$$

$$= \frac{1}{L}J_{D1}(x_1-x_2,\mathrm{C}_0) + \frac{2}{L}\sum_{n=1}^{\infty}\cos(n\pi y_1/L)\cos(n\pi y_2/L)\,J_{D2}(x_1-x_2,n,\mathrm{C}_0)\ , \qquad \text{(C.416)}$$

where J_{D1} and J_{D2} have been introduced in Sect. C.10.4. Separation of G_{3D} into two parts according to Eq. (C.416) gives rise to the zero mode contribution p_D^{aI} and non-zero mode contribution p_D^{aS}:

$$p_D^a(k_x,t) = p_D^{aI}(k_x,t) + p_D^{aS}(k_x,t)\ . \qquad \text{(C.417)}$$

Functions p_D^{aI} and p_D^{aS} can be obtained immediately now that we have knowledge of the behaviour of the terms I'_B and I'_C. Substitution of Eq. (C.416) into Eq. (C.413) gives for the zero mode term

$$p_D^{aI}(k_x,t) = \frac{1}{L}J_{D1}(k_x,\mathrm{C}_0)\int_0^L dy_1\, g^a(k_x,y_1)\int_0^L dy_1\, g^a(k_x,y_1) \qquad \text{(C.418)}$$

$$= \frac{1}{L}\frac{(1-e^{-2\mathrm{C}_0|k_x|})}{2|k_x|}\left[\frac{\cosh(|k_x|L)-1}{|k_x|\sinh(|k_x|L)}\right]^2 . \qquad \text{(C.419)}$$

The Fourier transform, $J_{D1}(k_x, \mathrm{c}_0)$ has been calculated in Sect. C.10.5. In the limit $L \to \infty$ the contribution from this term vanishes because of the factor $1/L$. For p_D^{aS} we obtain

$$\begin{aligned} p_D^{aS}(k_x, t) \equiv \frac{2}{L} \int_0^L dy_1 \int_0^L dy_2 \Big\{ g^a(k_x, y_1) g^a(k_x, y_2) \qquad\qquad (\mathrm{C}.420) \\ \times \mathcal{F}_{x_1/k_x} \Big\{ \sum_{n=1}^{\infty} \cos\Big(\frac{n\pi y_1}{L}\Big) \cos\Big(\frac{n\pi y_2}{L}\Big) J_{D2}(x_1, n, \mathrm{c}_0) \Big\} \Big\} \ . \end{aligned}$$

Interchanging the order of the Fourier transformation, and summation over n gives the following expression

$$p_D^{aS}(k_x, t) = \frac{2}{L} \sum_{n=1}^{\infty} J_{D2}(k_x, n, \mathrm{c}_0) \left[\int_0^L dy_1 \, g^a(k_x, y_1) \cos\Big(\frac{n\pi y_1}{L}\Big) \right]^2 . \qquad (\mathrm{C}.421)$$

The integral over y_1 (y_2) is familiar from previous sections and the $J_{D2}(k_x, n, \mathrm{c}_0)$ is given in Eq. (C.285). Plugging these into the previous equation gives

$$p_D^{aS}(k_x, t) = \frac{2}{L} \sum_{n=1}^{\infty} \frac{1 - e^{-2\mathrm{c}_0 \sqrt{k_x^2 + (n\pi/L)^2}}}{2\sqrt{k_x^2 + (n\pi/L)^2}} U^2(k_x, n, L) \ . \qquad (\mathrm{C}.422)$$

This term does not vanish in the limit of large L but gives something finite, which will be later on shown to be the single wall result.

The remaining expressions p_D^{bI} and p_D^{bS} appearing in the decomposition of the coefficient function $p_D^b = p_D^{bI} + p_D^{bI}$ are readily obtained since the corresponding expression of the contact line profile c^a are known:

$$\begin{aligned} p_D^{bI}(k_x, t) &= \frac{1}{L} J_{D1}(k_x, \mathrm{c}_0) \int_0^L dy_1 \, g^a(k_x, y_1) \int_0^L dy_2 \, g^b(k_x, y_1) \qquad (\mathrm{C}.423) \\ &= \frac{1}{L} \frac{(1 - e^{-2|k_x|\mathrm{c}_0})}{2|k_x|} \left[\frac{\cosh(|k_x|L) - 1}{|k_x| \sinh(|k_x|L)} \right]^2 . \qquad (\mathrm{C}.424) \end{aligned}$$

The only difference as compared to Eq. (C.418) is that in the latter integral g^a has changed to g^b. Due to the prefactor $1/L$ p_D^{bI} vanishes for large L unlike the term p_D^{bS} which reads

$$\begin{aligned} p_D^{bS}(k_x, t) &= \frac{2}{L} \sum_{n=1}^{\infty} J_{D2}(k_x, n, \mathrm{c}_0) \int_0^L dy_1 \, g^a(k_x, y_1) \cos\Big(\frac{n\pi y_1}{L}\Big) \qquad (\mathrm{C}.425) \\ &\quad \times \int_0^L dy_2 \, g^b(k_x, y_2) \cos\Big(\frac{n\pi y_2}{L}\Big) \\ &= \frac{2}{L} \sum_{n=1}^{\infty} \frac{1 - e^{-2\mathrm{c}_0 \sqrt{k_x^2 + (n\pi/L)^2}}}{2\sqrt{k_x^2 + (n\pi/L)^2}} \cos(n\pi) U^2(k_x, n, L) \ . \qquad (\mathrm{C}.426) \end{aligned}$$

The Fourier transformation and integrals over y_1 and y_2 were performed prior to the summation over n as in the case of p_D^{aS}. As expected, this term vanishes in the limit $L \to \infty$.

C.14.4 Single wall limit

Let us collect the results of the three previous sections. The Fourier transform of I'_B can be decomposed as $\mathcal{F}_{x/k_x}\{I'_B\} = p^a_B c^a + p^b_B c^b$, where $p^a_B = p^{aI}_B + p^{aS}_B$. The explicit representation of the coefficient functions is given below.

$$\begin{cases} p^{aI}_B(k_x,t) = \dfrac{1}{2}\partial_t \mathrm{C}_0 \dfrac{\sinh(2|k_x|L) - 2|k_x|L}{4|k_x|\sinh^2(|k_x|L)} \ ; \\ p^{aS}_B(k_x,t) = 0 \ . \end{cases} \tag{C.427}$$

$$\begin{cases} p^{bI}_B(k_x,t) = \dfrac{1}{2}\partial_t \mathrm{C}_0 \dfrac{L|k_x|\cosh(|k_x|L) - \sinh(|k_x|L)}{2|k_x|\sinh^2(|k_x|L)} \ ; \\ p^{bS}_B(k_x,t) = 0 \ . \end{cases} \tag{C.428}$$

The Fourier transform of I'_C can be decomposed as $\mathcal{F}_{x/k_x}\{I'_C\} = p^a_C c^a + p^b_C c^b$, where $p^a_C = p^{aI}_C + p^{aS}_C$. Explicitly,

$$\begin{cases} p^{aI}_C(k_x,t) = \partial_t \mathrm{C}_0 \dfrac{1}{2L} e^{-2\mathrm{C}_0|k_x|}\, U^2(k_x,0,L) \ ; \\ p^{aS}_C(k_x,t) = \partial_t \mathrm{C}_0 \dfrac{1}{L} \displaystyle\sum_{n=1}^{\infty} e^{-2\mathrm{C}_0\sqrt{k_x^2+(n\pi/L)^2}}\, U^2(k_x,n,L) \ . \end{cases} \tag{C.429}$$

$$\begin{cases} p^{bI}_C(k_x,t) = \partial_t \mathrm{C}_0 \dfrac{1}{2L} e^{-2\mathrm{C}_0|k_x|}\, U^2(k_x,0,L) \ ; \\ p^{bS}_C(k_x,t) = \partial_t \mathrm{C}_0 \dfrac{1}{L} \displaystyle\sum_{n=1}^{\infty} e^{-2\mathrm{C}_0\sqrt{k_x^2+(n\pi/L)^2}}\, \cos(n\pi)\, U^2(k_x,n,L) \ . \end{cases} \tag{C.430}$$

The Fourier transform of I'_D can be decomposed as $\mathcal{F}_{x/k_x}\{I'_D\} = p^a_D c^a + p^b_D c^b$, where $p^a_D = p^{aI}_D + p^{aS}_D$. Explicitly,

$$\begin{cases} p^{aI}_D(k_x,t) = \dfrac{1}{L}\dfrac{(1 - e^{-2\mathrm{C}_0|k_x|})}{2|k_x|}\, U^2(k_x,0,L) \ ; \\ p^{aS}_D(k_x,t) = \dfrac{2}{L}\displaystyle\sum_{n=1}^{\infty} \dfrac{(1 - e^{-2\mathrm{C}_0\sqrt{k_x^2+(n\pi/L)^2}})}{2\sqrt{k_x^2+(n\pi/L)^2}}\, U^2(k_x,n,L) \ . \end{cases} \tag{C.431}$$

$$\begin{cases} p^{bI}_D(k_x,t) = \dfrac{1}{L}\dfrac{(1 - e^{-2\mathrm{C}_0|k_x|})}{2|k_x|}\, U^2(k_x,0,L) \ ; \\ p^{bS}_D(k_x,t) = \dfrac{2}{L}\displaystyle\sum_{n=1}^{\infty} \dfrac{(1 - e^{-2\mathrm{C}_0\sqrt{k_x^2+(n\pi/L)^2}})}{2\sqrt{k_x^2+(n\pi/L)^2}}\, \cos(n\pi)\, U^2(k_x,n,L) \ . \end{cases} \tag{C.432}$$

Let us extract the scaling behaviour of the various functions above. For $|k_x|L \to 0$, $p^{aI}_B \to L\partial_t \mathrm{C}_0/3$. For $L \to \infty$, $p^{aI}_B \to \partial_t \mathrm{C}_0/(4|k_x|)$. The contact line of the other wall situated at $y = L$ does not contribute in the infinite wall separation limit. Therefore $p^{bI}_B \to 0$ for $L \to \infty$. In the opposite limit, $|k_x|L \to 0$ there is a finite contribution $p^{bI}_B \to \partial_t \mathrm{C}_0/24$. To study the behaviour of the coefficient functions originated from the Fourier transforms of terms I'_C and I'_D it suffices to study the limiting behaviour of the function U defined in Eq. (C.405). For infinite wall separation $L \to \infty$, $U(k_x,n,L) \to |k_x|/(k_x^2 + (n\pi/L)^2)$ and we can replace $(n\pi/L)$ with k_y. Obviously, $U(k_x,0,L) \to 1/|k_x|$ in this limit. When $|k_x|L \to 0$, $U(k_x,n,L) \to L(1 - \cos(n\pi))/(n\pi)^2$.

In the single wall limit, $L \to \infty$ all terms associated with the contact line profile c^b vanish, as they should. Terms p_C^{bI} and p_D^{bI} vanish being proportional to $1/L$. Terms p_C^{bS} and p_D^{bS} disappear because they contain summation over an alternating factor $\cos(n\pi)$ which renders the limit of the sum zero. From the coefficient functions associated with the contact line c^a only the terms p_B^{aI}, p_C^{aS} and p_D^{aS} survive for $L \to \infty$; terms p_C^{aI} and p_D^{aI} vanish because of their proportionality to $1/L$. Thus,

$$\mathcal{F}_{x/k_x}\{I'_B\} \longrightarrow \frac{1}{4|k_x|}\partial_t \mathrm{C}_0\, c^a(k_x,t) \ ; \tag{C.433}$$

$$\mathcal{F}_{x/k_x}\{I'_C\} \longrightarrow \partial_t \mathrm{C}_0 \frac{1}{\pi}\int_0^\infty dk_y\; e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}}\; \frac{k_x^2}{(k_x^2+k_y^2)^2}\, c^a(k_x,t) \ ; \tag{C.434}$$

$$\mathcal{F}_{x/k_x}\{I'_D\} \longrightarrow \frac{2}{\pi}\int_0^\infty dk_y\; \frac{(1-e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}})}{2\sqrt{k_x^2+k_y^2}}\; \frac{k_x^2}{(k_x^2+k_y^2)^2}\, \partial_t c^a(k_x,t) \ . \tag{C.435}$$

The summation has been replaced with integration, $(1/L)\sum_{n=1}^{\infty} \to (1/\pi)\int_0^\infty dk_y$ and the variable $n\pi/L$ has been replaced with k_y. The results of Eq. (C.433) – Eq. (C.435) should be compared with those presented in Sect. C.15

C.14.5 Restoring forces for double wall system

In this section we derive the right hand side of the contact line equation of motion. Eq. (C.370) contains the deterministic forces acting on the contact line c^a. The random contribution will be taken into account in the Sect. C.14.6. Fourier transformation gives

$$\begin{aligned} -M\mathcal{F}_{x/k}\Big\{\delta F_{1D}^a[c^a,c^b]\Big/\,\delta c^a(x,t)\Big\} = \qquad\qquad\qquad\qquad & \qquad\qquad\qquad \text{(C.436)}\\ -2M\int_0^L dy_1\,\Big\{\,(+\imath k)g^a(k,y_1)\,(-\imath k)g^a(k,y_1)\,c^a(k,t) + \partial_{y_1}g^a(k,y_1)\,\partial_{y_1}g^a(k,y_1)\,c^a(k,t) &\\ +\,(+\imath k)g^a(k,y_1)\,(-\imath k)g^b(k,y_1)\,c^b(k,t) + \partial_{y_1}g^a(k,y_1)\,\partial_{y_1}g^b(k,y_1)\,c^a(k,t)\Big\} & \end{aligned}$$

For shortness, we write k instead of k_x in this section. The signs of the factors in the expression $(\pm\imath k)$ appear because in the real space convolution product the argument of the first Green's function is $g^{a,b}(x_1-x,y_1)$ instead of $g^{a,b}(x-x_1,y_1)$, see Eq. (C.370). By grouping similar terms

$$-M\mathcal{F}_{x/k}\left\{\frac{\delta F_{1D}^a[c^a,c^b]}{\delta c^a(x,t)}\right\} = -2M\,\Big[\tilde{g}^a(k,t,L)\,c^a(k,t) + \tilde{g}^b(k,t,L)\,c^b(k,t)\Big] \tag{C.437}$$

The new coefficient functions $\tilde{g}^a$ and $\tilde{g}^a$ are expressed in terms of the Green's functions as

$$\tilde{g}^a(k,t,L) \equiv \int_0^L dy_1\,\Big(k^2 g^a(k,y_1)g^a(k,y_1) + \partial_{y_1}g^a(k,y_1)\partial_{y_1}g^a(k,y_1)\Big) \ ; \tag{C.438}$$

$$\tilde{g}^b(k,t,L) \equiv \int_0^L dy_1\,\Big(k^2 g^a(k,y_1)g^b(k,y_1) + \partial_{y_1}g^a(k,y_1)\partial_{y_1}g^b(k,y_1)\Big) \ . \tag{C.439}$$

Contributions to $\tilde{g}^a$ will be calculated first. Integrals can be decomposed to elementary ones by representing the integrands with the aid of exponential functions. Substitution of

Eq. (C.376) results in

$$\int_0^L dy_1\, k^2 g^a(k,y_1) g^a(k,y_1) \;=\; k^2\Big(\sinh(2|k|L) - 2|k|L\Big)\Big/\Big(4|k|\sinh^2(|k|L)\Big)\,; \quad \text{(C.440)}$$

$$\int_0^L dy_1\, \partial_{y_1} g^a(k,y_1)\partial_{y_1} g^a(k,y_1) \;=\; k^2\Big(\sinh(2|k|L) + 2|k|L\Big)\Big/\Big(4|k|\sinh^2(|k|L)\Big)\,. \quad \text{(C.441)}$$

Thus, we get $\tilde{g}^a = \sigma|k|\coth(|k|L)$. In the limit of infinite wall separation $\tilde{g}^a \to \sigma|k|$, which is the familiar single wall result of Ref. [355]. Performing the integrals of $\tilde{g}^b$ gives

$$\int_0^L dy_1\, k^2 g^a(k,y_1) g^b(k,y_1) \;=\; k^2\Big(L|k|\cosh(|k|L) - \sinh(|k|L)\Big)\Big/\Big(2|k|\sinh^2(|k|L)\Big)\,; \text{(C.442)}$$

$$\int_0^L dy_1\, \partial_{y_1} g^a(k,y_1)\partial_{y_1} g^a(k,y_1) = -k^2\Big(L|k|\cosh(|k|L) + \sinh(|k|L)\Big)\Big/\Big(2|k|\sinh^2(|k|L)\Big)\,. \text{(C.443)}$$

Combining the right hand sides of the previous equations yields $\tilde{g}^b = -|k|/\sinh(|k|L)$. Since the denominator goes like $e^{-|k|L}$ for large L, the coefficient function $\tilde{g}^b$ of the second wall vanishes for large separation as it should.

C.14.6 Two interacting contact lines

In the previous section we computed the deterministic forces acting on the line c^a. Inclusion of random contribution due to the fluctuating surface tensions of the walls gives rise to a stochastic force. The full free energy containing the random part has been presented in Sect. C.5.1. Variation with respect to c^a gives

$$\frac{\delta}{\delta c^a(x,t)} \int\limits_{-\infty}^{\infty} dt \int\limits_{-\infty}^{\infty} dx \int\limits_{0}^{\mathrm{C}^a(x,t)} dz\, \left(\sigma_{sl}(x,z) - \sigma_{sg}(x,z)\right) = A(x,0,\mathrm{c}_0(t) + c^a(x,t))\;, \qquad \text{(C.444)}$$

where we have defined $A(x,0,z) \equiv \sigma_{sl}(x,z) - \sigma_{sg}(x,z)$ to be the noise field evaluated at the wall. Notice that the other wall does not contribute since the variation of the last term in Eq. (C.86) with respect to c^a is zero. Denoting the Fourier transform

$$\mathcal{F}_{x/k}\{A(x,0,\mathrm{c}_0(t) + c^a(x,t))\} \equiv A_k(c^a)\;, \qquad \text{(C.445)}$$

we obtain the full equation of motion for the contact line c^a by setting the sum of the stochastic (Eq. (C.444)) and deterministic forces (Eq. (C.437)) equal to the Rayleigh terms (Eq. (C.377)):

$$\begin{aligned} & p_D^a(k,t)\,\partial_t c^a(k,t) + p_D^b(k,t)\,\partial_t c^b(k,t) \\ &+\, \Big(p_B^a(k,t) + p_C^a(k,t)\Big)\, c^a(k,t) + \Big(p_B^b(k,t) + p_C^b(k,t)\Big)\, c^b(k,t) \\ &= -(M/2)\tilde{g}^a(k,t,L)\, c^a(k,t) - (M/2)\tilde{g}^b(k,t,L)\, c^b(k,t) + (M/4)A_k(c^a)\;. \end{aligned} \qquad \text{(C.446)}$$

Naturally, there is also a similar equation for the contact line c^b. With Green's functions g^a and g^b defined in Eq. (C.376) the values of the integrals over y_1 stay the same even though we exchange g^a and g^b in the defining expressions. Therefore,

$$\begin{aligned} & p_D^a(k,t)\,\partial_t c^a(k,t) + p_D^b(k,t)\,\partial_t c^b(k,t) \\ &+\, \Big(p_B^a(k,t) + p_C^a(k,t)\Big)\, c^a(k,t) + \Big(p_B^b(k,t) + p_C^b(k,t)\Big)\, c^b(k,t) \\ &= -(M/2)\tilde{g}^a(k,t,L)\, c^a(k,t) - (M/2)\tilde{g}^b(k,t,L)\, c^b(k,t) + (M/4)A_k(c^b)\;. \end{aligned} \qquad \text{(C.447)}$$

Thus, the only difference between Eq. (C.446) and Eq. (C.447) is lies in the quenched noise term. This set of coupled equations is too difficult to solve for general purposes and therefore we will concentrate more effort in understanding the single wall, $L \to \infty$, limit. In this limit the equations decouple as explained in Sect. C.15.2.

C.15 Contact line dynamics: single wall

Let us first derive the term on the left hand side of the equation of motion of the contact line for the single wall set-up and compare the results with those of the double wall set-up in the limit of wall separation approaching infinity. Thanks to the formulation we are using, it is easy to change the physical set-up of the system we are modelling just by altering the form of the relevant Green's functions in the dissipation and free energy functionals. All we have to do now is to take Eq. (C.373) – Eq. (C.375) and replace G_{3D} with G_{3D}^{1W} and g^a with g^{1W} leaving out g^b which is irrelevant when focusing on contact line c^a. We define $\mathcal{F}_{x/k_x}\{I_B'\} \equiv p_B^{1W}(k_x,t)\, c(k_x,t)$, and

$$p_B^{1W}(k_x,t) \approx \int_0^\infty dy_1 \int_0^\infty dy_2\, G^{1W}(k_x,y_1)\, G^{1W}(k_x,y_1) \int_{-\infty}^\infty dx_2\, \partial_{z_1} G_{3D}^{1W}(1;2;t)\, \partial_t \textsc{c}_0 \ . \tag{C.448}$$

We have used the approximation $\textsc{h}_0 \approx \textsc{c}_0$. The contact line profile is denoted by $c(k_x,t)$. In terms of the kernel function i_B presented in Eq. (C.213) we can express

$$\partial_{z_1} G_{3D}^{1W}(1;2;t) = \left(i_B(x-x_1, y-y_1, t) + i_B(x-x_1, y+y_1, t)\right)/(4\pi) \ . \tag{C.449}$$

As explained in Sect. C.11.1, the quasi-stationary meniscus solution is related to the contact line profile through $h_{qs}(k_x,y_1,t) = \int dk_x\, e^{-\imath k_x x} e^{-|k_x| y_1} c(k_x,t)$, which leads to the identification $G^{1W}(k_x,y_1) = e^{-|k_x|y_1}$. Substitution of these results back into Eq. (C.448) gives

$$\begin{aligned} p_B^{1W}(k_x,t) &= \partial_t \textsc{c}_0 \int_0^\infty dy_1 \int_0^\infty dy_2\, e^{-2|k_x|y_1} \frac{1}{4\pi} \int_{-\infty}^\infty dx_2 \Big(i_B(x_2, y_1-y_2, t) \\ &\qquad + i_B(x_2, y_1+y_2, t)\Big) && \text{(C.450)} \\ &= \partial_t \textsc{c}_0 \frac{1}{4\pi} \int_{-\infty}^\infty dx_2 \int_0^\infty dy_2\, \cos(ky_2) \int_0^\infty dy_1\, e^{-2|k_x|y_1} \Big(i_B(x_2, y_1-y_2, t) \\ &\qquad + i_B(x_2, y_1+y_2, t)\Big)\Big|_{k=0} \ . && \text{(C.451)} \end{aligned}$$

The second equality follows from switching the order of the integrals and setting $k=0$ in the argument of the term $\cos(ky_2)$ which has been added to make the expression appear as the cosine transform of the convolution. Indeed, we can write

$$\begin{aligned} p_B^{1W} &= \partial_t \textsc{c}_0 \frac{1}{4\pi} \int_{-\infty}^\infty dx_2 \left\{ 2\int_0^\infty dy_2' \cos(ky_2')\, e^{-2|k_x|y_2'} \int_0^\infty dy_2\, \cos(ky_2)\, i_B(x_2,y_2,t) \right\}\Bigg|_{k=0} && \text{(C.452)} \\ &= 2\partial_t \textsc{c}_0 \frac{1}{4\pi} \int_{-\infty}^\infty dx_2\, \frac{1}{2|k_x|} \int_0^\infty dy_2\, i_B(x_2,y_2,t) = \frac{1}{4|k_x|} \partial_t \textsc{c}_0 \ . && \text{(C.453)} \end{aligned}$$

The integrals over x_2 and y_2 of i_B can be easily done in polar coordinates. We see that the final result is consistent with Eq. (C.433), which was derived for double wall set-up letting the separation of the walls to go to infinity.

The Fourier transform of the term I'_C in the single wall case defines a new coefficient function: $\mathcal{F}_{x/k_x}\{I'_C\} \equiv p_C^{1W}(k_x,t)\,c(k_x,t)$. Using the approximation $\mathrm{H}_0 \approx \mathrm{C}_0$ leads to

$$p_C^{1W}(k_x,t) \approx \int_0^\infty dy_1 \int_0^\infty dy_2\, G^{1W}(k_x,y_1)\, G^{1W}(k_x,y_2) \mathcal{F}_{x_1/k_x}\Big\{\partial_{z_2} G_{3D}^{1W}(1;2;t)\Big\}\, \partial_t \mathrm{C}_0 \ . \qquad \text{(C.454)}$$

The Fourier integral representation is found most convenient for manipulation of the expression $\partial_{z_2} G_{3D}^{1W}(1;2;t)$:

$$\begin{aligned}\mathcal{F}_{x_1/k_x}\Big\{\partial_{z_2} G_{3D}^{1W}(1;2;t)\Big\} = -\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z\, &\left(\frac{e^{-\imath k_y(y_1-y_2)} e^{-\imath k_z 2\mathrm{C}_0}\,(-\imath k_z)}{k_x^2+k_y^2+k_z^2}\right. \\ &+ \left.\frac{e^{-\imath k_y(y_1+y_2)} e^{-\imath k_z 2\mathrm{C}_0}\,(-\imath k_z)}{k_x^2+k_y^2+k_z^2}\right) .\end{aligned} \qquad \text{(C.455)}$$

It should be noted that we are using the same representation of the Green's function as given in Sect. C.6 which means that in addition to k_x also integrals over k_y and k_z run from $-\infty$ to ∞. Integration over k_z gives rise to a familiar looking exponential function:

$$\mathcal{F}_{x_1/k_x}\Big\{\partial_{z_2} G_{3D}^{1W}(1;2;t)\Big\} = \frac{1}{4\pi}\int_{-\infty}^{\infty} dk_y \Big(e^{-\imath k_y(y_1-y_2)} + e^{-\imath k_y(y_1+y_2)}\Big)\, e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}} \ . \qquad \text{(C.456)}$$

Substituting this result into Eq. (C.454) and performing the integrals over y_1 and y_2 prior to k_y-integration we obtain

$$p_C^{1W}(k_x,t) = \frac{1}{4\pi}\partial_t \mathrm{C}_0 \int_{-\infty}^{\infty} dk_y\, e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}}\, \frac{2k_x^2 - 2\imath k_x k_y}{(k_x^2+k_y^2)^2} \qquad \text{(C.457)}$$

Since we are integrating over symmetric interval, the monomial $-2\imath k_x k_y$ in the numerator of the integrand gives zero contribution to the integral. Thus, we see that we have arrived at the same result as in Eq. (C.434).

Precisely in the same manner as in the previous case, we compute the Fourier transform of the term I'_D. We introduce a coefficient function $\mathcal{F}_{x/k_x}\{I'_D\} \equiv p_D^{1W}(k_x,t)\,\partial_t c(k_x,t)$. Using the approximation $\mathrm{H}_0 \approx \mathrm{C}_0$ leads to

$$p_D^{1W}(k_x,t) \approx \int_0^\infty dy_1 \int_0^\infty dy_2\, G^{1W}(k_x,y_1)\, G^{1W}(k_x,y_2) \mathcal{F}_{x_1/k_x}\Big\{G_{3D}^{1W}(1;2;t)\Big\} \ . \qquad \text{(C.458)}$$

The Fourier integral representation is similar to the one that appeared above except that there are more terms involved:

$$\begin{aligned}&\mathcal{F}_{x_1/k_x}\Big\{G_{3D}^{1W}(1;2;t)\Big\} = \qquad \text{(C.459)}\\ &\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \left(\frac{e^{-\imath k_y(y_1-y_2)} e^{-\imath k_z(z_1-z_2)}}{k_x^2+k_y^2+k_z^2} - \frac{e^{-\imath k_y(y_1-y_2)} e^{-\imath k_z(z_1+z_2)}}{k_x^2+k_y^2+k_z^2}\right)\Bigg|_{\mathrm{C}_0} \\ &+ \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \left(\frac{e^{-\imath k_y(y_1+y_2)} e^{-\imath k_z(z_1-z_2)}}{k_x^2+k_y^2+k_z^2} - \frac{e^{-\imath k_y(y_1+y_2)} e^{-\imath k_z(z_1+z_2)}}{k_x^2+k_y^2+k_z^2}\right)\Bigg|_{\mathrm{C}_0} .\end{aligned}$$

The substitution symbol $|_{\mathrm{C}_0}$ means that the expression is evaluated at the linearization point $z_1 = z_2 = \mathrm{C}_0$. Once this has been done and the integral over k_y performed, we obtain after substitution of the resulting expression into Eq. (C.458),

$$p_D^{1W}(k_x,t) = \frac{1}{2\pi}\int_0^\infty dy_1 \int_0^\infty dy_2\, e^{-|k_x|(y_1+y_2)} \int_{-\infty}^{\infty} dk_y \Big\{ \big(e^{-\imath k_y(y_1-y_2)} + e^{-\imath k_y(y_1+y_2)} \big) \times \big(1 - e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}}\big) \Big/ \big(2\sqrt{k_x^2+k_y^2}\,\big) \Big\} . \tag{C.460}$$

Assuming that the integrals over y_1 and y_2 can be done before the integration over k_y, we get

$$p_D^{1W}(k_x,t) = \frac{2}{\pi}\int_0^\infty dk_y\, \frac{1-e^{-2\mathrm{C}_0\sqrt{k_x^2+k_y^2}}}{2\sqrt{k_x^2+k_y^2}}\, \frac{k_x^2}{(k_x^2+k_y^2)^2} . \tag{C.461}$$

This is the same result as in Eq. (C.435). All in all, we conclude that the double wall results reduce to those of the single wall set-up in the limit $L \to \infty$.

C.15.1 Representation of coefficient functions

Let us try to cast the functions p_B^{1W}, p_C^{1W} and p_D^{1W} into simple form which facilitates further analytic investigations. We concentrate on p_D^{1W} with the aid of which we construct the others. Eq. (C.461) yields

$$p_D^{1W} = \frac{2}{\pi k_x^2}\int_1^\infty ds\, \frac{1}{\sqrt{s^2-1}}\frac{1-e^{-2Us}}{s^4} , \tag{C.462}$$

where we have defined $U \equiv |k_x|\mathrm{C}_0$. We have also changed to dimensionless variable of integration: $s = (k_x^2+k_y^2)^{1/2}/|k_x|$. The integral is well defined, of course, as the divergence at $s = 1$ is integrable. For physics purposes it suffices to know how the integral in Eq. (C.462) behaves in the limits U very large or small. For $U \gg 1$ we can drop the exponential and we get

$$p_D^{1W} \approx \frac{2}{\pi k_x^2}\int_1^\infty ds\, \frac{1}{s^4\sqrt{s^2-1}} \equiv \frac{1}{k_x^2} I_> . \tag{C.463}$$

To get the behaviour in the limit $U \ll 1$ we split the integral into two parts. Choose a constant E such that $U \ll E \ll 1$. It holds that $Us \ll 1$ for all $s < s_m \equiv E/U$. Then, $p_D^{1W} = (2/\pi k_x^2)(A_1 + A_2)$, where

$$A_1 \equiv \int_1^{s_m} ds\, \frac{1}{\sqrt{s^2-1}}\frac{1-e^{-2Us}}{s^4} \approx 2U\int_1^{s_m} ds\, \frac{1}{s^3\sqrt{s^2-1}} \tag{C.464}$$

where we Taylor expanded the exponential as its argument is always small in the given domain. The other term,

$$A_2 \equiv \int_{s_m}^\infty ds\, \frac{1}{\sqrt{s^2-1}}\frac{1-e^{-2Us}}{s^4} = s_m^{-3}\int_1^\infty dr\, \frac{1}{\sqrt{(s_m r)^2-1}}\frac{1-e^{-2Er}}{r^4} . \tag{C.465}$$

The second equality was obtained by making the variable transformation $s \equiv s_m r$. Because $s_m \gg 1$ and the lower limit of integration is one, it holds for all r that $s_m r \gg 1$. Therefore, we can approximate the factor $((s_m r)^2 - 1)^{-1/2} \approx s_m r$.

$$A_2 \le s_m^{-3}\int_1^\infty dr\, \frac{1}{s_m r}\frac{1}{r^4} \propto s_m^{-4} , \tag{C.466}$$

which means that A_2 vanishes much faster than $A_1 \propto s_m^{-1}$. Leaving it out, we can write for $U \ll 1$,

$$p_D^{1W} \approx \frac{2}{\pi k_x^2} A_1 \approx \frac{4U}{\pi k_x^2} \int_1^{\infty} ds\, s^{-3}(s^2-1)^{-1/2} \equiv \frac{\mathrm{C}_0}{|k_x|} I_< \ , \tag{C.467}$$

where we have defined a new constant $I_<$. Combination of the limiting behaviours of Eq. (C.467) and Eq. (C.463) gives rise to an interpolating expression,

$$p_D^{1W} \approx \frac{2I_>}{\pi k_x^2}\left(1 - e^{-(I_</I_>)\mathrm{C}_0|k_x|}\right) \approx \frac{1 - e^{-2\mathrm{C}_0|k_x|}}{4k_x^2} \ . \tag{C.468}$$

There will be small error induced via replacement of $I_</I_>$ by factor of 2 and $2I_>/\pi$ by 1/4 but the limiting behaviour in powers of $|k_x|$ stays intact, which is important for large scale analysis. With the aid of Eq. (C.468) we also obtain an approximation for the coefficient

$$p_C^{1W} = \frac{1}{2}\partial_t \mathrm{C}_0 \frac{\partial p_D^{1W}}{\partial \mathrm{C}_0} \approx \partial_t \mathrm{C}_0 \, \frac{e^{-2\mathrm{C}_0|k_x|}}{4|k_x|} \ , \tag{C.469}$$

where the second approximative equality was obtained by differentiating the expression of far right of Eq. (C.468). Since p_B^{1W} calls for no approximations, we have been able calculate all the terms on the left hand side of the equation of motion of the contact line in the single wall case.

C.15.2 Contact line equation for single wall

Explicit expressions for the coefficient functions arising from the Rayleigh dissipation functional have been derived in Sect. C.15.1. The right hand side of the equation of motion of the contact line can be generated by substituting the single wall Green's functions into the free energy functional F_{1D} and taking the variation with respect to the contact line profile c. However, since the resulting expressions are more trivial than in the case of the dissipation functional, we will not perform a similar analysis as in Sect. C.15.1 but instead we make use of the results of Sect. C.14.5 where the restoring forces were derived for double wall set-up. Taking the limit $L \to \infty$ of Eq. (C.446) and setting it equal to expression $\mathcal{F}_{x/k_x}\{I'_B + I'_C + I'_D\}$ yields

$$p_D^{1W}(k,t)\, \partial_t c(k,t) + \left(p_B^{1W}(k,t) + p_C^{1W}(k,t)\right) c(k,t) = -\frac{M}{2}\sigma|k|\, c(k,t) + \frac{M}{4} A_k(c) \ , \tag{C.470}$$

where we use k instead of k_x. Substitution of the approximative coefficient functions given in Eq. (C.468) and Eq. (C.469) together with the representation of p_B^{1W} given in Eq. (C.453) yields

$$\frac{1 - e^{-2\mathrm{C}_0|k|}}{4k^2}\, \partial_t c(k,t) + \frac{\partial_t \mathrm{C}_0}{4|k|}\left(1 + e^{-2\mathrm{C}_0|k|}\right) c(k,t) = -\frac{M}{2}\sigma|k|\, c(k,t) + \frac{M}{4} A_k(c) \ , \tag{C.471}$$

As compared to the meniscus equation of motion (C.289) the coefficient functions on the left hand side are divergent when $k \to 0$. This observation does not render the theory useless, however. Divergent terms in the equation of motion are familiar from other fields of physics, think of Schrödinger equation with Coulomb potential, for example. Of course, differences remain since the coefficient function of the time derivative term is also divergent in the contact line equation. We could have avoided the divergences had we multiplied both sides of the 3D phase field evolution equation not by operator $(\nabla^2)^{-1}$ but by something else which would have made the left hand side of the contact line equation not divergent, if only we had known how to project the meniscus equation in this case. However, we can still remove the apparent divergence for small wave vectors by multiplying both sides of Eq. (C.471) by $2|k|$:

$$\frac{1-e^{-2\mathrm{C}_0|k|}}{2|k|}\,\partial_t c(k,t)+\frac{\partial_t \mathrm{C}_0}{2}\left(1+e^{-2\mathrm{C}_0|k|}\right)c(k,t)=-M\sigma k^2\,c(k,t)+\tilde{A}_k(c)\ , \tag{C.472}$$

where $\tilde{A}_k \equiv (M/2)|k|A_k$ behaves like conserved quenched noise. Apart from the noise, the equation is similar to the equation of motion of the meniscus with finite coefficient functions for all values of k. Moreover, if the original noise A_k is split into its constant average $(\bar{A}\delta(k))$ and fluctuating parts $(\Delta A_k \equiv A_k - \bar{A}\delta(k))$, the new noise $\tilde{A}_k = (M/2)|k|(\bar{A}\delta(k)+\Delta A_k)$ will effectively have zero average, because $|k|\,\delta(k)=0$.

Problems with direct projection

For comparison, let us demonstrate what kind of dimensional problems arise if, instead of using the Rayleigh dissipation functional to derive the equation of motion for the noise induced fluctuations of the contact line, we try to generate the contact line equation of motion by applying the direct projection method on the left hand side of the equation of motion of the meniscus fluctuations (C.64). This procedure can not be ruled out right away since it produces a sensible equation of motion in the case of a pure system as shown in Sect. C.12.1. To obtain the contact line equation of motion we define a projector which casts out the bulk dynamics of the fluids and only takes into account what happens at the walls bounding the fluids., Therefore, we define a new projection operator, which is rather trivial in form:

$$P_y(\cdot) \equiv \int dy'\,\delta(y'-y)\ . \tag{C.473}$$

Projecting Eq. (C.63) and Eq. (C.64) onto the wall(s) at $y=0$ $(y=L)$ and setting $\tilde{\Lambda}=0$, leads to the equations of motion of the contact line:

$$P_0 I_A = (M\sigma/4)\,P_0\partial_y^2 \mathrm{H}_0 = (M\sigma/4)\,\partial_y^2 \mathrm{H}_0|_0\ ; \tag{C.474}$$

$$P_0 I_B + P_0 I_C + P_0 I_D \overset{?}{=} \frac{\delta F_{1D}[c]}{\delta c}\ . \tag{C.475}$$

Later on we show what destroys the validity of Eq. (C.475). To be able to do this, we have to consider the units and scaling of the four integral expressions resulting from first linearizing and then applying the projection operator on the left hand side of the equation of motion of the meniscus fluctuations:

$$P_0 I_A = \int_{-\infty}^{\infty}\!dx_1\int_0^{\infty}\!dy_1\,G_{3D}(x,0,\mathrm{C}_0(t);x_1,y_1,\mathrm{H}_0(y_1,t))\,\partial_t \mathrm{H}_0(y_1,t)\ ; \tag{C.476}$$

$$P_0 I_B = \int_{-\infty}^{\infty}\!dx_1\int_0^{\infty}\!dy_1\,\partial_z G_{3D}(x,0,z;x_1,y_1,\mathrm{H}_0(y_1,t))|_{\mathrm{C}_0(t)}\,c(x,t)\,\partial_t \mathrm{H}_0(y_1,t)\ ; \tag{C.477}$$

$$P_0 I_C = \int_{-\infty}^{\infty}\!dx_1\int_0^{\infty}\!dy_1\,\partial_{z_1} G_{3D}(x,0,\mathrm{C}_0(t);x_1,y_1,z_1)|_{\mathrm{H}_0(y_1,t)}\,h(x_1,y_1,t)\,\partial_t \mathrm{H}_0(y_1,t)\ ; \tag{C.478}$$

$$P_0 I_D = \int_{-\infty}^{\infty}\!dx_1\int_0^{\infty}\!dy_1\,G_{3D}(x,0,\mathrm{C}_0(t);x_1,y_1,\mathrm{H}_0(y_1,t))\,\partial_t h(x_1,y_1,t)\ . \tag{C.479}$$

In deriving these expressions we have used the facts that $P_0\mathrm{H}_0(y,t)$ will be equal to $\mathrm{H}_0(0,t) = \mathrm{C}_0(t)$, and $\partial_t\mathrm{H}_0(y,t) = \partial_t\mathrm{C}_0(t)$. In case the curvature is time dependent, the present derivation shows that depending on whether we first linearize and the project, or vice versa, the results will be different. However, for constant curvature these operations commute, which is proved below by by interchanging the order of the projection and linearization

Project the left hand side of Eq. (8.47) first and then linearize around *both* C_0 *and* H_0. To get a condition for the validity of the expansion, it suffices to require $h \ll \mathrm{H}_0$. If this holds for all x and y, then $h(x, y = 0, t) \ll \mathrm{H}_0(y = 0, t) \Leftrightarrow c(x, t) \ll \mathrm{C}_0(t)$. Next, let us concentrate on deriving the contact line equation of motion using the variations c and h as small variations around the zeroeth order solutions. The right hand side of the equation of motion of the meniscus stays the same irrespective of the order of linearization and projections when $\tilde{\Lambda} = 0$. Projection of the left hand side yields:

$$P_0 \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, G_{3D}(x, y, \mathrm{H}(x, y, t); x_1, y_1, \mathrm{H}(x_1, y_1, t))\, \partial_t \mathrm{H}(x_1, y_1, t) \tag{C.480}$$

$$= \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \Big\{ G_{3D}(x, y, \mathrm{C}_0(t) + c(x, t); x_1, y_1, \mathrm{H}_0(y_1, t) + h(x_1, y_1, t)) \times \Big[\partial_t \mathrm{H}_0(y_1, t) + \partial_t h(x_1, y_1, t)\Big]\Big\}. \tag{C.481}$$

As before, we expand the Green function to first order in the fluctuations h and c. Thus, the last two lines of the previous equation become

$$\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1 \Big\{\Big[G_{3D} + \partial_z G_{3D}|_{\mathrm{C}_0}\, c(x, t) + \partial_{z_1} G_{3D}|_{\mathrm{H}_0}\, h(x_1, y_1, t)\Big] \times \Big[\partial_t \mathrm{H}_0(y_1, t) + \partial_t h(x_1, y_1, t)\Big]\Big\}. \tag{C.482}$$

Analogously to equations (C.55) – (C.57), the following short-hand symbols were introduced:

$$G_{3D} = G_{3D}(x, 0, \mathrm{C}_0(t); x_1, y_1, \mathrm{H}_0(y_1, t)) \;; \tag{C.483}$$

$$\partial_z G_{3D}|_{\mathrm{C}_0} = \partial_z G_{3D}(x, 0, z; x_1, y_1, \mathrm{H}_0(y_1, t))|_{\mathrm{C}_0(t)} \;; \tag{C.484}$$

$$\partial_{z_1} G_{3D}|_{\mathrm{H}_0} = \partial_{z_1} G_{3D}(x, 0, \mathrm{C}_0(t); x_1, y_1, z_1)|_{\mathrm{H}_0(y_1,t)} \;. \tag{C.485}$$

Expansion of the square brackets in expression (C.482) gives rise to a term $h\partial_t h$ which is of second order in the fluctuations h. Neglecting it, the previous expression reduces to

$$\int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, G_{3D}\, \partial_t \mathrm{H}_0(y_1, t) + \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, \partial_z G_{3D}|_{\mathrm{C}_0}\, c(x, t)\, \partial_t \mathrm{H}_0(y_1, t) + \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, \partial_{z_1} G_{3D}|_{\mathrm{H}_0}\, h(x_1, y_1, t)\, \partial_t \mathrm{H}_0(y_1, t) + \int_{-\infty}^{\infty} dx_1 \int_0^{\infty} dy_1\, G_{3D}\, \partial_t h(x_1, y_1, t)$$

$$= P_0 I_A + P_0 I_B + P_0 I_C + P_0 I_D \;, \tag{C.486}$$

where the terms $P_0 I_s$, $s = A, B, C, D$ coincide with those given in Eq. (C.476) - (C.479). Hence, we observe that for time independent curvature linearization and projection commute.

Even though we have shown that the direct projection method has to convenient feature of being commutative with respect to linearization of the Green's function, we encounter problems when setting the projected left hand side of the meniscus equation of motion equal to $-M\delta F_{1D}[c]/\delta c$: the two sides of the equation have different dimensionality. In other words, if we assume (erroneously) that $P_0(I_B+I_C+I_D) = -M\delta F_{1D}[c]/\delta c$, where P_0 is a projector which basically sets the y-coordinate of any function equal to zero: $P_0 f \equiv \int dy'\, \delta(y')f(y') = f(0)$, we obtain essentially something like

$$\frac{1-e^{-2\mathrm{C}_0|k|}}{4k}\,\partial_t c(k,t) + \frac{\partial_t \mathrm{C}_0}{4}\left(1+e^{-2\mathrm{C}_0|k|}\right) c(k,t) \overset{?}{=} -2M\sigma|k|\, c(k,t) + MA_k(c) \ , \qquad \text{(C.487)}$$

which should be compared with the dimensionally correct Eq. (C.471). On the left there is one power of length missing. If one compares the equations of motion for the double wall set-up, the main difference in addition to the the factor $1/|k|$ is that the dimensionally correct equation contains more terms as the projection onto the plane $y = 0$ makes some of them to vanish. The only possibility to fix the problem with units is to assume that on the right hand side of the equation of motion the dimensionality of the dissipative coefficient M changes when going from two dimensions to one: $-M\delta F_{2D}[h]/\delta h \to -M'\delta F_{1D}[c]/\delta c$, such that $[M] = m^3/s$ and $[M'] = m^2/s$. However, this is not very good idea because the number of parameters of the theory increases and there is no obvious way of relating M' to M, not to mention any attempts to derive its value from microscopics. Also the reduction of dimensionality of the right hand side of the equation of motion remains more mysterious than in the present derivation utilizing the dissipation and free energy functionals. Therefore, we prefer to stick to the present variational derivation, which seems to give at least the units correctly.

C.16 Contact line dynamics: memory effects

The results of the previous section have been derived using the quasi-stationary approximation which means that the meniscus follows the movement of the contact line instantaneously without any delays. In reality this assumption becomes progressively worse the smaller the effective surface tension $\tilde{\sigma}$ is in Eq. (C.303). Alternatively, we can use the curvature expansion parameter $\epsilon \equiv KL^2/\mathrm{C}_0 \propto L^2/(\tilde{\sigma}\tau)$ defined in Sect. C.11.2: the bigger the curvature, the more important memory effects become.

The approximation we have used, namely the replacement of $\mathrm{H}_0 \approx \mathrm{C}_0$ in the Green's functions, would suggest to use only the first order terms in ϵ of the memory expansion of the meniscus presented in Sect. C.11.2. Substitution of $\tilde{h} \approx \tilde{h}_{qs} + \epsilon\tilde{h}_1$ into the dissipation and free energy functionals according to the recipe given in Sect. C.13 would produce the history dependent equation of motion for the contact line. However, the memory kernels would have no interesting time dependence due to the truncation of the perturbation series. Therefore, to make closer contact with memory functions of generalized Langevin equations, we prefer to use the full time dependent solution of the (linearized) meniscus fluctuations. Using the single wall theory,

$$h(x_1,y_1,t_1) = \int_0^{t_1} dt_1' \int_{-\infty}^{\infty} dx_1'\, R_1(x_1-x_1',y_1,t_1,t_1')\, c(x_1',t_1') \ , \qquad \text{(C.488)}$$

For simplicity one can use the kernel $R_1(x_1,y_1,t_1,t_1') \equiv (\partial\tau(t_1')/\partial t_1')\, g^a(x_1,y_1,\tau(t_1)-\tau(t_1'))$ where g^a is defined in Eq. (C.334). For the single wall set-up, the superscript a plays no role, of course. To take into account all terms of the linearized theory, one should use $R_1(x_1,y_1,t_1,t_1') \equiv (\partial\tau(t_1')/\partial t_1')\, g^a(x_1,y_1,\tau(t_1),\tau(t_1'))$ where this time the definition of g^a is given in Eq. (C.331). Assuming that we can differentiate the integral representation of h

with respect to t_1 in the elementary manner (with contributions generated by the fact that the upper limit of time integration is dependent on t_1 and the fact that the kernel R_1 is also dependent on t_1), we get the following results in the Fourier space:

$$h(k_x, y_1, t_1) = \int_0^{t_1} dt'_1 \, R_1(k, y_1, t_1, t'_1) \, c(k, t'_1) \tag{C.489}$$

$$\partial_{t_1} h(k_x, y_1, t_1) = \int_0^{t_1} dt'_1 \, R_2(k, y_1, t_1, t'_1) \, \partial_{t'_1} c(k, t'_1) \ , \tag{C.490}$$

where R_2 can be straightforwardly related to R_1. The following prescription can be used for taking the functional derivative of R_{1D} (cf. Eq. (C.360)) with respect to $\dot{c}$:

$$\frac{\delta \dot{h}(x_1, y_1, t_1)}{\delta \dot{c}(x, t)} = \theta(t_1 - t) \, R_2(x_1 - x, y_1, t_1, t) \equiv \tilde{R}_2(x_1 - x, y_1, t_1, t) \ . \tag{C.491}$$

The Heaviside's step function is denoted by θ. To compactify notation we defined a new function $\tilde{R}_2$. The left hand side of the equation of motion of the contact line is readily obtained with the aid of the previous result and Eq. (C.360) from which we drop the coupling terms to h^b which are irrelevant for the single-wall set-up we are considering:

$$\begin{aligned}\frac{\delta R^a_{1D}[\,\dot{c}^a\,]}{\delta \dot{c}^a(x,t)} &\equiv \frac{4}{M} \int dA_1 \int dt_1 \int dA_2 \Big\{ \tilde{R}_2(x_1 - x, y_1, t_1, t) \, G^{\mathrm{H}_0}_{3D}(1;2;t_1) \dot{h}^a_{\mathrm{C}}(2, t_2) \\ &+ \tilde{R}_2(x_1 - x, y_1, t_1, t) \Big[\partial_{z_1} G^{\mathrm{H}_0}_{3D}(1;2;t_1) h_{\mathrm{C}}(1, t_1) + \partial_{z_2} G^{\mathrm{H}_0}_{3D}(1;2;t_1) h_{\mathrm{C}}(2, t_2) \Big] \dot{\mathrm{H}}_0(2, t_2) \Big\} \ ,\end{aligned} \tag{C.492}$$

where we have used the same short-hand notation for the arguments of the Green's function and its derivatives as in Sect. C.14. It is important to notice that in principle we can define h^a_{C} to be a function of the contact line velocity $\partial_t c^a$ through

$$h^a_{\mathrm{C}}(x_1, y_1, t_1) = \int_0^{t_1} dt'_1 \int_{-\infty}^{\infty} dx'_1 \, R_1(x_1 - x'_1, y_1, t_1, t'_1) \int_0^{t'_1} dt'_2 \, \partial_{t'_2} c(x'_1, t'_2) \ , \tag{C.493}$$

thus making it legitimate to generate new terms in the equation of motion by taking functional derivative of h^a_{C} with respect to $\dot{c}^a$ in addition to functional differentiation of $\dot{h}^a_{\mathrm{C}}$, which led to Eq. (C.492). However, it is easy to show by substituting the memory expansion $h_{\mathrm{C}} \approx h_{qs} + \epsilon h_1$ into the dissipation functional that allowing the functional differentiation of the functions h_{qs} and h_1 with respect to contact line velocity based on the representation of Eq. (C.493), we do not recover the correct quasi-stationary limit when we take ϵ to zero. Restricting the functional differentiation only to terms $\dot{h}^a$ appearing in R^a_{1D}, we do recover the quasi-stationary limit correctly when taking $\epsilon \to 0$. The situation is analogous to the fact that on should not act on the position coordinate when taking variation of the Lagrangian with respect to momentum coordinate even though the latter can be represented as the time integral of the former. In the field theoretical setting this needed to be clarified a bit further as we did above by setting the requirement of the correct quasi-stationary limit. After all this said and done we obtain

$$\mathcal{F}_{x/k_x} \Big\{ \frac{\delta R^a_{1D}[\,\dot{c}^a(x,t)\,]}{\delta \dot{c}^a(x,t)} \Big\} = \int_{-\infty}^{\infty} dt'_1 \, S_1(k_x, t, t'_1) \partial_{t'_1} c^a(k_x, t'_1) + \int_{-\infty}^{\infty} dt'_1 \, S_2(k_x, t, t'_1) c^a(k_x, t'_1) \ , \tag{C.494}$$

where S_1 and S_2 are new integral kernels whose lengthy expressions are not shown explicitly as only their dependence on the time arguments is important here. Even though the integration limits run from $-\infty$ to ∞ it does not automatically mean that the resulting equation of motion would be non-causal. For example, if we have a non-causal looking equation of motion, $\partial_t c^a - \gamma_1 c^a = \int_{-\infty}^{\infty} dt'_1\, S_1(t,t'_1) c^a(t'_1)$, where $S_1 = -\gamma_2 \theta(t'_1 - t)$, differentiating with respect to time brings it back into the typical causal Langevin type of form: $\partial_t^2 c^a - \gamma_1 \partial_t c^a = \gamma_2 c^a$, where $\gamma_{1,2}$ are some constants.

The right hand side of the equation of motion is obtained in an analogous manner. We substitute Eq. (C.488) into the free energy Eq. (C.368), neglect the terms related to the second wall and take the variational derivative with respect to c^a. After Fourier transform we obtain

$$\mathcal{F}_{x/k_x}\left\{\frac{\delta F^a_{1D}[\,\dot{c}^a(x,t)\,]}{\delta c^a(x,t)}\right\} = \int_{-\infty}^{\infty} dt'_1\, S_3(k_x,t,t'_1)\, c^a(k_x,t'_1)\ , \tag{C.495}$$

where S_3 is another new kernel function. Assuming that the operator with kernel S_1 is invertible, we can formally write the full contact line equation of motion in the following form

$$\partial_t c^a(k_x,t) + \int dt'\, S(k_x,t,t')\, c^a(k_x,t') = f_r\ . \tag{C.496}$$

We have added to the right hand side the stochastic force f_r due to the fluctuations of the surface tensions of the wall. It is a function of the old noise $A_{k_x}(c^a)$: $f_r = \hat{S}_1^{-1} A_{k_x}$. The kernel $S(k_x,t,t') \equiv \int dt'\, S_1^{-1}(k_x,t,t'_1)(S_2(k_x,t'_1,t') - S_3(k_x,t'_1,t'))$, where S_1^{-1} is the kernel of the inverse operator $\hat{S}_1^{-1}$. The remarkable thing is that Eq. (C.496) looks like a generalized Langevin equation. In principle such an equation could be obtained by projecting out the microscopic details, but in practice it would be very difficult to do. We have arrived at a similar looking equation via a different route. Of course there are important differences like the wave vector dependence typical of spatially extended objects and the quenched nature of the noise. However, for pure systems with only thermal noise Eq. (C.496) is exactly the generalized Langevin equation if S can be shown to be a causal kernel. Fluctuation-dissipation theorem in the context of this type of complicated quenched process are not guaranteed to hold but more generally, steady states can be produced as pointed out in Sect. 12.3.

C.17 Meniscus shape for regular defects

In this section we study the equilibrium shape of a meniscus whose shape is distorted from the parabolic due to the effect of a regular domain on the wall at $y = 0$ having different wetting properties than the rest of the wall. Typically, we are thinking of a stripe like defect with no variation in the wetting properties in z-direction. Neglecting the time dependence of the phase field in Eq. (8.43) leads to de Gennes's theory in the limit of small slopes $\nabla \mathrm{H} \ll 1$:

$$\sigma \nabla \cdot \frac{\nabla \mathrm{H}}{\sqrt{1 + |\nabla \mathrm{H}|^2}} \approx \sigma \nabla^2 \mathrm{H} = 0\ . \tag{C.497}$$

This is a straightforward consequence of the free energy minimization of the free energy of the meniscus (drumhead free energy [337]), which is given by

$$F_{2D} = \sigma \int dS\, \sqrt{1 + |\nabla \mathrm{H}|^2}\ . \tag{C.498}$$

The surface element is denoted by dS. Extension of the free energy to account for gravity would have an additional term in the free energy of the liquid-gas interface:

$$F^g_{2D} \equiv \sigma \int dS\, \sqrt{1 + |\nabla \mathrm{H}|^2} + \int dS\, \frac{1}{2} \mathrm{H}^2\ . \tag{C.499}$$

In Eq. (C.499) we have expressed the free energy in the units of capillary length $l_c \equiv \sigma_{lv}/(\rho g)$. Use of F^g_{2D} leads to the result of Pomeau and Vannimenus for the kernel Γ mentioned in Sect. 8.5. The presence of the gravitational interaction guarantees that Γ^{-1} is not singular on large scales $k \to 0$, which is a problem in the basic theory of de Gennes. We will see next how Γ can be made well-defined for all wave vectors even *without* gravity. This is achieved by confinement of the fluid between two vertical walls.

C.17.1 Equilibrium derivation

We'll show first that in the quasi-stationary approximation with no connection to external fluid reservoir the meniscus satisfies Poisson's equation having the contact line position as the boundary value. We assume that we have no-flux boundary conditions for the chemical potential which means that the *global* mass of the fluid between the walls is conserved. To incorporate this into the expression of free energy, we introduce a Lagrange multiplier Υ:

$$F^{2W}_{2D} \equiv \sigma \int_{-\infty}^{\infty} dx \int_0^L dy \, \frac{1}{2} |\nabla \textsc{h}(x,y)|^2 + \Upsilon \int_{-\infty}^{\infty} dx \int_0^L dy \, \textsc{h}(x,y) \ , \tag{C.500}$$

where we have subtracted the constant bulk contribution from the first term on the right hand side and kept only the leading contribution for small slopes. Had the boundary condition been chosen as the usual one $\mu = 0$ at the reservoir boundary, the Lagrange's term would be missing because the global mass would not be conserved. It should also be noted that we have not derived the Lagrange's term here through projection starting from F^{2W}_{3D} and keeping only such order parameter profiles which satisfy global mass conservation requirements producing a linear term in $\textsc{h}$ in the expression of F^{2W}_{2D}.

Since there is no macroscopic motion in equilibrium we leave out the Rayleigh dissipation functional. Minimizing $F^{2W}_{2D}[\textsc{h}]$ with respect to the shape $\textsc{h}$ yields Poisson equation for the height field:

$$\sigma \nabla^2 \textsc{h} = \Upsilon \ . \tag{C.501}$$

The Poisson equation is supplemented with Dirichlet boundary conditions.

$$\begin{cases} \textsc{h}(x, L) = B = const \ ; \\ \textsc{h}(x, 0) = c(x) \ . \end{cases} \tag{C.502}$$

In the x-direction the solution should be well-behaved for $x \to \pm\infty$, or periodic boundaries can be used as in the computer simulations. The boundary conditions have been tailored to model a situation where one of the walls at $y = L$ is pure and the other one at $y = 0$ has spatially varying wetting conditions reflected in the x-dependence of the contact line height c. This choice is useful for discussion of stripe defects, for example. In case both walls are chemically inhomogeneous the first condition just has to be replaced by $\textsc{h}(x, L) = c_2(x)$ where $c_2(x)$ is the spatially varying contact line configuration at $y = L$. The physics regarding the form of the restoring force, which we are going to derive, doesn't change, though. Therefore we stick the simpler choice of Eq. (C.502) for now. To get rid of the Lagrange multiplier, set

$$\textsc{h} \equiv h + \textsc{h}_0 \tag{C.503}$$

where $\textsc{h}_0 = \Upsilon y^2/(2\sigma)$. In this case $h(x, y, t)$ is induced by the surface tension change of the wall-liquid and wall-gas tensions in the x-direction.

It would be more consistent with the notation of the rest of the work to choose $\textsc{h}_0 = \textsc{c}_0 - KLy + Ky^2$, where the curvature $K = \Upsilon/(2\sigma)$. Moreover, since we have set the global height $H(x, L) = B$ in Eq. (C.502) we should set $\textsc{c}_0 = 0$. Thus, $\textsc{h}$ reduces to $\Upsilon y^2/(2\sigma) - \Upsilon Ly/(2\sigma)$. Despite the ambiguity in the choice of $\textsc{h}_0$, the unique global solution $\textsc{h}$ does not change since it is a sum of h and $\textsc{h}_0$: Adding something to $\textsc{h}_0$ results in subtraction of the same thing from h. For simplicity, we stick to the definition $\textsc{h}_0 = \Upsilon y^2/(2\sigma)$ in the subsequent sections. The new function h satisfies Laplace's equation with modified boundary conditions:

$$\nabla^2 h = 0 \quad ; \quad \begin{cases} h(x, L) = B' = const \ ; \\ h(x, 0) = c(x) \ . \end{cases} \tag{C.504}$$

The constant B' is related to the other parameters of the problem through $B' = B - \Upsilon L^2/(2\sigma)$. Solution of the inhomogeneous problem of Eq. (C.504) is expressible with the aid of the Green function G_0 of the corresponding homogeneous problem:

$$\begin{aligned} h(x, y) &= -\int_S dS' \, \partial_{y'} G_0(\mathbf{r}, \mathbf{r}') \, h_S(\mathbf{r}') && \text{(C.505)} \\ &= -\int_{-\infty}^{\infty} dx' \, \partial_{y'} G_0(\mathbf{r}; \mathbf{r}')|_0 \, c(x') + \int_{-\infty}^{\infty} dx' \, \partial_{y'} G_0(\mathbf{r}; \mathbf{r}')|_L \, B' \ , && \text{(C.506)} \end{aligned}$$

where $\mathbf{r} = (x, y)$ and S denotes the boundary coordinates.

Let us next study the Green function G_0 of the homogeneous problem. It can be constructed using the method of images. Summing over an infinite alternating series of mirror charge potentials one obtains [357]

$$G_0(\mathbf{r}; \mathbf{r}') = \frac{1}{4\pi} \ln \left[\frac{\cosh(\pi(x' - x)/L) - \cos(\pi(y' - y)/L)}{\cosh(\pi(x' - x)/L) - \cos(\pi(y' + y)/L)} \right] \ . \tag{C.507}$$

In the limit of the wall separation L going to infinity we correctly recover the good old half-plane propagator which we have been using in our imbibition model. Evaluation of $\partial_{y'} G_0(\mathbf{r}; \mathbf{r}')$ is performed at the wall positions $y' = 0$ and $y' = L$. We obtain

$$\begin{aligned} \partial_{y'} G_0(x, y; x', y')|_0 &= -\frac{\sin(\pi y/L)}{2L} \frac{1}{\cosh(\pi(x' - x)/L) - \cos(\pi y/L)} \ ; && \text{(C.508)} \\ \partial_{y'} G_0(x, y; x', y')|_L &= \frac{\sin(\pi y/L)}{2L} \frac{1}{\cosh(\pi(x' - x)/L) + \cos(\pi y/L)} \ . && \text{(C.509)} \end{aligned}$$

In the next section we will compute the Fourier transforms of the two kernels above and confirm with explicit calculation that the boundary values set for h are respected.

C.17.2 Validation of the boundary conditions

The explicit form of the meniscus in Eq. (C.506) defines two new functions $h^a(x, y)$ and $h^b(y)$, which should not be confused with the average meniscus position and the fluctuations around it.

$$\begin{aligned} h(x, y) &= h^a(x, y) + h^b(y) \ . && \text{(C.510)} \\ h^a(x, y) &\equiv \frac{\sin(\pi y/L)}{2L} \int_{-\infty}^{\infty} dx' \frac{1}{\cosh(\pi(x' - x)/L) - \cos(\pi y/L)} c(x') && \text{(C.511)} \\ h^b(y) &\equiv \frac{B' \sin(\pi y/L)}{2L} \int_{-\infty}^{\infty} dx' \frac{1}{\cosh(\pi x'/L) + \cos(\pi y/L)} \ . && \text{(C.512)} \end{aligned}$$

First, consider the limiting limiting values of h^a. The dominant contribution to the convolution come from the neighbourhood of $x \approx x'$ for $y = 0$. Therefore,

$$\begin{aligned}
\lim_{y\to 0} h^a &= \lim_{y\to 0} \frac{\sin(\pi y/L)}{2L} \int_{-\infty}^{\infty} dx' \, \frac{1}{1 + \frac{1}{2}(\frac{\pi}{L})^2 (x-x')^2 - 1 + \frac{1}{2}(\frac{\pi}{L})^2 y^2} \, c(x') && \text{(C.513)} \\
&= \lim_{y\to 0} \frac{(\pi y/L)}{2L} \int_{-\infty}^{\infty} dx' \, \frac{1}{\frac{1}{2}(\frac{\pi}{L})^2 \left[(x-x')^2 + y^2\right]} \, c(x') && \text{(C.514)} \\
&= \lim_{y\to 0} \int_{-\infty}^{\infty} dx' \, \frac{1}{\pi} \frac{y}{(x-x')^2 + y^2} \, c(x') && \text{(C.515)} \\
&= \int_{-\infty}^{\infty} dx' \, \delta(x-x') \, c(x') = c(x) \ . && \text{(C.516)}
\end{aligned}$$

In the first line we Taylor expand $\cosh(\pi(x-x')/L)$, and the last line follows from the Poisson representation of the delta function. The correct boundary condition is revived at $y = 0$. For $y \to L$,

$$\lim_{y\to L} h^a \propto \frac{\sin(\pi L/L)}{2L} = 0 \ . \qquad \text{(C.517)}$$

Thus, the effect of h^a vanishes at the other boundary as it should; the correct boundary value B' at $y = L$ is produced by the other term h^b.

It turns out that the expression of h^b can be reduced to a much less complicated form which allows us to see the limiting behaviour immediately. We first remove the redundant coordinate x In Eq. (C.512) from the integral kernel of h^b by shifting $x'_{old} - x \equiv x'_{new}$. The integration can be readily performed:

$$\begin{aligned}
&\int_{-\infty}^{\infty} dx' \, \frac{1}{\cosh(\pi x'/L) + A} \\
&\quad = \frac{L}{\pi} \int_{-\infty}^{\infty} dx_1 \, \frac{1}{\cosh(x_1) + A} = \frac{2L}{\pi} \int_{-\infty}^{\infty} dx_1 \, \frac{1}{e^{x_1} + e^{-x_1} + 2A} && \text{(C.518)} \\
&\quad = \frac{2L}{\pi} \int_0^{\infty} \frac{dz}{z} \, \frac{1}{z + z^{-1} + 2A} = \frac{2L}{\pi} \int_0^{\infty} dz \, \frac{1}{z^2 + 2Az + 1} \ , && \text{(C.519)}
\end{aligned}$$

where we have used the short-hand notation $A \equiv \cos(\pi y/L)$. In the last line we performed the change of variables $\exp(x) \equiv z$. The last integral can be done in a closed form with the result,

$$\begin{aligned}
\int_{-\infty}^{\infty} dx' \, \frac{1}{\cosh(\pi x'/L) + A} &= \frac{2L}{\pi\sqrt{1-A^2}} \left[\frac{\pi}{2} - \arctan\left(\frac{A}{\sqrt{1-A^2}}\right)\right] && \text{(C.520)} \\
&= \frac{2L}{\pi \sin(\pi y/L)} \left[\frac{\pi}{2} - \arctan(\cot(\pi y/L))\right] && \text{(C.521)} \\
&= \frac{2L}{\sin(\pi y/L)} \, \frac{y}{L} \ . && \text{(C.522)}
\end{aligned}$$

The second equality follows from the fact that $\sqrt{1-A^2} = |\sin(\pi y/L)| = \sin(\pi y/L)$ for $y \in [0, L]$. The last line is obtained by shifting the argument of the cotangent by $\pi/2$: $\cot(x + \pi/2) = -\tan(x)$. Therefore,

$$h^b(y) = B' \frac{y}{L} \ . \qquad \text{(C.523)}$$

The linear relationship was to be expected since the curvature should be zero for the solution satisfying a constant boundary condition. The limits are obviously correct:

$$\lim_{y\to 0} h^b(y) = 0 \;\; ; \;\; \lim_{y\to L} h^b(y) = B' \; . \tag{C.524}$$

We notice that the desired boundary value $c(x)$ is produced by the term $h^a(x,0) = c(x)$ whereas $h^b(0) = 0$. At the other boundary the situation is reversed: $h^a(x,L) = 0$ and $h^b(L) = B'$.

C.18 Force kernel and mass conservation

In the quasi stationary approximation with constant contact line profile at $y = L$ we obtain the following decomposition of the meniscus after taking the Fourier transform of h with respect to variable x:

$$\begin{aligned} \mathrm{H}(x,y,t) &= h(x,y,t) + \Upsilon y^2/(2\sigma) \; ; & \text{(C.525)} \\ h(k,y,t) &= h^a(k,y,t) + h^b(k,y,t) \; , & \text{(C.526)} \end{aligned}$$

where we have split h into two parts named h^a and h^b the superscripts of whom indicate at which wall they are fulfil the boundary condition. In the Fourier space

$$\begin{aligned} h^a(k,y,t) &= \frac{\sinh(|k|(L-y))}{\sinh(|k|L)}\, c_k(t) \; ; & \text{(C.527)} \\ h^b(k,y,t) &= \delta(k)\, B' y/L \; . & \text{(C.528)} \end{aligned}$$

Expressions for h^a and h^b have been derived in Sect. C.17.2 and Sect. C.11. As mentioned in the previous section, instead of $\mathrm{H}_0 = \Upsilon y^2/(2\sigma)$ which leads to Eq. (C.525), choosing $\mathrm{H}_0 = \Upsilon y^2/(2\sigma) - \Upsilon L y/(2\sigma)$ gives $\mathrm{H} = h^a + h^b + \mathrm{H}_0$, where $h^b = \delta(k) B y/L$ instead of Eq. (C.528).

The force f_{CL} density per unit length on the contact line is by definition given by the expression

$$\mathrm{f}_{CL} \equiv \frac{\delta}{\delta c}(F - F_0) \; , \tag{C.529}$$

F_0 being a reference free energy which absorbs factors independent of the contact line position c. To eliminate unnecessary terms from Eq. (C.529) we shall use the real space representation first, and switch over to Fourier space only after things have simplified enough. The force f_{CL} is then given by

$$\mathrm{f}_{CL} = \frac{\partial}{\partial c}\left\{ \int_{-\infty}^{\infty} dx \int_0^L dy \; \left[\frac{\sigma}{2} |\nabla \mathrm{H}(x,y)|^2 + \Upsilon \mathrm{H}(x,y) - f_0 \right] \right\} \; , \tag{C.530}$$

where f_0 is the density of F_0. The gradient of the meniscus H is $\nabla \mathrm{H} = \nabla h + \mathbf{e}_y\,(\Upsilon/\sigma) y$, and $\nabla \equiv \mathbf{e}_x\,\partial_x + \mathbf{e}_y\,\partial_y$. Therefore,

$$|\nabla \mathrm{H}|^2 = |\nabla h|^2 + 2(\Upsilon/\sigma) y\, \partial_y h + (\Upsilon y/\sigma)^2 \; . \tag{C.531}$$

After substitution of the expansion $h = h^a(x,y) + h^b(y)$ into the expression we can write the free energy density f as

$$f = \frac{\sigma}{2}|\nabla h^a|^2 + \sigma \partial_y h^a\, \partial_y h^b + \frac{\sigma}{2}(\partial_y h^b)^2 + \Upsilon y\, \partial_y h + \frac{\sigma}{2}(\Upsilon y/\sigma)^2 + \Upsilon \mathrm{H} - f_0 \; . \tag{C.532}$$

Somewhat surprisingly, all the terms on the right hand side of the previous equation except for the first one will turn out to have no effect on the restoring force f_{CL}. Let us prove this term by term in Fourier space. Starting with $\sigma\partial_y h^a\,\partial_y h^b$, we get

$$\frac{\partial}{\partial c_k}\int_0^L dy\;\sigma\partial_y h^a(k=0,y)\,\partial_y h^b(y) = 0\;, \tag{C.533}$$

where we have utilized the fact that $h^b(y)$ is a function of y only (and therefore proportional to $\delta(k)$). Thus, the integral of h^a over x can be represented as $\int dx\, h^a(x,y) = h^a(k=0,y)$. As the functional derivative is taken with respect to c_k, Eq. (C.533) holds since there is no dependence on c in $\partial_y h^a\,\partial_y h^b$ for $k \neq 0$. This term will not vanish if the contact line fluctuations c_k^b on the second wall at $y = L$ are non-zero. In that case $h^b = \sinh(|k|y)/\sinh(|k|L)c_k^b$ instead of $h^b = \delta(k)\,B'y/L$, and consequently there will be non-zero modes.

The next term on the right hand side of Eq. (C.532) is $(\sigma/2)(\partial_y h^b(y))^2$. When integrated over x and y it gives a constant (no dependence on c) which can be absorbed into f_0 (infinities cancel out). Similar argument holds for the fifth term $(\sigma/2)(\Upsilon y/\sigma)^2$. The fourth term on the right hand side of the free energy density, $2\Upsilon y\,\partial_y h$, requires a bit more work. By partial integration we get,

$$\Upsilon\int_{-\infty}^{\infty}dx\int_0^L dy\,y\,\partial_y h = \Upsilon\int_{-\infty}^{\infty}dx\;[y\,h]_0^L - \Upsilon\int_{-\infty}^{\infty}dx\int_0^L dy\,h(x,y) \tag{C.534}$$

$$= \Upsilon\int_{-\infty}^{\infty}dx\,LB' - \Upsilon\int_{-\infty}^{\infty}dx\int_0^L dy\,\left(\mathrm{H}(x,y) - \Upsilon y^2/(2\sigma)\right)\;. \tag{C.535}$$

In the first line we used the boundary condition for h to evaluate the substitution term $[y\,h]_0^L \equiv 0\,h(x,0) - L\,h(x,L)$, and in the second line we expanded $\mathrm{H} = h + \Upsilon y^2/(2\sigma)$. The first and third terms in Eq. (C.535) are just constants. The second term is seen to exactly cancel out the mass conservation term

$$+\int_{-\infty}^{\infty}dx\int_0^L dy\,\Upsilon\mathrm{H}(x,y)\;, \tag{C.536}$$

which also appears in Eq. (C.532). The mass conservation term could also be forced to vanish by considering no-flux boundary conditions and by setting the initial height of the fluid between the walls properly. This situation is relevant for defect studies discussed in Sect. 8.8.

We have now shown that the only nontrivial dependence on the contact line position of the restoring force f_{CL} originates from the first term on the right hand side of Eq. (C.532). Thus,

$$\mathrm{f}_{CL}(k) = \mathcal{F}_{x/k}\left\{\frac{\partial}{\partial c(x)}\int_{-\infty}^{\infty}dx\int_0^L dy\,\frac{\sigma}{2}|\nabla h^a|^2\right\} \tag{C.537}$$

$$= \frac{\sigma}{2}\frac{\partial}{\partial c_k}\int_{-\infty}^{\infty}dk\int_0^L dy\,\left[k^2|h^a(k,y)|^2 + |\partial_y h^a(k,y)|^2\right] \tag{C.538}$$

Substitution of $h^a(k,y)$ given in Eq. (C.527) yields

$$\mathrm{f}_{CL}(k) = \frac{\sigma}{2}\frac{\partial}{\partial c_k}\int_{-\infty}^{\infty}dk\int_0^L dy\,k^2|c_k|^2\,\Gamma'(k,y)\;. \tag{C.539}$$

In the previous equation we have defined a new function

$$\Gamma'(k,y) \equiv \left(\frac{\sinh(|k|(L-y))}{\sinh(|k|L)}\right)^2 + \left(\frac{\cosh(|K|(L-y))}{\sinh(|k|L)}\right)^2 = \frac{\cosh(2|k|(L-y))}{\sinh^2(|k|L)} \ . \tag{C.540}$$

To relate $\Gamma'(k,y)$ with $\Gamma_{2W}(k)$ appearing in evolution equation of the contact line, we consider the integral of $\Gamma'(k,y)$ over y:

$$\begin{aligned}\int_0^L dy\, \Gamma'(k,y) &= \int_0^L dy\, \frac{\cosh(2|k|(L-y))}{\sinh^2(|k|L)} = \frac{1}{\sinh^2(|k|L)} \int_0^L dy\, \cosh(2|k|y) &\text{(C.541)}\\ &= \frac{1}{2|k|}\,\frac{\sinh(2|k|L)}{\sinh^2(|k|L)} = \frac{1}{|k|}\,\coth(|k|L) \ . &\text{(C.542)}\end{aligned}$$

The restoring force (cf. Eq (C.539)) can now be conveniently represented as

$$\mathrm{f}_{CL}(k) = \frac{\partial}{\partial c_k} \int_{-\infty}^{\infty} dk\, \tfrac{1}{2}\Gamma_{2W}(k)\,|c_k|^2 \ , \tag{C.543}$$

where we have defined the kernel

$$\Gamma_{2W}(k) \equiv \sigma k^2 \int_0^L dy\, \Gamma'(k,y) = \sigma|k|\coth(|k|L) \ . \tag{C.544}$$

The inverse of $\Gamma_{2W}(k)$ is needed in Sect. 8.8 to relate the fluctuations of the local wetting properties to the shape of the contact line. Let us therefore study the behaviour of the inverse for $k \to 0$.

$$\lim_{k\to 0} \Gamma_{2W}^{-1}(k) = \frac{L}{\sigma} \ . \tag{C.545}$$

The limiting value of Γ_{2W}^{-1} is finite for finite plate separation L and the inverse is well-defined for all values of k. Consideration of very large values of kL, or more precisely $k_x L_y$, leads us back to de Gennes's result *if* the walls have finite length in x-direction: $\Gamma_{2W} \to \sigma|k_x|$ when $k_x L_y \gg 1$, or $(2\pi/L_x)\,L_y \gg 1$.

C.19 Dynamic critical properties of contact line

In this section we study dynamic critical properties (kinetic roughening) of the contact line the kinetic roughening of the contact line and compute the lowest order approximation to roughness exponents in different scaling regimes. In Sect. 8.8 we have shown that the restoring force for the two wall set-up (Eq. (8.80)) can be approximated with de Gennes's result of Eq. (8.78) for large enough k-vectors: $\Gamma(k) \approx \sigma|k|$ for $|k| \gg 1/L_y$. Let us rewrite the evolution equation of the contact line in a simplified form (reminiscent of imbibition), which we will use for the fluctuation analysis:

$$\frac{1 - e^{-\mathrm{C}_0|k|}}{|k|}\,\partial_t c_k(t) = -\sigma_1 k^2\, c_k(t) + \tilde{A}_k(t) \ . \tag{C.546}$$

There appears a new constant in Eq. (C.546), σ_1, which is defined with the aid of the mobility M and the liquid-gas surface tension σ: $\sigma_1 \equiv M\sigma$. The quenched noise field $\tilde{A}_k \equiv M|k|A_k$

represents the Fourier transform of the projection of the random field $A(x, y, z)$ present in the bulk free energy of the model:

$$A_k(t) = \int dx\, e^{\imath kx} A(x, 0, \textsc{c}(x, t)) \ . \tag{C.547}$$

Redefine the time to simplify the subsequent calculations:

$$\tau(k, t) \equiv \int_0^t dt' \, \frac{|k|}{1 - e^{-\mathrm{C}_0(t')|k|}} \ . \tag{C.548}$$

Depending on whether we are in the local or nonlocal regime, τ takes on the values

$$\tau \to \begin{cases} 2\sqrt{t/(M\sigma K)} \ , & \text{for } \textsc{c}_0|k| \ll 1 \text{ (local regime)} \ . \\ |k|t \ , & \text{for } \textsc{c}_0|k| \gg 1 \text{ (nonlocal regime)} \ . \end{cases} \tag{C.549}$$

The constant K appearing above is the curvature of the zeroeth order meniscus position $\textsc{h}_0(y, t) = \underline{c(t)} + K(t)(y - L/2)^2$. The explicit formula for $\textsc{c}_0(t)$ used in Eq. (C.548) is, $\textsc{c}_0(t) = \sqrt{M\sigma K t}$ which should hold for larger times when the curvature K doesn't depend on time so strongly. In terms of the redefined time we have

$$\partial_\tau c_k(\tau) = -\sigma_1 k^2 \, c_k(\tau) + \tilde{A}_k(\tau) \ . \tag{C.550}$$

The formal solution is simply

$$c_k(\tau) = \int_0^\tau ds\, e^{-\sigma_1 k^2 (t-s)} \, \tilde{A}_k(s) \ . \tag{C.551}$$

Using the effective noise approximation for the quenched noise we can write the first approximation of the noise correlator as

$$\langle \tilde{A}_k \tilde{A}_{k'} \rangle \approx k^2 \delta(k + k') D/W \ , \tag{C.552}$$

where D is the (constant) strength of the impurity correlations on the wall and W is the r.m.s. width of the fluctuating contact line. The structure factor is given by

$$S(k, \tau) = e^{-2\sigma_1 k^2 \tau} \int_0^\tau ds_1 \, e^{\sigma_1 k^2 s_1} \int_0^\tau ds_2 \, e^{\sigma_1 k^2 s_1} \, Dk^2/W \ . \tag{C.553}$$

Roughness exponent χ and the time correlation exponent β can be obtained by studying the time-like and length-like scaling of the structure factor in the limits $\sigma_1 \tau k^2 \gg 1$ and $\sigma_1 \tau k^2 \ll 1$.

$$\text{For } \sigma_1 \tau k^2 \gg 1, \ \ S(k, t) \ \sim \ k^{-2} W^{-1} \sim k^{-2} L^{-\chi} \sim k^{\chi - 2} \sim k^{-(2\chi + d)} \ . \tag{C.554}$$

$$\text{For } \sigma_1 \tau k^2 \ll 1, \ \ S(k, t) \ \sim \ k^2 \tau^2 W^{-1} \sim \tau^2 \tau^{-2\beta} \sim t^{1-\beta} \sim t^{2\beta + d/z} \ . \tag{C.555}$$

The last scaling relations on the right in Eq. (C.554) and Eq. (C.555) are the self-consistency requirements based on the definitions of exponents χ and β. The dynamic exponent z is defined through $z = \chi/\beta$. Substituting this together with $d = 1$ into the last scaling relation of Eq. (C.555) yields $\beta = \chi/(3\chi + 1)$. The roughness exponent is solved from Eq. (C.554) with the result $\chi = 1/3$ in $d = 1$. Therefore, $\beta = 1/6$ and $z = 2$.

In the nonlocal regime where $\tau \to kt$ we can similarly divide the analysis into two parts:

$$\text{For } \sigma_1 \tau k^2 \gg 1, \quad S(k,t) \sim k^{-2} W^{-1} \sim k^{-2} L^{-\chi} \sim k^{\chi-2} \sim k^{-(2\chi+d)} \, . \tag{C.556}$$

$$\text{For } \sigma_1 \tau k^2 \ll 1, \quad S(k,t) \sim k^2 \tau^2 W^{-1} \sim k^2 \tau^2 (\tau/k)^{-\beta} \sim t^{2-\beta} \sim t^{2\beta+d/z} \, . \tag{C.557}$$

Matching aging the powers in scaling relation of Eq. (C.556) gives $\chi = 1/3$. From the lengthwise scaling we obtain $\beta = 2\chi/(3\chi+1)$. Substitution of $\chi = 1/3$ gives $\beta = 1/3$ and $z = 1$.

Another possibility to perform the analysis is to work with the real time and consider the nonlocal and local limits of Eq. (C.546) separately. This leads to the same results as the method above. It remains to be checked more thoroughly if the simple power counting arguments can be applied to the noise correlator of quenched 'conserved' noise field $\tilde{A}_k = M|k|A_k$. For other models with simpler noise A_k (no factor of $|k|$) we have found good correspondence between analytic results obtained in the manner described above and direct numerical integration (Sect. 12.3). However, the dynamic critical properties of the contact line are more difficult to determine because of the non-linear mean velocity of the line (in the non-driven case) in addition to the different noise properties. Preliminary numerics contradicts strongly the analytic prediction for the roughness exponent χ. Numerically, there should be a regime where the line is super-rough with $\chi \approx 1.25$.

Appendix D

Details of hydrodynamics

D.1 Evaluation of Poisson brackets

Let us start with the simplest possible system with one chemical species of molecules (particles) in the fluid state. The microscopic expressions of the conserved observables which are the mass density ϕ, the momentum density $\mathbf{j}$ and the internal energy density $\mathcal{E}$ are:

$$\phi(\mathbf{x},t) \equiv \sum_{\alpha} m\, \delta(\mathbf{x}-\mathbf{x}^{\alpha}(t)) \ . \tag{D.1}$$

$$\mathbf{j}(\mathbf{x},t) \equiv \sum_{\alpha} \mathbf{p}^{\alpha}(t)\, \delta(\mathbf{x}-\mathbf{x}^{\alpha}(t)) \ . \tag{D.2}$$

$$\mathcal{E}(\mathbf{x},t) \equiv \Big(\textstyle\sum_{\alpha}(p^{\alpha})^2/(2m) + (1/2)\sum_{\alpha\neq\beta} V(\mathbf{x}^{\alpha\beta})\Big)\, \delta(\mathbf{x}-\mathbf{x}^{\alpha}(t)) \ . \tag{D.3}$$

The mass of the fluid molecule is m and the instantaneous position and momenta are $\mathbf{x}^{\alpha}(t)$ and $\mathbf{p}^{\alpha}(t)$. The superscript α runs over all fluid particles in the system. In the argument of the interparticle potential energy V we have abbreviated $\mathbf{x}^{\alpha\beta} \equiv \mathbf{x}^{\alpha} - \mathbf{x}^{\beta}$. Finally, the component notation of the momentum vector is given by $\mathbf{p}^{\alpha} \equiv (p_x^{\alpha}, p_y^{\alpha}, p_z^{\alpha})$, where instead of subscripts x, y, z numbers $1, 2, 3$ is used. Angular momentum density, $\mathbf{L} = \sum_{\alpha}(\mathbf{x}^{\alpha} \wedge \mathbf{p}^{\alpha})\, \delta(\mathbf{x}-\mathbf{x}^{\alpha})$ ($\wedge$ denotes the vector product), is also a conserved quantity. However, it does not give rise to any new hydrodynamic modes (p. 441, Ref. [5]). This is generally true for theories with symmetric stress tensor.

The value of the Poisson bracket is a function of the arguments of the observables: $Q_{\mu\nu}(\mathbf{x},\mathbf{x}') \equiv \{\psi_{\mu}(\mathbf{x}), \psi_{\nu}(\mathbf{x}')\}$. This equation can be interpreted either as a time independent Poisson bracket for static fields $\psi_{\mu}(\mathbf{x})$ and $\psi_{\nu}(\mathbf{x}')$, or as an equal time Poisson bracket for time dependent fields $\psi_{\mu}(\mathbf{x},t)$ and $\psi_{\nu}(\mathbf{x}',t)$ with time dependence suppressed. To be able to interpret the meaning of the Poisson bracket of two fields evaluated at different times, $\{\psi_{\mu}(\mathbf{x},t), \psi_{\nu}(\mathbf{x}',t')\}$ we first note that there are two equivalent ways of obtaining the evolution equations for the coarse-grained variables ψ_{μ}. As explained in App. D.4, the Langevin equation of the macro variables is given by

$$\partial_t \psi_{\mu}(\mathbf{x}) = N_{\mu}(\mathbf{x}) - \Gamma_{\mu\nu}\frac{\delta F[\psi]}{\delta\psi_{\nu}(\mathbf{x})} + \eta_{\mu}(\mathbf{x},t) \ . \tag{D.4}$$

Because this equation utilizes the stationary probability distribution P_{eq}, the field ψ_{ν} appearing in the term $\delta F[\psi]/\delta\psi_{\nu}(\mathbf{x})$ is only a function of $\mathbf{x}$. This is due to the fact that

$P_{eq}(\psi(\mathbf{x}), t|\psi_0(\mathbf{x}), t_0)$ tells the probability of the macro variable operator $\hat{\psi}(\mathbf{x}, t)$ obtaining the value $\psi(\mathbf{x})$ at time t (given that it had the value $\psi_0(\mathbf{x})$ at the initial time t_0). Thus, for static free energy,

$$F[\psi] = \int d\mathbf{x}\, f(\psi(\mathbf{x})) \ , \tag{D.5}$$

the variational derivative becomes a function of $\mathbf{x}$ only: $\delta F[\psi]/\delta\psi(\mathbf{x}) = f'(\psi(\mathbf{x}))$. Therefore, in Eq. (D.4), we have to add the time dependence to the argument of ψ by hand. In other words, we replace $f'(\psi(\mathbf{x}))$ with $f'(\psi(\mathbf{x}, t))$ to justify the time differentiation on the left hand side of Eq. (D.4). Using this method it suffices to compute the static Poisson brackets without any time dependence in the fields. Moreover, the integrals included in the expression of the force N_μ (see Eq. (D.134) and Eq. (D.119)) are over the $\mathbf{x}'$-coordinate only:

$$N_\mu = U_\mu + T\int d\mathbf{x}'\, \frac{\delta Q_{\mu\nu}}{\delta\psi_\nu(\mathbf{x}')} = -\int d\mathbf{x}'\, Q_{\mu\nu}(\mathbf{x}, \mathbf{x}')\frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x}')} + T\int d\mathbf{x}'\, \frac{\delta Q_{\mu\nu}}{\delta\psi_\nu(\mathbf{x}')} \ . \tag{D.6}$$

The second possibility, which gives identical results with the procedure explained above, is to generalize the free energy, which only had static fields as its arguments before, in such a way that its argument functions can be time dependent:

$$F = \int d\mathbf{x}\int dt\, f(\psi(\mathbf{x}, t)) \equiv \int dx\, f(\psi(x)) \ , \tag{D.7}$$

where $dx \equiv d\mathbf{x}\, dt$ and $x = (\mathbf{x}, t)$. With this generalization, it would be more appropriate to talk about action instead of free energy since the units of F given in Eq. (D.7) are the unit of energy times the unit of time. Naturally, the integrals in the expression of the force N_μ include also time integration:

$$N_\mu = -\int d\mathbf{x}'\int dt\ Q_{\mu\nu}(\mathbf{x}, t; \mathbf{x}', t')\frac{\delta F_t[\psi]}{\delta\psi_\nu(\mathbf{x}', t')} + T\int d\mathbf{x}'\int dt\ \frac{\delta Q_{\mu\nu}}{\delta\psi_\nu(\mathbf{x}', t')} \ . \tag{D.8}$$

If we choose to use the time dependent arguments of fields and wish to obtain the same result as with time independent arguments, the Poisson brackets will acquire an additional delta function factor as compared to the time independent case:

$$\{A(\mathbf{x}, t), B(\mathbf{x}', t')\} \quad \equiv \quad \sum_{\alpha,j}\left[\frac{\partial A(\mathbf{x}, t)}{\partial p_j^\alpha(t)}\frac{\partial B(\mathbf{x}', t')}{\partial x_j^\alpha(t)} - \frac{\partial A(\mathbf{x}, t)}{\partial x_j^\alpha(t)}\frac{\partial B(\mathbf{x}', t')}{\partial p_j^\alpha(t)}\right] \tag{D.9}$$

$$\longrightarrow \quad \sum_{\alpha,j}\left[\frac{\partial A(\mathbf{x})}{\partial p_j^\alpha}\frac{\partial B(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial A(\mathbf{x})}{\partial x_j^\alpha}\frac{\partial B(\mathbf{x}')}{\partial p_j^\alpha}\right]\delta(t - t') \ . \tag{D.10}$$

In Eq. (D.10) we have suppressed the time dependence of all functions as the delta function forces the time arguments to be the same. So, as a *mnemonical rule* we can use $\{A(\mathbf{x}, t), B(\mathbf{x}', t')\} = \{A(\mathbf{x}), B(\mathbf{x}')\}\ \delta(t - t')$. The delta function $\delta(t - t')$ takes care of the extra time integral present in Eq. (D.8) making the results of the time independent theory and the functional derivative calculus with time dependent arguments identical. To summarize, at the level of the Langevin equation there is no difference, which method we use, if replace the unequal time commutator with the form (D.10). This is just a trick, however. Strictly speaking our mnemonic rule contradicts the correct definition of the unequal time commutator, which must be calculated from the time-dependent solutions of evolution equations of motion of the dynamic variables A and B [70]. For classical variables we should write

$$A(\mathbf{x}, t) = e^{\imath t\hat{L}}A(\mathbf{x}, 0) \equiv \sum_{n=0}^{\infty}\frac{t^n}{n!}(\imath\hat{L})^n A(\mathbf{x}, 0) \ , \tag{D.11}$$

where $A(\mathbf{x}, 0)$ is the given initial value of A. Similar relation holds for the variable B. The action of the Liouville operator is defined in terms of the microscopic Hamiltonian H:

$$\imath\hat{L}A = \{A, H\} \ . \tag{D.12}$$

Constructing $A(\mathbf{x}, t)$ and $B(\mathbf{x}, t')$ in this manner and computing their Poisson bracket will obviously produce a more complicated time dependence than given by the replacement rule of Eq. (D.10). This result seems to indicate that when constructing the Langevin equation for macro variables it is fundamentally more correct to use the time independent fields which can be read of from the stationary free energy to compute the (equal time) commutators. Once the Poisson brackets have been computed, one should put in the time dependence by hand through replacement $\phi(\mathbf{x}) \longrightarrow \phi(\mathbf{x}, t)$. One should be careful with the dimensional analysis, though. In the equation of motion the free energy should have units of action.

D.1.1 Mass and momentum density

First we compute the Poisson brackets between the mass density and momentum density. As pointed out above, when all the fields and variables are determined at the same instant of time, we do not have to write down the time arguments explicitly. Therefore, suppressing time arguments in Eq. (D.10) and substituting $A = \phi(\mathbf{x})$ and $B = j_i(\mathbf{x}')$ we get

$$\{\phi(\mathbf{x}), j_i(\mathbf{x}')\} \equiv \sum_{\alpha,j}\left[\frac{\partial\phi(\mathbf{x})}{\partial p_j^\alpha}\frac{\partial j_i(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial\phi(\mathbf{x})}{\partial x_j^\alpha}\frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha}\right] = -\sum_{\alpha,j}\frac{\partial\phi(\mathbf{x})}{\partial x_j^\alpha}\frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha} \ , \tag{D.13}$$

because the mass density is independent of momenta, $\partial\phi(\mathbf{x})/\partial p_j^\alpha = 0$. Next, we use the fact that $\partial j_i(\mathbf{x})/\partial p_j^\alpha = (\partial/\partial p_j^\alpha)\sum_\beta p_i^\beta\delta(\mathbf{x}' - \mathbf{x}^\beta) = \delta_{ij}\delta(\mathbf{x}' - \mathbf{x}^\beta)$:

$$\{\phi(\mathbf{x}), j_i(\mathbf{x}')\} = -\sum_{\alpha,j}\frac{\partial\phi(\mathbf{x})}{\partial x_j^\alpha}\delta_{ij}\delta(\mathbf{x}' - \mathbf{x}^\beta) = -\sum_\alpha\left(\frac{\partial}{\partial x_i^\alpha}\sum_\beta m\,\delta(\mathbf{x} - \mathbf{x}^\beta)\right)\delta(\mathbf{x} - \mathbf{x}^\beta) \ , \tag{D.14}$$

The action of the derivative on the multidimensional delta function can be easily seen. For $i = 1$, $(\partial/\partial x_i^\alpha)\delta(\mathbf{x} - \mathbf{x}^\beta) = (\partial\delta(x_1 - x_1^\beta)/\partial x_1^\alpha)\,\delta(x_2 - x_2^\beta)\delta(x_3 - x_3^\beta)\,\delta_{\alpha\beta}$, and so on. Keeping the index $i = 1$ fixed, we obtain

$$\{\phi(\mathbf{x}), j_1(\mathbf{x}')\} =$$

$$\sum_\alpha m\,\delta'(x_1 - x_1^\alpha)\delta(x_2 - x_2^\alpha)\delta(x_3 - x_3^\alpha)\,[\delta(x_1' - x_1^\alpha)\delta(x_2' - x_2^\alpha)\delta(x_3' - x_3^\alpha)] \tag{D.15}$$

$$= \sum_\alpha m\,\delta'(x_1 - x_1')\delta(x_2 - x_2')\delta(x_3 - x_3')\,\delta(\mathbf{x}' - \mathbf{x}^\alpha) \tag{D.16}$$

$$= \delta'(x_1 - x_1')\delta(x_2 - x_2')\delta(x_3 - x_3')\sum_\alpha m\,\delta(\mathbf{x}' - \mathbf{x}^\alpha) \ , \tag{D.17}$$

where the delta function $\delta(\mathbf{x}' - \mathbf{x}^\alpha)$, which is expanded in the square brackets on the first line, was used to replace the variables x_s^α with x_s', $s = 1, 2, 3$. The previous calculation was done for index $i = 1$ but similar argumentation holds for the remaining indices, too. Therefore,

$$\{\phi(\mathbf{x}), j_i(\mathbf{x}')\} = \partial_i\delta(\mathbf{x} - \mathbf{x}')\,\phi(\mathbf{x}') \ , \tag{D.18}$$

which is seen from Eq. (D.17) by pulling out the delta factors which do not depend on the summation index α and using the definition of the density ϕ. By interchanging arguments $\mathbf{x}$ and $\mathbf{x}'$ and multiplying the previous equation by -1 gives

$$\{j_i(\mathbf{x}), \phi(\mathbf{x}')\} = -\partial_i' \delta(\mathbf{x}' - \mathbf{x})\, \phi(\mathbf{x}) = \partial_i \delta(\mathbf{x}' - \mathbf{x})\, \phi(\mathbf{x})\ . \tag{D.19}$$

The fact that the argument of ϕ has changed has an effect of the action of the Poisson bracket kernels on a function f as demonstrated below:

$$\begin{cases} \displaystyle\int d\mathbf{x}'\, \{\phi(\mathbf{x}), \mathbf{j}(\mathbf{x}')\}\, f(\mathbf{x}') = \nabla\left(\phi(\mathbf{x}) f(\mathbf{x})\right)\ . \\ \displaystyle\int d\mathbf{x}'\, \{\mathbf{j}(\mathbf{x}), \phi(\mathbf{x}')\}\, f(\mathbf{x}') = \phi(\mathbf{x}) \nabla f(\mathbf{x})\ . \end{cases} \tag{D.20}$$

As will be shown later, the upper equation enables us to compute the Poisson bracket of the velocity (not momentum) field and the density field ϕ which is needed in evaluation of Eq. (9.31).

D.1.2 Components of momentum density

Unlike the Poisson brackets of the density field, $\{\phi(\mathbf{x}), \phi(\mathbf{x}')\} = 0$, the Poisson brackets of the different momentum field components do not vanish since the fields j_i $(i = 1, 2, 3)$ do depend on the microscopic momenta. Starting from the defining equation,

$$\{j_s(\mathbf{x}), j_i(\mathbf{x}')\} \equiv \sum_{\alpha j} \left[\frac{\partial j_s(\mathbf{x})}{\partial p_j^\alpha} \frac{\partial j_i(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial j_s(\mathbf{x})}{\partial x_j^\alpha} \frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha} \right] \tag{D.21}$$

$$\begin{aligned} = \sum_{\alpha j} \Bigg[& \frac{\partial}{\partial p_j^\alpha} \left(\textstyle\sum_{\beta_1} p_s^{\beta_1} \delta(\mathbf{x} - \mathbf{x}^{\beta_1}) \right) \frac{\partial}{\partial x_j^\alpha} \left(\textstyle\sum_{\beta_2} p_i^{\beta_2} \delta(\mathbf{x}' - \mathbf{x}^{\beta_2}) \right) \\ & - \frac{\partial}{\partial x_j^\alpha} \left(\textstyle\sum_{\beta_1} p_s^{\beta_1} \delta(\mathbf{x} - \mathbf{x}^{\beta_1}) \right) \frac{\partial}{\partial p_j^\alpha} \left(\textstyle\sum_{\beta_2} p_i^{\beta_2} \delta(\mathbf{x}' - \mathbf{x}^{\beta_2}) \right) \Bigg]\ . \end{aligned} \tag{D.22}$$

The first factor on the right hand side of Eq. (D.22) is readily obtained: $(\partial/\partial p_j^\alpha)(\sum_{\beta_1} p_s^{\beta_1} \delta(\mathbf{x} - \mathbf{x}^{\beta_1})) = \delta_{js} \delta(\mathbf{x} - \mathbf{x}')$. In the same way we can compute the last factor on the right in the second line of Eq. (D.22). Let us now concentrate on the factors in the middle: $(\partial/\partial x_j^\alpha)(\sum_{\beta_2} p_i^{\beta_2} \delta(\mathbf{x}' - \mathbf{x}^{\beta_2})) = (\sum_{\beta_2} p_i^{\beta_2} (\partial/\partial x_j^\alpha) \delta(\mathbf{x}' - \mathbf{x}^{\beta_2}))$. The differentiation of the delta function gives

$$\frac{\partial}{\partial x_j^\alpha} \prod_{k=1}^{3} \delta(x_k' - x_k^{\beta_2}) = \sum_{k=1}^{3} \delta\,'(x_k' - x_k^{\beta_2})(-1)\, \delta_{jk} \delta_{\alpha\beta_2} \prod_{r \neq k} \delta(x_r' - x_r^{\beta_2}) \tag{D.23}$$

The expression $(\partial/\partial x_j^\alpha)(\sum_{\beta_1} p_s^{\beta_1} \delta(\mathbf{x} - \mathbf{x}^{\beta_1}))$ is treated similarly. Substitution of the previous results back into Eq. (D.22) yields

$$\begin{aligned} \{j_s(\mathbf{x}), j_i(\mathbf{x}')\} \equiv \sum_{\alpha j} \Bigg[& \Big(\delta_{js} \delta(\mathbf{x} - \mathbf{x}^\alpha) \Big) \sum_{\beta_2} p_i^{\beta_2} (-1) \delta\,'(x_j' - x_j^{\beta_2}) \delta_{\alpha\beta_2} \prod_{r \neq j} \delta(x_r' - x_r^{\beta_2}) \\ & - \sum_{\beta_1} p_s^{\beta_1} (-1) \delta\,'(x_j' - x_j^{\beta_1}) \delta_{\alpha\beta_1} \prod_{r \neq j} \delta(x_r' - x_r^{\beta_1}) \Big(\delta_{ij} \delta(\mathbf{x}' - \mathbf{x}^\alpha) \Big) \Bigg]\ . \end{aligned} \tag{D.24}$$

Summation over indices β_1 and β_2 is carried out next. Due to the Dirac deltas δ_{js} and δ_{ij} we can also perform the summation over j:

$$\begin{aligned}\{j_s(\mathbf{x}), j_i(\mathbf{x}')\} = \sum_\alpha \Big[& \delta(\mathbf{x}-\mathbf{x}^\alpha)(-p_i^\alpha)\delta\,'(x_s'-x_s^\alpha)\prod_{r\neq s}\delta(x_r'-x_r^\alpha) \\ & + p_s^\alpha\delta\,'(x_i-x_i^\alpha)\prod_{r\neq i}\delta(x_r-x_r^\alpha)\;\delta(\mathbf{x}'-\mathbf{x}^\alpha)\Big] .\end{aligned} \tag{D.25}$$

We can again use the same trick which was introduced in the context of Eq. (D.15). Thanks to the delta function $\delta(\mathbf{x}-\mathbf{x}^\alpha)$ in the first line of Eq. (D.25), we can replace the particle coordinates x_s^α and x_r^α appearing in the consecutive terms $\delta\,'(x_s'-x_s^\alpha)\prod_{r\neq s}\delta(x_r'-x_r^\alpha)$ with the components of $\mathbf{x}$. Similar arguments apply the the second line of the right hand side of Eq. (D.25) as well:

$$\begin{aligned}\{j_s(\mathbf{x}), j_i(\mathbf{x}')\} = \sum_\alpha \Big[& \delta(\mathbf{x}-\mathbf{x}^\alpha)(-p_i^\alpha)\delta\,'(x_s'-x_s)\prod_{r\neq s}\delta(x_r-x_r') \\ & + p_s^\alpha\delta\,'(x_i-x_i')\prod_{r\neq i}\delta(x_r-x_r')\;\delta(\mathbf{x}'-\mathbf{x}^\alpha)\Big] .\end{aligned} \tag{D.26}$$

The summation over index α can now be performed. In the first and the second term of the previous equation this gives rise to factors $j_i(\mathbf{x})$ and $j_s(\mathbf{x}')$, respectively:

$$\{j_s(\mathbf{x}), j_i(\mathbf{x}')\} = -j_i(\mathbf{x})\;\delta\,'(x_s'-x_s)\prod_{r\neq s}\delta(x_r'-x_r) + \delta\,'(x_i-x_i')\prod_{r\neq i}\delta(x_r-x_r')\;j_s(\mathbf{x}') \;. \tag{D.27}$$

Both terms can be further simplified by extracting the derivative operator as shown for the first term on the right: $\delta\,'(x_s'-x_s)\prod_{r\neq s}\delta(x_r'-x_r) = \partial_s'\delta(\mathbf{x}'-\mathbf{x})$. Hence,

$$\{j_s(\mathbf{x}), j_i(\mathbf{x}')\} = -j_i(\mathbf{x})\,\partial_s'\delta(\mathbf{x}'-\mathbf{x}) + \partial_i\delta(\mathbf{x}-\mathbf{x}')\,j_s(\mathbf{x}') \;, \tag{D.28}$$

where the order of the arguments $\mathbf{x}$ and $\mathbf{x}'$ in the arguments of the delta functions should be noted. The abbreviations $\partial_s' \equiv \partial/\partial x_s'$ and $\partial_i \equiv \partial/\partial x_i$.

What remains to be calculated is the action of the Poisson bracket kernels on an arbitrary function $f(\mathbf{x})$. By partial integration it is easy to show that

$$\int d\mathbf{x}'\,\{j_s(\mathbf{x}), j_i(\mathbf{x}')\}\,f(\mathbf{x}') = j_i(\mathbf{x})\,\partial_s f(\mathbf{x}) + \partial_i\Big(j_s(\mathbf{x})f(\mathbf{x})\Big) \;. \tag{D.29}$$

It is particularly interesting to apply this result to the case $f = \delta F_k/\delta j_i(\mathbf{x})$ where the momentum density dependent part of $F_k = \int d\mathbf{x}\, j^2(\mathbf{x})/(2\phi)$ where $\phi = \mathit{const}$ is the average density, which does not have any spatial dependence. Since ϕ is just a constant, we can scale it away as far as the following calculation goes. Substitution of $f(\mathbf{x}) = \delta F_k[\mathbf{j}]/\delta j_i(\mathbf{x}) = j_i(\mathbf{x})$ into Eq. (D.29) gives

$$\int d\mathbf{x}'\,\{j_s(\mathbf{x}), j_i(\mathbf{x}')\}\,\frac{\delta F_k[\mathbf{j}]}{\delta j_i(\mathbf{x})} = j_i(\mathbf{x})\,\partial_s j_i(\mathbf{x}) + \partial_i\Big(j_s(\mathbf{x})j_i(\mathbf{x})\Big) \tag{D.30}$$

$$= \frac{1}{2}\partial_s j^2(\mathbf{x}) + j_s(\mathbf{x})\,\nabla\cdot\mathbf{j}(\mathbf{x}) + (\mathbf{j}(\mathbf{x})\cdot\nabla)\,j_s(\mathbf{x}) \;. \tag{D.31}$$

The last equality follows by expanding the Einstein summation in Eq. (D.30). The first term on the right hand side of Eq. (D.30) is $j_i \partial_s j_i = (1/2)\, \partial_s j^2$ with $j^2 = j_1^2 + j_2^2 + j_3^2$. The second term on the right is $\partial_i (j_s j_i) = \partial_1 (j_s j_1) + \partial_2 (j_s j_2) + \partial_3 (j_s j_3) = j_s \nabla \cdot \mathbf{j} + (\mathbf{j} \cdot \nabla)\, j_s$. Summing up these contributions gives Eq. (D.31). The result of Eq. (D.31) should be compared with the same calculation performed with a spatially varying density field in the expression of the free energy: $F_k = \int d\mathbf{x}\, j^2(\mathbf{x})/(2\phi(\mathbf{x}))$. As will be demonstrated later on, there will be no term present in the final equation of motion of the momentum density (or velocity) which would be proportional to the divergence of momentum density ($j_s \nabla \cdot \mathbf{j}$). To obtain the model H of critical dynamics [297], where ϕ is replaced with the average constant critical density of the fluids one should make the additional assumption that $\nabla \cdot \mathbf{j} = 0$. This condition cannot be derived in the present formalism as an additional constraint independent of the mass conservations equation. Though, it is true that the latter reduces to the incompressibility condition if we assume that the density is constant everywhere and that there is no diffusive nor random mass flux.

D.1.3 From momentum to velocity representation

Since the equations of fluid dynamics are more frequently written using velocity field as the primary variable, we re-derive the Poisson bracket relations of the previous sections in terms of $\mathbf{v}$. This cannot be done directly since we do not know what is the form of the velocity field in terms of the microscopic coordinate and momenta. We have to use the identification,

$$\phi(\mathbf{x})\, \mathbf{v}(\mathbf{x}) \equiv \mathbf{j}(\mathbf{x}) \ , \tag{D.32}$$

which is a nontrivial relation as it relates the *product* of two macroscopic (averaged) fields to a third one [244]. In far from equilibrium situation it is not obvious that such a relation holds (p. 50, Ref. [45]). It should also be noted that $\mathbf{v}$ is a function all microscopic coordinate and momenta of the fluid particles and in that sense a macroscopic quantity. In the single particle limit it obviously reduces to the standard form $mv(t) = p(t)$ relating the momentum of the particle to its velocity. Since we know the microscopic expressions of ϕ and $\mathbf{j}$, we can formally solve for the velocity:

$$\mathbf{v}(\mathbf{x}) \equiv \frac{\mathbf{j}(\mathbf{x})}{\phi(\mathbf{x})} \ . \tag{D.33}$$

Despite the delta function nature of the denominator the quotient on the right should be well defined formally, since both $\mathbf{j}$ and ϕ have their zeroes at the same places thereby ' they cancel each other out'. Using Eq. (D.33) and the identity of Poisson brackets, $\{A, BC\} = B\{A, C\} + \{A, B\}C$, gives

$$\{\phi(\mathbf{x}), v_i(\mathbf{x}')\} = \left\{\phi(\mathbf{x}), \frac{1}{\phi(\mathbf{x}')} j_i(\mathbf{x}')\right\} = \frac{1}{\phi(\mathbf{x}')} \{\phi(\mathbf{x}), j_i(\mathbf{x}')\} \ , \tag{D.34}$$

because $\{\phi(\mathbf{x}), 1/\phi(\mathbf{x}')\} = 0$ as there is no dependence on the microscopic momenta in ϕ. The bracket between ϕ and j_i has been computed in Eq. (D.18). Thus,

$$\left\{ \begin{array}{l} \{\phi(\mathbf{x}), v_i(\mathbf{x}')\} = \partial_i \delta(\mathbf{x} - \mathbf{x}') \ . \\ \{v_i(\mathbf{x}), \phi(\mathbf{x}')\} = -\partial_i' \delta(\mathbf{x}' - \mathbf{x}) \ . \end{array} \right. \tag{D.35}$$

The latter equation follows directly from the first one by interchanging $\mathbf{x}$, $\mathbf{x}'$ and by multiplying both sides of the equation with (-1). When operating on an arbitrary function f, we get

$$\begin{cases} \displaystyle\int d\mathbf{x}' \, \{\phi(\mathbf{x}), v_i(\mathbf{x}')\} \, f(\mathbf{x}') = \partial_i f(\mathbf{x}) \ . \\ \displaystyle\int d\mathbf{x}' \, \{v_i(\mathbf{x}), \phi(\mathbf{x}')\} \, f(\mathbf{x}') = \partial_i f(\mathbf{x}) \ . \end{cases} \tag{D.36}$$

Irrespective of the order of the fields ϕ and v_i, the operation of both kernels on f gives the same result. Next, we produce the Poisson brackets between two components of the velocity field. Using the identity for the brackets we can write

$$\{v_s(\mathbf{x}), v_i(\mathbf{x}')\} = \left\{ \frac{1}{\phi(\mathbf{x})} j_s(\mathbf{x}), \frac{1}{\phi(\mathbf{x}')} j_i(\mathbf{x}') \right\} = \tag{D.37}$$

$$j_s(\mathbf{x}) \left\{ \frac{1}{\phi(\mathbf{x})}, j_i(\mathbf{x}') \right\} \frac{1}{\phi(\mathbf{x}')} + j_i(\mathbf{x}') \left\{ j_s(\mathbf{x}), \frac{1}{\phi(\mathbf{x}')} \right\} \frac{1}{\phi(\mathbf{x})} + \{j_s(\mathbf{x}), j_i(\mathbf{x}')\} \frac{1}{\phi(\mathbf{x}')} \frac{1}{\phi(\mathbf{x})} . \tag{D.38}$$

In Eq. (D.38) there is also a fourth term which vanishes since it is proportional to the Poisson bracket of the inverse densities $\{1/\phi(\mathbf{x}), 1/\phi(\mathbf{x}')\} = 0$. Let us start working on the two bracket expressions whose value we do not know yet. First, by definition

$$\left\{ \frac{1}{\phi(\mathbf{x})}, j_i(\mathbf{x}') \right\} \equiv \sum_{\alpha j} \left[\frac{\partial \phi^{-1}(\mathbf{x})}{\partial p_j^\alpha} \frac{\partial j_i(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial \phi^{-1}(\mathbf{x})}{\partial x_j^\alpha} \frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha} \right] \tag{D.39}$$

$$= \frac{1}{\phi^2(\mathbf{x})} \sum_{\alpha j} \frac{\partial \phi(\mathbf{x})}{\partial x_j^\alpha} \frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha} = -\frac{1}{\phi^2(\mathbf{x})} \{\phi(\mathbf{x}), j_i(\mathbf{x}')\} = -\frac{1}{\phi^2(\mathbf{x})} \partial_i \delta(\mathbf{x} - \mathbf{x}') \, \phi(\mathbf{x}') \ , \tag{D.40}$$

where we used Eq. (D.18). Since the density ϕ does not contain microscopic momenta, the first term in the square brackets on the right hand side of the Eq. (D.39) vanishes. We have also used the chain rule: $\partial \phi^{-1}(\mathbf{x}) / \partial x_j^\alpha = (-1) \phi^{-2}(\mathbf{x}) \partial \phi(\mathbf{x}) / \partial x_j^\alpha$. Similarly we obtain

$$\left\{ j_i(\mathbf{x}), \frac{1}{\phi(\mathbf{x}')} \right\} = \frac{1}{\phi^2(\mathbf{x}')} \phi(\mathbf{x}) \, \partial_s' \delta(\mathbf{x}' - \mathbf{x}) \ . \tag{D.41}$$

Now all the Poisson brackets appearing in Eq. (D.38) are known. Substitution gives

$$\begin{aligned} \{v_s(\mathbf{x}), v_i(\mathbf{x}')\} = {} & \frac{j_s(\mathbf{x})}{\phi(\mathbf{x}')} \left[-\frac{\phi(\mathbf{x}')}{\phi^2(\mathbf{x})} \partial_i \delta(\mathbf{x} - \mathbf{x}') \right] + \frac{j_i(\mathbf{x}')}{\phi(\mathbf{x})} \left[-\frac{\phi(\mathbf{x})}{\phi^2(\mathbf{x}')} \partial_s' \delta(\mathbf{x}' - \mathbf{x}) \right] \\ & + \frac{1}{\phi(\mathbf{x}) \phi(\mathbf{x}')} \left[-j_i(\mathbf{x}) \partial_s' \delta(\mathbf{x}' - \mathbf{x}) + \partial_i' \delta(\mathbf{x} - \mathbf{x}') \, j_s(\mathbf{x}') \right] . \end{aligned} \tag{D.42}$$

Using the definition $j_i(\mathbf{x}) = \phi(\mathbf{x}) v_i(\mathbf{x})$ and cancelling out the common factors we simplify the previous equation and obtain

$$\{v_s(\mathbf{x}), v_i(\mathbf{x}')\} = \tag{D.43}$$

$$= -\frac{v_s(\mathbf{x})}{\phi(\mathbf{x})} \partial_i \delta(\mathbf{x} - \mathbf{x}') + \frac{v_i(\mathbf{x}')}{\phi(\mathbf{x}')} \partial_s' \delta(\mathbf{x}' - \mathbf{x}) - \frac{v_i(\mathbf{x})}{\phi(\mathbf{x}')} \partial_s' \delta(\mathbf{x}' - \mathbf{x}) + \frac{v_s(\mathbf{x}')}{\phi(\mathbf{x})} \partial_i \delta(\mathbf{x} - \mathbf{x}') \ .$$

Grouping the terms finally gives the result which has been quoted in Eq. (9.18). The action of this kernel on $\delta F_k / \delta v_j$ has been given in Eq. (9.22). Indeed, it should be noticed that there is no term which is proportional to $\nabla \cdot \mathbf{v}$ as there is a term $\nabla \cdot \mathbf{j}$ in Eq. (D.31). This is because in the latter case the density ϕ in the free energy functional $F_k = \int d\mathbf{x} \, j^2(\mathbf{x})/2$ was assumed to be a constant, so it can be scaled out. Contrary to that, in the former case we allowed $\phi(\mathbf{x})$ to vary spatially, which leads to $F_k = \int d\mathbf{x} \, j^2(\mathbf{x})/(2\phi(\mathbf{x})) = \int d\mathbf{x} \, \phi(\mathbf{x}) v^2(\mathbf{x})/2$. In Sect. D.2.1 we demonstrate in more detail that both variables $\mathbf{v}$ and $\mathbf{j}$ are good macroscopic variables in the sense that they produce the same deterministic part of the equation of motion for mass and momentum densities.

D.1.4 Poisson brackets involving energy density

Let us first work out the Poisson bracket of the energy density and the mass density. We divide the internal energy, given by Eq. (D.3), into two parts: $\mathcal{E} = \mathcal{E}_k + \mathcal{E}_p$ where $\mathcal{E}_k \equiv \sum_\alpha (\mathbf{p}^\alpha)^2/(2m)$ and $\mathcal{E}_p(\mathbf{x}) \equiv (1/2)\sum_{\alpha\neq\beta} V(\mathbf{x}^{\alpha\beta})\,\delta(\mathbf{x}-\mathbf{x}^\alpha(t))$. First, we notice that $\{\mathcal{E}_p(\mathbf{x}), \phi(\mathbf{x}')\} = 0$ as there is no dependence on the microscopic momenta in either of the functions. The bracket including the $\mathcal{E}_k$ gives:

$$\{\mathcal{E}_k(\mathbf{x}), \phi(\mathbf{x}')\} \equiv \sum_{\alpha j}\left[\frac{\partial \mathcal{E}_k(\mathbf{x})}{\partial p_j^\alpha}\frac{\partial \phi(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial \phi(\mathbf{x}')}{\partial p_j^\alpha}\frac{\partial \mathcal{E}_k(\mathbf{x})}{\partial x_j^\alpha}\right] = \sum_{\alpha j}\frac{\partial \mathcal{E}_k(\mathbf{x})}{\partial p_j^\alpha}\frac{\partial \phi(\mathbf{x}')}{\partial x_j^\alpha} \tag{D.44}$$

$$= \sum_{\alpha j}\frac{1}{m}p_j^\alpha\delta(\mathbf{x}-\mathbf{x}^\alpha)\,(-m)\partial'_j\delta(\mathbf{x}'-\mathbf{x}^\alpha) = -\sum_j\sum_\alpha p_j^\alpha\delta(\mathbf{x}-\mathbf{x}^\alpha)\partial'_j\delta(\mathbf{x}'-\mathbf{x})\ , \tag{D.45}$$

where we have used the fact that $\partial\phi/\partial p_j^\alpha = 0$. Combining the results for $\mathcal{E}_k$ and $\mathcal{E}_p$, we write in vector notation

$$\{\mathcal{E}(\mathbf{x}), \phi(\mathbf{x}')\} = -\mathbf{j}(\mathbf{x})\cdot\nabla'\delta(\mathbf{x}'-\mathbf{x})\ , \tag{D.46}$$

where $\nabla' \equiv \sum_{i=1}^3 \mathbf{e}_i\partial'_i$. Similarly, one obtains $\{\phi(\mathbf{x}), \mathcal{E}(\mathbf{x}')\} = \mathbf{j}(\mathbf{x}')\cdot\nabla\delta(\mathbf{x}-\mathbf{x}')$. The Poisson bracket of the mass and energy density is expressible in terms of the coarse-grained variables ($\mathbf{j}$) but this is not true for the Poisson bracket of energy and momentum density.

Next, we calculate $\{\mathcal{E}(\mathbf{x}), j_i(\mathbf{x}')\} = \{\mathcal{E}_k(\mathbf{x}), j_i(\mathbf{x}')\} + \{\mathcal{E}_p(\mathbf{x}), j_i(\mathbf{x}')\}$. As in the previous case, we compute the first bracket on the right hand side yielding

$$\{\mathcal{E}_k(\mathbf{x}), j_i(\mathbf{x}')\} \equiv \sum_{\alpha j}\left[\frac{\partial \mathcal{E}_k(\mathbf{x})}{\partial p_j^\alpha}\frac{\partial j_i(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha}\frac{\partial \mathcal{E}_k(\mathbf{x})}{\partial x_j^\alpha}\right] \tag{D.47}$$

$$= \sum_{\alpha j}\frac{1}{m}p_j^\alpha\delta(\mathbf{x}-\mathbf{x}^\alpha)\frac{\partial j_i(\mathbf{x}')}{\partial x_j^\alpha} + \frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha}\frac{1}{2m}(\mathbf{p}^\alpha)^2\,\partial_j\delta(\mathbf{x}-\mathbf{x}^\alpha)\ . \tag{D.48}$$

where we used $\partial\mathcal{E}_k(\mathbf{x})/\partial p_j^\alpha = (1/m)p_j^\alpha\delta(\mathbf{x}-\mathbf{x}^\alpha)$ and $\partial\mathcal{E}_k(\mathbf{x})/\partial x_j^\alpha = -(1/2m)(\mathbf{p}^\alpha)^2\,\partial_j\delta(\mathbf{x}-\mathbf{x}^\alpha)$. Substitution of the expressions, $\partial j_i(\mathbf{x}')/\partial x_j^\alpha = -p_i^\alpha\partial'_j\delta(\mathbf{x}'-\mathbf{x}^\alpha)$ and $\partial j_i(\mathbf{x}')/\partial p_j^\alpha = \delta_{ij}\delta(\mathbf{x}'-\mathbf{x}^\alpha)$ into Eq. (D.48) gives

$$\{\mathcal{E}_k(\mathbf{x}), j_i(\mathbf{x}')\} = -\sum_j\partial'_j\delta(\mathbf{x}'-\mathbf{x})\sum_\alpha\frac{1}{m}p_j^\alpha p_i^\alpha\delta(\mathbf{x}-\mathbf{x}^\alpha) + \mathcal{E}_k(\mathbf{x}')\,\partial_i\delta(\mathbf{x}-\mathbf{x}')\ . \tag{D.49}$$

The first term on the right hand side is not representable in terms of the fields (ϕ, $\mathbf{j}$, $\mathcal{E}$). Similar thing happens for the Poisson bracket of $\mathcal{E}_p$ and j_i, which we calculate next.

$$\{\mathcal{E}_p(\mathbf{x}), j_i(\mathbf{x}')\} \equiv \sum_{\alpha j}\left[\frac{\partial \mathcal{E}_p(\mathbf{x})}{\partial p_j^\alpha}\frac{\partial j_i(\mathbf{x}')}{\partial x_j^\alpha} - \frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha}\frac{\partial \mathcal{E}_p(\mathbf{x})}{\partial x_j^\alpha}\right] = -\sum_{\alpha j}\frac{\partial j_i(\mathbf{x}')}{\partial p_j^\alpha}\frac{\partial \mathcal{E}_p(\mathbf{x})}{\partial x_j^\alpha} \tag{D.50}$$

The first equality follows because $\mathcal{E}_p$ is only a function of the coordinates $\mathbf{x}^\alpha$. The first factor, $\partial j_i(\mathbf{x}')/\partial p_j^\alpha$ has been given above. Concentrating on the second,

$$\frac{\partial\mathcal{E}_p(\mathbf{x})}{\partial x_j^\alpha} = \left(\frac{\partial}{\partial x_j^\alpha}\frac{1}{2}\sum_{\alpha_1\neq\alpha_2}V(\mathbf{x}^{\alpha_1\alpha_2})\right)\delta(\mathbf{x}-\mathbf{x}^\alpha) + \frac{1}{2}\sum_{\alpha_1\neq\alpha_2}V(\mathbf{x}^{\alpha_1\alpha_2})\frac{\partial\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})}{\partial x_j^\alpha}\ . \tag{D.51}$$

The derivative appearing in the second term on the right is given by $\partial\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})/\partial x_j^\alpha = (-1)\delta_{\alpha\alpha_1}\partial_j\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})$. The derivative of the potential term gives the total force on particle at $\mathbf{x}^\alpha$:

$$\frac{\partial}{\partial x_j^\alpha}(1/2)\sum_{\alpha_1\neq\alpha_2} V(\mathbf{x}^{\alpha_1\alpha_2}) = \sum_{\alpha_1(\neq\alpha_2)} \tilde{V}_j'(\mathbf{x}^{\alpha\alpha_1}) \ , \tag{D.52}$$

where we have defined $\tilde{V}_j'(\mathbf{x}^{\alpha\alpha_1}) \equiv (x_j^\alpha - x_j^{\alpha_1})[(dV(r)/dr)r^{-1}]_{r=|\mathbf{x}^{\alpha_1\alpha_2}|}$. Therefore, the Poisson bracket can be written as

$$\{\mathcal{E}_p(\mathbf{x}), j_i(\mathbf{x}')\} = -\delta(\mathbf{x}'-\mathbf{x})\sum_{\alpha_1\neq\alpha_2}\tilde{V}_i'(\mathbf{x}^{\alpha_1\alpha_2})\delta(\mathbf{x}-\mathbf{x}^{\alpha_1}) + \mathcal{E}_p(\mathbf{x}')\,\partial_i\delta(\mathbf{x}-\mathbf{x}') \ . \tag{D.53}$$

Combining the previous equation with Eq. (D.49) gives the final answer

$$\{\mathcal{E}(\mathbf{x}), \mathbf{j}(\mathbf{x}')\} = -\mathbf{P}^\ddagger(\mathbf{x})\cdot\nabla'\delta(\mathbf{x}'-\mathbf{x}) - \mathbf{W}(\mathbf{x})\,\delta(\mathbf{x}'-\mathbf{x}) + \mathcal{E}(\mathbf{x}')\,\nabla\delta(\mathbf{x}-\mathbf{x}') \ , \tag{D.54}$$

where we have defined the momentum flux density tensor $\mathbf{P}^\ddagger$ (which is a function of the microscopic coordinate and momenta as opposed to $\mathbf{P}$ introduced in Eq. (D.72)) and a vector quantity $\mathbf{W}(\mathbf{x})$ which represents the total force acting on all the molecules inside the (infinitesimal) fluid element situated at $\mathbf{x}$ arising from the pairwise interaction with the other molecules outside of the element:

$$\mathbf{P}_{ij}^\ddagger(\mathbf{x}) \equiv \sum_\alpha \frac{1}{m}p_i^\alpha p_j^\alpha\,\delta(\mathbf{x}-\mathbf{x}^\alpha) \ \ ; \ \ W_i(\mathbf{x}) \equiv \sum_{\alpha_1\neq\alpha_2}\tilde{V}_i'(\mathbf{x}^{\alpha_1\alpha_2})\,\delta(\mathbf{x}-\mathbf{x}^{\alpha_1}) \ . \tag{D.55}$$

Thus, we have introduced two new macro fields $\mathbf{P}^\ddagger$ and $\mathbf{W}$ whose microscopic expressions given in Eq. (D.55) are not directly expressible in terms of the other macroscopic variables (ϕ, $\mathbf{j}$, $\mathcal{E}$).

D.2 Comparison of momentum and velocity representations

First we show that the same equations of motion are generated in both the momentum and velocity representations if the dissipative and stochastic terms are left out. Inclusion of them makes the two representations inequivalent. In other words, starting from the momentum balance equation (which we consider more fundamental than the velocity) and using the identification $\mathbf{j} = \phi\mathbf{v}$ leads to a different equation of motion for the velocity as compared to the equation, which emerges when we treat velocity as the fundamental variable and apply the Poisson bracket formalism to it.

D.2.1 Galilean invariant part of the equation of motion

We derive the deterministic part of the momentum and mass balance equations. Eq. (9.10) reduces to the form $\partial_t\psi_\mu(\mathbf{x},t) = N_\mu$, where $N_\mu = -\int d\mathbf{x}' Q_{\mu\nu}(\mathbf{x},\mathbf{x}')\delta F_k[\psi]/\delta\psi_\mu(\mathbf{x}')$ when the dissipative and random fluxes are left out. In terms of variable $\mathbf{j}$ the kinetic part of the free energy is

$$F_k[\phi,\mathbf{j}] \equiv \int d\mathbf{x}\,\frac{1}{2\phi(\mathbf{x})}j^2(\mathbf{x}) \ . \tag{D.56}$$

The deterministic part of the equation of motion of mass density, $\psi_u = \phi$, becomes

$$\partial_t\phi + \int d\mathbf{x}' \, \{\phi(\mathbf{x}), j_s(\mathbf{x}')\} \, \frac{\delta F_k[\phi,\mathbf{j}]}{\delta j_s(\mathbf{x}')} = \partial_t\phi + \int d\mathbf{x}' \, \{\phi(\mathbf{x}), j_s(\mathbf{x}')\} \left(\frac{1}{\phi(\mathbf{x})} j_s(\mathbf{x})\right) \quad (D.57)$$

$$= \partial_t\phi + \partial_s \left[\phi(\mathbf{x}) \left(\frac{1}{\phi(\mathbf{x})} j_s(\mathbf{x})\right)\right] = 0 \ , \quad (D.58)$$

where we have used Eq. (D.18). In other words,

$$\partial_t\phi + \nabla \cdot \mathbf{j} = 0 \ . \quad (D.59)$$

Changing the fundamental variable of the free energy from $\mathbf{j}$ to $\mathbf{v}$ means that the form of the kinetic part of the free energy functional changes. Instead of Eq. (D.56) we must use

$$F_k[\phi, \mathbf{v}] = \int d\mathbf{x} \, \frac{1}{2} \phi(\mathbf{x}) v^2(\mathbf{x}) \ . \quad (D.60)$$

The equation of motion, $\partial_t\psi_\mu - N_\mu = 0$, now reads

$$\partial_t\phi + \int d\mathbf{x}' \, \{\phi(\mathbf{x}), v_s(\mathbf{x}')\} \, \frac{\delta F_k[\phi,\mathbf{v}]}{\delta v_s(\mathbf{x}')} = \partial_t\phi + \int d\mathbf{x}' \, \{\phi(\mathbf{x}), v_s(\mathbf{x}')\} \, (\phi(\mathbf{x}') v_s(\mathbf{x}')) \quad (D.61)$$

$$= \partial_t\phi + \partial_s \left(\phi(\mathbf{x}) v_s(\mathbf{x})\right) = 0 \ , \quad (D.62)$$

where we used Eq. (D.35). In the vector notation we can express the previous relation as

$$\partial_t\phi + \nabla \cdot (\phi\mathbf{v}) = 0 \ , \quad (D.63)$$

which is the same as the equation of motion (D.59) in terms of the momentum density variable.

Let us now turn to the momentum balance equation. Using first the momentum density $\mathbf{j}$ as the basic variable we start with the equation of motion $\partial_t\psi_\mu(\mathbf{x},t) - N_\mu = 0$ where $\psi_\mu = j_s$. Then,

$$\partial_t j_s + \int d\mathbf{x}' \, \{j_s(\mathbf{x}), \phi(\mathbf{x}')\} \, \frac{\delta F_k[\phi,\mathbf{j}]}{\phi(\mathbf{x}')} + \int d\mathbf{x}' \, \{j_s(\mathbf{x}), j_i(\mathbf{x}')\} \, \frac{\delta F_k[\phi,\mathbf{j}]}{j_i(\mathbf{x}')} = 0 \ . \quad (D.64)$$

Let us first compute the second term on the left hand side. Using Eq. (D.56) and the fact that $\delta F_k[\phi,\mathbf{j}]/\delta\phi(\mathbf{x}') = (-1/2)(j^2(\mathbf{x}')/\phi^2(\mathbf{x}'))$ it can be written as

$$\int d\mathbf{x}' \, \{j_s(\mathbf{x}), \phi(\mathbf{x}')\} \, \frac{\delta F_k[\phi,\mathbf{j}]}{\phi(\mathbf{x}')} = -\frac{1}{2}\phi(\mathbf{x}) \, \partial_s \left(\frac{1}{\phi^2(\mathbf{x})} j^2(\mathbf{x})\right) \ . \quad (D.65)$$

Since $\delta F_k[\phi,\mathbf{j}]/\delta j_i(\mathbf{x}') = j_i(\mathbf{x}')/\phi(\mathbf{x}')$ the third term on the left hand side of Eq. (D.64) becomes

$$\int d\mathbf{x}' \, \{j_s(\mathbf{x}), j_i(\mathbf{x}')\} \, \frac{\delta F_k[\phi,\mathbf{j}]}{j_i(\mathbf{x}')} = j_i(\mathbf{x}) \, \partial_s \left(\frac{1}{\phi(\mathbf{x})} j_i(\mathbf{x})\right) + \partial_i \left(j_s(\mathbf{x}) \, \frac{1}{\phi(\mathbf{x})} j_i(\mathbf{x})\right) . \quad (D.66)$$

Substitution of Eq. (D.65) and Eq. (D.66) into Eq. (D.64) gives the deterministic part of the momentum balance equation expressed in variable $\mathbf{j}$. It can be recast into the more familiar form by substituting $\mathbf{j} = \phi\mathbf{v}$. We obtain

$$\partial_t(\phi v_s) - \frac{1}{2}\phi \, \partial_s(v^2) + \phi v_i \, \partial_s v_i + \partial_i(\phi v_s v_i) = 0 \ , \quad (D.67)$$

where $v^2 \equiv v_1^2 + v_2^2 + v_3^2$. Using the deterministic part of the equation of motion of the mass density, which we have shown to be the same in both $\mathbf{j}$ and $\mathbf{v}$ representations, we can rewrite the first term on the left as $\partial_t(\phi v_s) = -\partial_i(\phi v_i) + \phi\, \partial_t v_s$. Substitution of this result back into Eq. (D.67) and cancelling out a few terms it becomes

$$\phi \left(\partial_t v_s + v_i\, \partial_i v_s \right) = 0 \ . \tag{D.68}$$

This says just that the acceleration of the fluid element is zero when there are no forces acting on it. If we prefer to use $F_k[\phi, \mathbf{v}]$ given in Eq. (D.60) instead of $F_k[\phi, \mathbf{j}]$, we obtain

$$\partial_t v_s + \int d\mathbf{x}' \left\{ v_s(\mathbf{x}), \phi(\mathbf{x}') \right\} \frac{\delta F_k[\phi, \mathbf{v}]}{\phi(\mathbf{x}')} + \int d\mathbf{x}' \left\{ v_s(\mathbf{x}), v_i(\mathbf{x}') \right\} \frac{\delta F_k[\phi, \mathbf{v}]}{v_i(\mathbf{x}')} = 0 \ . \tag{D.69}$$

as compared to Eq. (D.64). Because $\delta F_k[\phi, \mathbf{v}]/\phi(\mathbf{x}') = (1/2)\, v^2(\mathbf{x})$, the second term on the left hand side becomes

$$\int d\mathbf{x}' \left\{ v_s(\mathbf{x}), \phi(\mathbf{x}') \right\} \frac{\delta F_k[\phi, \mathbf{v}]}{\phi(\mathbf{x}')} = \frac{1}{2} \partial_s v^2(\mathbf{x}) \ , \tag{D.70}$$

where we have also used Eq. (D.36). Based on Eq. (9.20) we can write the third term on the left hand side of Eq. (D.69) as

$$\int d\mathbf{x}' \left\{ v_s(\mathbf{x}), v_i(\mathbf{x}') \right\} \frac{\delta F_k[\phi, \mathbf{v}]}{v_i(\mathbf{x}')} = -v_s \frac{1}{\phi} \partial_i(\phi v_i) - \partial_s v^2 + v_i \partial_s v_i + \frac{1}{\phi} \partial_i(v_s\, \phi v_i) \ . \tag{D.71}$$

Finally, substitution of Eq. (D.70) and Eq. (D.71) into Eq. (D.69) gives again the zero force condition of Eq. (D.68). All in all we have established the momentum density and velocity representations are tied together through

$$\partial_t \mathbf{j} + \nabla \cdot \mathbf{P} = \phi \left(\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) \ , \tag{D.72}$$

where $\mathbf{P}$ is the (macroscopic) momentum flux density tensor: $\mathbf{P}_{ij} = (1/\phi) j_i j_j$. It is very important to note that the macroscopic fields are replaced directly with their expectation values when forming the final equations of motion. All cross correlations present in nonlinear product terms are neglected in the process of coarse-graining through averaging over a suitable ensemble. There are situations, though, where this type of procedure can be justified. This happens can happen if the density matrix can be factorized for mutually commuting operators representing the relevant variables (cf. Sect. 3.2). Constitutive equations of hydrodynamics [1] are formed in such a way that the cross correlations do not have to be considered. It should also be noted that the constitutive equation $\mathbf{j} = \phi \mathbf{v}$, which we have used in this section and in Sect. D.1.3 can be derived using macroscopic arguments based on zero entropy production (p. 445 in Ref. [5]). This argument cannot be used, of course, when the fluids are viscous and there is dissipation. Alternatively, one can use Galilean invariance to fix the relationship between velocity and momentum.

D.2.2 Incompatibility of velocity and momentum density

We use the method of macroscopic Poisson brackets to derive the mass and momentum balance equations, as well as the equation of motion for the velocity field to make a quantitative comparison between the latter two. As we will see, there are considerable discrepancies, which call attention to the choice of the fundamental coarse-grained variables. The set $(\phi, \mathbf{j})$ is better suited for some purposes than $(\phi, \mathbf{v})$ but they cannot be made totally equivalent through identification $\phi\mathbf{v} = \mathbf{j}$ except in the simplest cases, as far as the Poisson bracket formalism is used to construct the hydrodynamic equations. Retaining just the mass and momentum density variables and leaving out energy, Eq. (9.35) gives

$$\partial_t \phi = -\int d\mathbf{x}' \left\{\phi(\mathbf{x}), j_s(\mathbf{x}')\right\} \frac{\delta F_t}{\delta j_s(\mathbf{x}')} + \Gamma_{00} \nabla^2 \frac{\delta F_t}{\delta \phi(\mathbf{x})} + \eta_0 \ . \tag{D.73}$$

The dissipative couplings Γ_{0i} $(i = 1, 2, 3)$ to momentum density have been set to zero. Using Eq. (D.20) and

$$\frac{\delta F_t}{\delta \phi} = -\frac{1}{2\phi^2} j^2 + \mu_2 \ , \tag{D.74}$$

where we have defined $\mu_2 \equiv \mu_f + V_S$, the mass balance equation becomes

$$\partial_t \phi = -\nabla \cdot \mathbf{j} + \Gamma_{00} \nabla^2 \Big(-\frac{1}{2\phi^2} j^2 + \mu_2 \Big) + \eta_0 \ . \tag{D.75}$$

From the momentum balance equation (9.36) the Poisson bracket with energy density is dropped and the dissipative coefficient Γ_{i0} is set to zero. The operator ∇^2 in front of the dissipative momentum term with coefficient Γ_{ii} implies certain properties of the momentum field. For simplicity, we retain it here, but for more general discussion the reader is referred to Sect. 9.5.2. Hence,

$$\partial_t j_i = \tag{D.76}$$

$$-\int d\mathbf{x}' \left\{j_i(\mathbf{x}), \phi(\mathbf{x}')\right\} \frac{\delta F_t}{\delta \phi(\mathbf{x}')} - \int d\mathbf{x}' \left\{j_i(\mathbf{x}), j_s(\mathbf{x}')\right\} \frac{\delta F_t}{\delta j_s(\mathbf{x}')} + \ \Gamma_{i\nu} \nabla^2 \frac{\delta F_t}{\delta j_\nu(\mathbf{x})} + \eta_i \ .$$

Plugging in the relevant brackets from Sect. D.2.1 we can rewrite the momentum equation:

$$\partial_t j_i = -\nabla_s \Big(\frac{1}{\phi} j_i j_s \Big) - \phi \nabla_i \mu_2 + \Gamma_{i\nu} \nabla^2 \frac{\delta F_t}{\delta j_\nu(\mathbf{x})} + \eta_i \ . \tag{D.77}$$

If $\Gamma_{i\nu} = \Gamma \delta_{i\nu}$ $(i, \nu = 1, 2, 3)$, then we can express the dissipative term as $\Gamma_{i\nu} \nabla^2 \delta F_t / \delta j_\nu(\mathbf{x}) = \Gamma \nabla^2 (j_i/\phi)$. Let us first consider the situation where continuity equation holds by dropping the the dissipative and stochastic terms from Eq. (D.75) which becomes $\partial_t \phi = -\nabla \cdot \mathbf{j}$. Using this and the identification $\mathbf{j} = \phi \mathbf{v}$, we can cast the momentum balance equation into the following form:

$$\phi \Big(\partial_t v_i + (\mathbf{v} \cdot \nabla) v_i \Big) = -\phi \nabla_i \mu_2 + \Gamma \nabla^2 v_i + \eta_i \tag{D.78}$$

If $\mathbf{v}$ is taken to the fundamental coarse-grained variable instead of the momentum density, we have to repeat the derivation and replace j_i with v_i in Eq. (D.76). Of coarse, the Poisson brackets will still have to be calculated with the aid of the momentum density as shown in App. D.1.3. The outcome is

$$\partial_t v_i + (\mathbf{v} \cdot \nabla) v_i = -\nabla_i \mu_2 + \hat{\Gamma} \nabla^2 (\phi v_i) + \tilde{\eta}_i \ . \tag{D.79}$$

Clearly the dissipative terms are different as compared to Eq. (D.78) unless the dissipative coefficient $\hat{\Gamma}$ is defined to be a non-local operator dependent on the density field ϕ in such a way that $\hat{\Gamma}(\phi)\nabla^2(\phi v_i) = (1/\phi)\Gamma\nabla^2 v_i$. However, this leads to multiplicative noise $\tilde{\eta}_i$ in order not to violate fluctuation-dissipation theorem. Thus, we clearly see that even when the mass balance equation reduces to the standard continuity equation, it does make a difference whether one first takes $\mathbf{j}$ to be the fundamental variable and later on obtains the evolution equation for $\mathbf{v}$ via substitution $\mathbf{j} = \phi\mathbf{v}$, or one treats $\mathbf{v}$ as the fundamental variable, and uses $\mathbf{j} = \phi\mathbf{v}$ only to be able to calculate the Poisson brackets of the velocity field with other relevant coarse-grained fields. When dissipation is left out of the description, everything works fine as shown in App. D.2.1.

We clearly see that when $\mathbf{v}$ is taken to be the fundamental variable, there will be no other interesting terms generated in the equation of motion except for those appearing in Eq. (D.79). However, if we treat $\mathbf{j}$ as the fundamental quantity (after all, we should, since it is the conserved variable), and derive an equation of motion for $\mathbf{v}$ as we did above, we do get new terms if the full form of the mass balance equation is used. In other words, the left hand side of the momentum balance equation gives $\partial_t j_i = \partial_t(\phi v_i) = (\partial_t\phi)v_i + \phi\partial_t v_i$. Substitution of the right hand side of mass balance Eq. (D.75) for $\partial_t\phi$ gives the following equation for the velocity field

$$\phi\Big(\partial_t v_i + (\mathbf{v}\cdot\nabla)v_i\Big) = -\phi\nabla_i\mu_2 - \Gamma_{00}\Big[\nabla^2\Big(-\frac{1}{2\phi^2}j^2 + \mu_2\Big)\Big]v_i - \eta_0 v_i + \Gamma\nabla^2 v_i + \eta_i \qquad \text{(D.80)}$$

What we have done here is exactly opposite to Ref. [303], where the momentum balance equation was used to give an expression for $\mathbf{j}(\phi)$, which was substituted back into the continuity equation $\partial_t\phi = -\nabla\cdot\mathbf{j}(\phi)$. The point is that the dissipative and stochastic elements contained in the momentum equation were transformed into corresponding elements of the order parameter (ϕ) equation. Going the other way around, we have managed to bring in some new dissipative and stochastic structure in the equation of motion of the velocity field. Of course, the structure of the stochastic and dissipative terms has changed, it is not easy to see by inspection if the fluctuation-dissipation theorem holds any more. In Ref. [303] the theorem was approximately shown to be true. However, the extra complication in the present case is that we have also utilized the identification $\mathbf{j}(\mathbf{x}) = \phi(\mathbf{x})\mathbf{v}(\mathbf{x})$, which complicates things. The properties of the term in square brackets are analyzed in Sect. 11.3.2.

D.3 Comparison with Hamiltonian formalisms

Having derived the necessary Poisson bracket relations in the previous sections we derive the reactive part of the equation of motion based on the representation given in Eq. (9.10): $\partial\psi_\mu = N_\mu$ when no dissipation or stochastic fluctuation is allowed. The full set of equations of motion for gross variables is given by

$$\begin{aligned}\partial_t\phi = &-\int d\mathbf{x}'\,\{\phi(\mathbf{x}),\phi(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}'\,\{\phi(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} \qquad \text{(D.81)}\\ &-\int d\mathbf{x}'\,\{\phi(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')}\;.\end{aligned}$$

$$\begin{aligned}\partial_t j_i = &-\int d\mathbf{x}'\,\{j_i(\mathbf{x}),\phi(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\phi(\mathbf{x}')} - \int d\mathbf{x}'\,\{j_i(\mathbf{x}),j_s(\mathbf{x}')\}\,\frac{\delta F_t}{\delta j_s(\mathbf{x}')} \qquad \text{(D.82)}\\ &-\int d\mathbf{x}'\,\{j_i(\mathbf{x}),\mathcal{E}(\mathbf{x}')\}\,\frac{\delta F_t}{\delta\mathcal{E}(\mathbf{x}')}\;.\end{aligned}$$

$$\begin{aligned}\partial_t \mathcal{E} = &- \int d\mathbf{x}' \left\{\mathcal{E}(\mathbf{x}), \phi(\mathbf{x}')\right\} \frac{\delta F_t}{\delta \phi(\mathbf{x}')} - \int d\mathbf{x}' \left\{\mathcal{E}(\mathbf{x}), j_s(\mathbf{x}')\right\} \frac{\delta F_t}{\delta j_s(\mathbf{x}')} \\ &- \int d\mathbf{x}' \left\{\mathcal{E}(\mathbf{x}), \mathcal{E}(\mathbf{x}')\right\} \frac{\delta F_t}{\delta \mathcal{E}(\mathbf{x}')} \ .\end{aligned} \tag{D.83}$$

These relations make only sense when the total free energy functional $F_t[\phi, \mathbf{j}, \mathcal{E}]$ has the correct dependence on all of its arguments. So far, the free energy, which we have derived and used in Sect. 9.1 has been of the form $F_t[\phi, \mathbf{j}]$, which means that none of the terms involving $\delta F_t/\delta\mathcal{E}$ can be evaluated at this point. Below we will settle for studying properties where we can make use of the microscopic expression of the energy density. For more discussion on how to obtain the correct energy dependence of the free energy, we refer the reader to Sect. 6.5.

In App. D.2.1 we have shown that if we replace F_t with $F_k[\phi, \mathbf{j}] \equiv \int d\mathbf{x} j^2(\mathbf{x})/(2\phi(\mathbf{x}))$, the correct reactive contributions to the equations of motion of the mass and momentum densities are recovered. All terms (Eq. (D.83) entirely) involving $\mathcal{E}$ above vanish in this case. To get an idea about the theory with five gross variables we can in the first approximation write

$$F_t[\phi, j, \mathcal{E}_p] \equiv \int d\mathbf{x} \left(\mathcal{E}_k(\mathbf{x}) + \mathcal{E}_p(\mathbf{x})\right) \equiv \int d\mathbf{x} \left(\frac{1}{2\phi(\mathbf{x})} j^2(\mathbf{x}) + \mathcal{E}_p(\mathbf{x})\right) . \tag{D.84}$$

One possible approximation is such that we set $\mathcal{E}_p(\mathbf{x}) = (1/2) \sum_{\alpha_1 \neq \alpha_2} V(\mathbf{x}^{\alpha_1\alpha_2}) \delta(\mathbf{x} - \mathbf{x}^{\alpha_1})$. More appropriately, the dependence of F_t on $\mathcal{E}_p$ is likely to be something more complicated than linear relationship of Eq. (D.84) but we can use this to start with. In a sense, it is not completely unjustified to choose the potential energy to be the primary coarse-grained variable of the theory instead of the full energy density $\mathcal{E}$ which also contains the kinetic energy. Even though, $\mathcal{E}_p$ is not conserved unlike $\mathcal{E}$, it is possible to express it as a function of the conserved variables: $\mathcal{E}_p(\mathbf{x}) = \mathcal{E}(\mathbf{x}) - j^2(\mathbf{x})/(2\phi(\mathbf{x}))$. In this sense the situation is analogous to the use of the velocity field determined with the aid of the conserved momentum field: $\mathbf{v}(\mathbf{x}) \equiv \mathbf{j}(\mathbf{x})/\phi(\mathbf{x})$. However, one should keep in mind that just like $\mathbf{v}$ and $\mathbf{j}$ can be noncompatible in the sense discussed in Sect. D.2.2, so are $\mathcal{E}$ and $\mathcal{E}_p$. Replacing $\mathcal{E}$ by $\mathcal{E}_p$ in the set of evolution equations above gives a fully reasonable result, though:

$$\partial_t \phi = -\nabla \cdot \mathbf{j}(\mathbf{x}) \ . \tag{D.85}$$

$$\partial_t \mathbf{j} = -\nabla \cdot \left(\frac{1}{\phi(\mathbf{x})} \mathbf{j}(\mathbf{x})\mathbf{j}(\mathbf{x})\right) - \sum_{\alpha_1 \neq \alpha_2} \tilde{\mathbf{V}}'(\mathbf{x}^{\alpha_1\alpha_2})\, \delta(\mathbf{x} - \mathbf{x}^{\alpha_1}) \ . \tag{D.86}$$

$$\partial_t \mathcal{E}_p = \nabla \cdot \left[\sum_{\alpha_1 \neq \alpha_2} \frac{1}{2} V(|\mathbf{x}^{\alpha_1\alpha_2}|) \delta(\mathbf{x} - \mathbf{x}^{\alpha_1}) \frac{\mathbf{p}^{\alpha_1}}{m}\right] + \sum_{\alpha_1 \neq \alpha_2} \tilde{\mathbf{V}}'(\mathbf{x}^{\alpha_1\alpha_2})\, \delta(\mathbf{x} - \mathbf{x}^{\alpha_1}) \cdot \frac{\mathbf{p}^{\alpha_2}}{m} \ . \tag{D.87}$$

To obtain the first equation notice that $\{\phi(\mathbf{x}), \phi(\mathbf{x}')\} = \{\mathcal{E}_p(\mathbf{x}), \mathcal{E}_p(\mathbf{x}')\} = 0$. Eq. (D.86) can also be written as $\partial_t \mathbf{j} = -\nabla \cdot \mathbf{P} - \mathbf{W}$, where $\mathbf{P}$ is the pressure tensor expressed in macro variables $\mathbf{j}$ and ϕ. Finally, in Eq. (D.87) the first term is the internal energy flux vector and the second describes the changes in internal energy due to the interaction forces. If we replace the macroscopic pressure tensor $\mathbf{P}$ in Eq. (D.86) with its microscopic counter part $\mathbf{P}^{\ddagger}_{ij} \equiv \sum_\alpha (1/m)\, p^\alpha_i p^\alpha_j \delta(\mathbf{x} - \mathbf{x}^\alpha)$, we obtain exactly the correct Hamiltonian equations of motion for the fields (ϕ, $\mathbf{j}$, $\mathcal{E}_p$). In other words, with the replacements mentioned, Eq. (D.85) - Eq. (D.87) are exactly the same as the ones below:

$$\partial_t \phi \quad = \quad \{\phi(\mathbf{x}), H\} \ . \tag{D.88}$$

$$\begin{aligned} \partial_t \mathbf{j} &= \{\mathbf{j}(\mathbf{x}), H\}\ . && \text{(D.89)}\\ \partial_t \mathcal{E}_p &= \{\mathcal{E}_p(\mathbf{x}), H\}\ . && \text{(D.90)} \end{aligned}$$

The Hamiltonian is not a function of position above as compared to the energy density given in Eq. (D.3):

$$H \equiv \sum_\alpha \frac{1}{2m}(p^\alpha)^2 + \frac{1}{2}\sum_{\alpha\neq\beta} V(|\mathbf{x}^{\alpha\beta}|)\ . \tag{D.91}$$

The reason why it is necessary to replace the $\mathbf{P}$ with $\mathbf{P}^\ddagger$ derives from the mixed representation used in the definition of the free energy (Eq. (D.84)): The kinetic energy part is given in terms of the macroscopic fields $\mathcal{E}_k(\mathbf{x}) = j^2(\mathbf{x})/(2\phi(\mathbf{x}))$ whereas the potential energy part has its exact microscopic form decorated by an additional delta function: $\mathcal{E}_p(\mathbf{x}) = (1/2)\sum_{\alpha_1\neq\alpha_2} V(|\mathbf{x}^{\alpha_1\alpha_2}|)\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})$.

Thus, with proper interpretation of the macroscopic fields, we can regenerate the equations of motion obtained from Hamiltonian formalism. If we want to obtain the Hamilton's equation of motion directly, without worrying about interpretation, we can redefine a non-coarse-grained free energy to be equal to the microscopic Hamiltonian,

$$F_t[\mathcal{E}] = \int d\mathbf{x} \sum_\alpha \left[\frac{1}{2m}(p^\alpha)^2 + \frac{1}{2}\sum_{\alpha(\neq\beta)} V(|\mathbf{x}^{\alpha\beta}|)\right]\delta(\mathbf{x}-\mathbf{x}^\alpha) \equiv \int d\mathbf{x}\, \mathcal{E}(\mathbf{x})\ , \tag{D.92}$$

where we have used the energy density defined in Eq. (D.3). Writing now the equations of motion for field variables (ϕ, $\mathbf{j}$, $\mathcal{E}$) we are going to show that the choice made in Eq. (D.92) leads to

$$\begin{aligned} \partial_t \phi &= -\int d\mathbf{x}'\, \{\phi(\mathbf{x}), \mathcal{E}(\mathbf{x}')\}\, \frac{\delta F_t[\mathcal{E}]}{\delta \mathcal{E}(\mathbf{x}')} = \{\phi(\mathbf{x}), H\}\ . && \text{(D.93)}\\ \partial_t j_i &= -\int d\mathbf{x}'\, \{j_i(\mathbf{x}), \mathcal{E}(\mathbf{x}')\}\, \frac{\delta F_t[\mathcal{E}]}{\delta \mathcal{E}(\mathbf{x}')} = \{j_i(\mathbf{x}), H\}\ . && \text{(D.94)}\\ \partial_t \mathcal{E} &= -\int d\mathbf{x}'\, \{\mathcal{E}(\mathbf{x}), \mathcal{E}(\mathbf{x}')\}\, \frac{\delta F_t[\mathcal{E}]}{\delta \mathcal{E}(\mathbf{x}')} = \{\mathcal{E}(\mathbf{x}), H\}\ . && \text{(D.95)} \end{aligned}$$

Thus, for the special case where the free energy is just a (linear) functional of the energy density (zero temperature limit), the Poisson bracket formalism is identical to the Hamiltonian formalism, as it should. As opposed to Eqs. (D.81) - (D.83), no other Poisson brackets emerge in Eqs. (D.93) - (D.95), except those with energy density, since it is the only variable in the free energy. Eqs. (D.93) - (D.95) can be easily confirmed since $\delta F_t[\mathcal{E}]/\delta\mathcal{E}(\mathbf{x}') = 1$ and in the remaining expressions the integration over $\mathbf{x}'$ destroys unwanted terms. Explicit computation based on the results of App. D.1.4 gives

$$\begin{aligned} \partial_t \phi &= -\nabla\cdot\Big(\sum_\alpha \mathbf{p}^\alpha \delta(\mathbf{x}-\mathbf{x}^\alpha)\Big)\ . && \text{(D.96)}\\ \partial_t j_i &= -\nabla\cdot\Big(\sum_\alpha \frac{1}{m} p_i^\alpha p_j^\alpha \delta(\mathbf{x}-\mathbf{x}^\alpha)\Big) - \sum_{\alpha_1\alpha_2} \tilde{\mathbf{V}}'(\mathbf{x}^{\alpha_1\alpha_2})\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})\ . && \text{(D.97)}\\ \partial_t \mathcal{E} &= -\nabla\cdot\Big(\sum_{\alpha_1}\left[\frac{(p^{\alpha_1})^2}{2m} + \frac{1}{2}\sum_{\alpha_2(\neq\alpha_1)} V(|\mathbf{x}^{\alpha_1\alpha_2}|)\right]\frac{\mathbf{p}^{\alpha_1}}{m}\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})\Big)\\ &\qquad + \sum_{\alpha_1\neq\alpha_2} \tilde{\mathbf{V}}'(\mathbf{x}^{\alpha_1\alpha_2})\left(\frac{\mathbf{p}^{\alpha_1}}{m} + \frac{\mathbf{p}^{\alpha_2}}{m}\right)\delta(\mathbf{x}-\mathbf{x}^{\alpha_1})\ . && \text{(D.98)} \end{aligned}$$

This result coincides with the Hamiltonian equations of motion which has been derived *e.g.* in Ref. [1]. In terms of the mass ($\mathbf{j}$), momentum ($\mathbf{\Pi}$) and energy fluxes ($\mathbf{j}^{\varepsilon}$) we can rewrite the Hamilton's equations of motion (Eq. (D.93) - (D.95)) as

$$\begin{aligned}
\partial_t \phi &= \{\phi(\mathbf{x}), H\} \equiv -\nabla \cdot \mathbf{j} \ . && \text{(D.99)} \\
\partial_t j_i &= \{j_i(\mathbf{x}), H\} \equiv -\nabla \cdot \mathbf{\Pi} \ . && \text{(D.100)} \\
\partial_t \mathcal{E} &= \{\mathcal{E}(\mathbf{x}), H\} \equiv -\nabla \cdot \mathbf{j}^{\varepsilon} \ . && \text{(D.101)}
\end{aligned}$$

Extraction of the divergence operator leads to the emergence of the delta function factor,

$$\Delta(\mathbf{x}, \mathbf{x}^{\alpha}, \mathbf{x}^{\beta}) \equiv \int_{-1}^{1} d\lambda \ \delta\Big(\mathbf{x} - \frac{1}{2}(\mathbf{x}^{\alpha} + \mathbf{x}^{\beta}) - \frac{\lambda}{2}\mathbf{x}^{\alpha\beta}\Big) \ , \tag{D.102}$$

which is present in the expressions of the momentum and energy fluxes. From Ref. [1] we get

$$\mathbf{\Pi}_{ij}(\mathbf{x}, t) \equiv \sum_{\alpha} \frac{1}{m} p_i^{\alpha} p_j^{\alpha} \delta(\mathbf{x} - \mathbf{x}^{\alpha}) - \frac{1}{2} \sum_{\alpha \neq \beta} x_j^{\alpha\beta} \tilde{V}_i'(\mathbf{x}^{\alpha\beta}) \, \Delta(\mathbf{x}, \mathbf{x}^{\alpha}, \mathbf{x}^{\beta}) \ . \tag{D.103}$$

$$\begin{aligned}
j_i^{\varepsilon}(\mathbf{x}, t) \equiv & \sum_{\alpha} \left[\frac{(p^{\alpha})^2}{2m} + \frac{1}{2} \sum_{\beta(\neq\alpha)} V(\mathbf{x}^{\alpha\beta}) \right] \frac{p_i^{\alpha}}{m} \delta(\mathbf{x} - \mathbf{x}^{\alpha}) \\
& - \frac{1}{4m} \sum_{\alpha \neq \beta} x_i^{\alpha\beta} \tilde{V}_j'(\mathbf{x}^{\alpha\beta}) (p_i^{\alpha} + p_i^{\beta}) \, \Delta(\mathbf{x}, \mathbf{x}^{\alpha}, \mathbf{x}^{\beta}) \ . && \text{(D.104)}
\end{aligned}$$

The momentum flux is given by Eq. (D.2) as in our case. Thus, we have been able to generate the correct Hamilton's equation of motion from the Poisson bracket formalism by defining the free energy to the integral over the internal energy density (Eq. (D.92)).

We conclude this section by considering the quantum mechanical equivalent of the equations of motion presented in Eq. (D.99) - (D.101). Use of the Heisenberg equation of motion for general observable $\hat{A}$, $\imath\hbar\partial_t \hat{A} = \left[\hat{A}, \hat{H}\right]$, leads to

$$\begin{aligned}
\partial_t \hat{\phi}(\mathbf{x}, t) &= -\frac{\imath}{\hbar} \left[\hat{\phi}(\mathbf{x}, t), \hat{H}\right] = -\nabla \cdot \hat{\mathbf{j}}(\mathbf{x}, t) \ . && \text{(D.105)} \\
\partial_t \hat{j}_i(\mathbf{x}, t) &= -\frac{\imath}{\hbar} \left[\hat{j}_i(\mathbf{x}, t), \hat{H}\right] = -\nabla \cdot \hat{\mathbf{\Pi}}(\mathbf{x}, t) \ . && \text{(D.106)} \\
\partial_t \hat{\mathcal{E}}(\mathbf{x}, t) &= -\frac{\imath}{\hbar} \left[\hat{\mathcal{E}}(\mathbf{x}, t), \hat{H}\right] = -\nabla \cdot \hat{\mathbf{j}}^{\varepsilon} \ . && \text{(D.107)}
\end{aligned}$$

The Hamiltonian is connected with the energy density through $\hat{H} = \int d\mathbf{x} \hat{\mathcal{E}}(\mathbf{x}, t)$, which is the quantum analogue of the non-coarse-grained classical relation of Eq. (D.92). The forms of the conserved observables are given by

$$\begin{aligned}
\hat{\phi}(\mathbf{x}, t) &\equiv \psi^{\dagger}(\mathbf{x}, t)\psi(\mathbf{x}, t) \ ; && \text{(D.108)} \\
\hat{\mathbf{j}}(\mathbf{x}, t) &\equiv \frac{\imath\hbar}{2m} \left[(\nabla\hat{\psi}^{\dagger})\hat{\psi} - \hat{\psi}^{\dagger}(\nabla\hat{\psi})\right] \ ; && \text{(D.109)} \\
\hat{\mathcal{E}}(\mathbf{x}, t) &\equiv \frac{\hbar^2}{2m}(\nabla\hat{\psi}^{\dagger}) \cdot (\nabla\hat{\psi}) + \frac{1}{2}\int d\mathbf{x}' \, V(|\mathbf{x} - \mathbf{x}'|)\hat{\psi}^{\dagger}(\mathbf{x}, t)\hat{\phi}(\mathbf{x}', t)\hat{\psi}(\mathbf{x}, t) \ . && \text{(D.110)}
\end{aligned}$$

where $\hat{\psi}$ and $\hat{\psi}^\dagger$ are the field annihilation and creation operators. The momentum flux density operator appearing in Eq. (D.106) is [245, 188]

$$\hat{\mathbf{\Pi}}_{ij}(\mathbf{x},t) \equiv \tag{D.111}$$
$$-\frac{\hbar^2}{4m}\left[(\nabla_i - \nabla'_i)(\nabla_j - \nabla'_j)\,\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\right]_{\mathbf{x}=\mathbf{x}'} - \frac{1}{4}\int d\mathbf{x}'\left[\frac{x'_i x'_j}{x'}\frac{dV(x')}{dx'}\right]\hat{\Delta}(\mathbf{x},\mathbf{x}',\hat{\phi})\ .$$

The current flux density operator given in Eq. (D.107) is [245]

$$\hat{j}^{\varepsilon}_i(\mathbf{x},t) \equiv \tag{D.112}$$
$$-\frac{\imath}{\hbar}(\hbar^2/(2m))^2\left[(\nabla_i - \nabla'_i)\nabla'\cdot\nabla\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\right]_{\mathbf{x}=\mathbf{x}'}$$
$$+\frac{1}{2}\int d\mathbf{x}'\,V(|\mathbf{x}-\mathbf{x}'|)\,\hat{\psi}^\dagger(\mathbf{x}')\hat{j}_i(\mathbf{x})\hat{\psi}(\mathbf{x}') - \frac{1}{4}\sum_s\int d\mathbf{x}'\left[\frac{x'_i x'_s}{x'}\frac{dV(x')}{dx'}\right]\hat{\Delta}(\mathbf{x},\mathbf{x}',\hat{j}_s)\ .$$

In both of the previous equations we have used an operator $\hat{\Delta}$ which for a general operator ($\hat{A} = \hat{\phi}$ or $\hat{A} = \hat{j}_s$) is defined through

$$\hat{\Delta}(\mathbf{x},\mathbf{x}',\hat{A}) \equiv \int_{-1}^{1} d\lambda\,\hat{\psi}^\dagger\Big(\mathbf{x}+\frac{1}{2}(1+\lambda)\mathbf{x}'\Big)\hat{A}\Big(\mathbf{x}-\frac{1}{2}(1-\lambda)\mathbf{x}'\Big)\hat{\psi}\Big(\mathbf{x}+\frac{1}{2}(1+\lambda)\mathbf{x}'\Big)\ . \tag{D.113}$$

The results given above have direct relevance not only for quantum objects, such as superfluids but also for classical fluids and many-body systems in general.

D.4 Fokker-Planck and Langevin descriptions

The fundamental equation of motion of the order parameter formalism given in Eq. (9.10). We will show that the requirement of relaxation to Gibbsian equilibrium state through a white noise process fixes the form of the evolution equation of the coarse-grained variables. Since the evolution equation will be of Langevin equation type the time evolution of the probability distribution of the system is given by a Fokker-Planck equation.

We start from microscopics and make use of the Hamilton's equation of motion, which for any component ψ_μ of the classical vector $\psi^\ddagger \equiv (\psi^\ddagger_1,\ldots,\psi^\ddagger_N)$, is given in terms of the Poisson bracket with the Hamiltonian H:

$$\partial_t\psi^\ddagger_\mu = \left\{H,\psi^\ddagger_\mu\right\}\ . \tag{D.114}$$

Both $\psi^\ddagger_\mu$ and H are non-coarse-grained functions of the microscopic coordinate and momenta, which is indicated explictly by the use of the symbol ‡. If, for simplicity, we neglect all correlations arising upon averaging $\langle\cdot\rangle_m$ over the probability density (non-equilibrium average in general) we can average all terms in the previous equation separately and obtain a coarse-grained evolution equation for the order parameter field $\psi \equiv \langle\psi^\ddagger\rangle_m$:

$$\partial_t\psi_\mu = \{F[\psi],\psi_\mu\}\ , \tag{D.115}$$

where $F[\psi] \equiv \langle H\rangle_m$ is the coarse-grained Hamiltonian or (generalized) free energy functional as we usually call it. As the Poisson bracket with the Hamiltonian (free energy functional) might be tedious to compute directly, it is advantageous to perform it with the aid of the Poisson brackets related to other components of the order parameter vector. Starting from microscopics we obtain

$$\partial_t \psi^\ddagger(\mathbf{x}) = \Big\{ H[\psi^\ddagger], \psi^\ddagger_\mu(\mathbf{x}) \Big\} \; \equiv \; \sum_{\alpha j} \left[\frac{\partial H[\psi^\ddagger]}{\partial p^\alpha_j} \frac{\partial \psi^\ddagger_\mu(\mathbf{x})}{\partial x^\alpha_j} - \frac{\partial H[\psi^\ddagger]}{\partial x^\alpha_j} \frac{\partial \psi^\ddagger_\mu(\mathbf{x})}{\partial p^\alpha_j} \right] \tag{D.116}$$

$$= \sum_{\alpha j} \int d\mathbf{x}' \left[\frac{\delta H[\psi^\ddagger]}{\delta \psi^\ddagger_\nu(\mathbf{x}')} \frac{\partial \psi^\ddagger_\nu(\mathbf{x}')}{\partial p^\alpha_j} \frac{\partial \psi^\ddagger_\mu(\mathbf{x})}{\partial x^\alpha_j} - \frac{\delta H[\psi^\ddagger]}{\delta \psi^\ddagger_\nu(\mathbf{x}')} \frac{\partial \psi^\ddagger_\nu(\mathbf{x}')}{\partial x^\alpha_j} \frac{\partial \psi^\ddagger_\mu(\mathbf{x})}{\partial p^\alpha_j} \right] . \tag{D.117}$$

In the last line we can separate out the the common factor $\delta H / \delta \psi^\ddagger_\nu$ which leads to

$$\partial_t \psi^\ddagger_\mu(\mathbf{x}) = - \int d\mathbf{x}' \, Q^\ddagger_{\mu\nu}(\mathbf{x}, \mathbf{x}') \frac{\delta H[\psi^\ddagger]}{\delta \psi^\ddagger_\nu(\mathbf{x}')} \equiv U^\ddagger_\mu(\mathbf{x}) \; , \tag{D.118}$$

where $Q^\ddagger_{\mu\nu}(\mathbf{x}, \mathbf{x}') \equiv \{\psi^\ddagger_\mu(\mathbf{x}), \psi^\ddagger_\nu(\mathbf{x}')\}$. The entire Poisson bracket contribution to time rate of change of the order operator $\psi^\ddagger_\mu$ is denoted with $U^\ddagger_\mu(\mathbf{x})$. As far as it is possible to present the microscopic Hamiltonian as a functional of the order field operators $\psi^\ddagger(\mathbf{x})$ the resulting Eq. (D.118) is exact. Depending on the choice of $\psi^\ddagger$ this may not always be possible. If the system is in contact with its surroundings the determination of hydrodynamically relevant variables valid for large length and time scales is discussed in Sect. 3.2. If we assume further that averages over an appropriate ensemble $\langle \cdot \rangle_m$ can be factorized and the cross correlations between various $\psi^\ddagger_\mu$ neglected, we can then rewrite Eq. (D.118) as

$$\partial_t \psi_\mu(\mathbf{x}) = - \int d\mathbf{x}' \, Q_{\mu\nu}(\mathbf{x}, \mathbf{x}') \frac{\delta F[\psi]}{\delta \psi_\nu(\mathbf{x}')} \equiv U_\mu(\mathbf{x}) \; , \tag{D.119}$$

where we have indicated the averages $\langle Q^\ddagger_{\mu\nu} \rangle_m = Q_{\mu\nu}$ and $\langle U^\ddagger_\mu \rangle_m = U_\mu$. As such, Eq. (D.119) does not describe the physical fact that left on their own devices many-body systems relax towards equilibrium state, the Gibbs equilibrium. To facilitate this we have to decorate Eq. (D.119) with dissipative and stochastic force terms:

$$\partial_t \psi_\mu(\mathbf{x}) = U_\mu(\mathbf{x}) - \Gamma_{\mu\nu} \frac{\delta F[\psi]}{\delta \psi_\nu(\mathbf{x})} + \eta_\mu(\mathbf{x}, t) \; . \tag{D.120}$$

The second term on the right represents the coarse-grained relaxational force with dissipative coefficient $\Gamma_{\mu\nu}$ and the last term η_μ describes interaction with the heat bath. The properties of the white noise term are given by

$$\left\{ \begin{array}{l} \langle \eta_\mu(\mathbf{x}, t) \rangle = 0 \; . \\ \langle \eta_\mu(\mathbf{x}, t) \eta_\nu(\mathbf{x}', t') \rangle = 2T\Gamma_{\mu\nu} \delta(\mathbf{x} - \mathbf{x}') \delta(t - t') \; . \end{array} \right. \tag{D.121}$$

It is important to keep in mind that $\langle \cdot \rangle$ is the average over the white noise process η_μ, which is different than the (nonequilibrium) average $\langle \cdot \rangle_m$ introduced when going from the microscopic representation $\psi^\ddagger$ to ψ.

The justification of Eq. (D.120) presented below is based on Ref. [5] with some intermediate steps added. The probability P_ψ of the macro variable field $\psi_\mu(\mathbf{x}, t)$ takes on the value $\psi_\mu(\mathbf{x})$ at time t, given that its initial value at t_0 was $\psi^0_\mu(\mathbf{x})$, is by definition

$$P_\psi\Big(\{\psi_\mu(\mathbf{x})\}, t \,|\, \{\psi^0_\mu(\mathbf{x})\}, t_0 \Big) \equiv \Big\langle \prod_{\mathbf{x}\mu} \delta(\psi_\mu(\mathbf{x}, t) - \psi_\mu(\mathbf{x})) \Big\rangle_{\psi^0_\mu} \; , \tag{D.122}$$

where the curly brackets around the field ($\{\psi_\mu(\mathbf{x})\}$) in the argument list of P_ψ denote the values of field ψ_μ at all points $\mathbf{x}$. The averaging $\langle\cdot\rangle_{\psi^0_\mu}$ is again different from the averages $\langle\cdot\rangle_m$ and $\langle\cdot\rangle$ introduced above. When represented as functional integral it means that only the paths $\psi_\mu(\mathbf{x},t)$ which obey the initial condition $\psi_\mu(\mathbf{x},t_0)=\psi^0_\mu(\mathbf{x})$ are to be included in the average. The average $\langle\cdot\rangle_{\psi^0_\mu}$ constrains in no way the final value the field ψ_μ takes at time t, contrary to the distribution P_ψ. The time evolution of P_ψ is given by the Smoluchowski equation,

$$\begin{aligned}
&P_\psi\Big(\{\psi_\mu(\mathbf{x})\},t+\Delta t\,|\,\{\psi^0_\mu(\mathbf{x})\},t_0\Big) \\
&= \int \mathcal{D}\psi'_\mu\, P_\psi\Big(\{\psi_\mu(\mathbf{x})\},t+\Delta t\,|\,\{\psi'_\mu(\mathbf{x})\},t\Big)\, P_\psi\Big(\{\psi'_\mu(\mathbf{x})\},t\,|\,\{\psi^0_\mu(\mathbf{x})\},t_0\Big)\ .
\end{aligned} \tag{D.123}$$

Functional integration measure is denoted with $\mathcal{D}\psi_\mu$. Based on Eq. (D.122) we can express the first factor appearing on the right hand side of the Smoluchowski equation in the following way:

$$P_\psi\Big(\{\psi_\mu(\mathbf{x})\},t+\Delta t\,|\,\{\psi'_\mu(\mathbf{x})\},t\Big) = \Big\langle \prod_{\mathbf{x}\mu}\delta(\psi_\mu(\mathbf{x},t+\Delta t)-\psi_\mu(\mathbf{x}))\Big\rangle_{\psi'_\mu}\ , \tag{D.124}$$

where the subscript ψ'_μ means initial condition $\{\psi'_\mu(\mathbf{x})\}$ at time t. Next, we make use of our ansatz, Eq. (D.120). Integrating it from time t to time $t+\Delta t$ we get

$$\psi_\mu(\mathbf{x},t+\Delta t) = \psi'_\mu(\mathbf{x}) + \left(U'_\mu - \Gamma_{\mu\nu}\frac{\delta F[\psi']}{\delta\psi'_\mu(\mathbf{x})}\right)\Delta t + \int_t^{t+\Delta t} ds\,\eta_\mu(\mathbf{x},s)\ , \tag{D.125}$$

where U'_μ denotes a functional that depends on ψ'_μ. A slight misuse of notation allows us to write directly $\psi'_\mu(\mathbf{x})$ instead of $\psi'_\mu(\mathbf{x},t)$ as the first term on the right. Substitution of Eq. (D.125) into Eq. (D.124) yields

$$\Big\langle \prod_{\mathbf{x}\mu}\delta(\psi_\mu(\mathbf{x},t+\Delta t)-\psi_\mu(\mathbf{x}))\Big\rangle_{\psi'_\mu} = \Big\langle \prod_{\mathbf{x}\mu}\delta(\psi'_\mu(\mathbf{x})-\psi_\mu(\mathbf{x})+\Delta\psi_\mu(\mathbf{x}))\Big\rangle_{\psi'_\mu} \tag{D.126}$$

where we have defined the change, which contains contributions that are essentially proportional to Δt and $\sqrt{\Delta t}$,

$$\Delta\psi_\mu(\mathbf{x}) \equiv \left(U'_\mu - \Gamma_{\mu\nu}\frac{\delta F[\psi']}{\delta\psi'_\mu(\mathbf{x})}\right)\Delta t + \int_t^{t+\Delta t} ds\,\eta_\mu(\mathbf{x},s)\ . \tag{D.127}$$

In terms of $\Delta\psi_\mu$ we can now expand the functional delta function to first order in time difference. Because the time integral of the noise term is effectively proportional to $\sqrt{\Delta t}$ we have to go to second order in $\Delta\psi_\mu$ to get a first order correct result in Δt when expanding the delta function in Eq. (D.126):

$$\begin{aligned}
&\Big\langle \prod_{\mathbf{x}\mu}\delta(\psi_\mu(\mathbf{x},t+\Delta t)-\psi_\mu(\mathbf{x}))\Big\rangle_{\psi'_\mu} \approx \\
&\Bigg\langle \Big[\prod_{\mathbf{x}\mu}\delta(\psi'_\mu(\mathbf{x})-\psi_\mu(\mathbf{x}))\Big] + \int d\mathbf{x}_1\,\frac{\delta}{\delta\psi'_\mu(\mathbf{x}_1)}\Big[\prod_{\mathbf{x}\mu}\delta(\psi'_\mu(\mathbf{x})-\psi_\mu(\mathbf{x}))\Big]\Delta\psi_\mu(\mathbf{x}_1) \\
&+\frac{1}{2}\int d\mathbf{x}_1\int d\mathbf{x}_2\,\frac{\delta}{\delta\psi'_\mu(\mathbf{x}_1)}\frac{\delta}{\delta\psi'_\nu(\mathbf{x}_2)}\Big[\prod_{\mathbf{x}\mu}\delta(\psi'_\mu(\mathbf{x})-\psi_\mu(\mathbf{x}))\Big]\,\Delta\psi_\mu(\mathbf{x}_1)\Delta\psi_\nu(\mathbf{x}_2)\ \Bigg\rangle_{\psi'_\mu}.
\end{aligned} \tag{D.128}$$

To proceed, we have to change the stochastic variable from $\Delta\psi_\mu(\mathbf{x})$ to $\eta_\mu(\mathbf{x},t)$. Assuming that the Jacobian resulting from the change of variables gives us no trouble (this should be true for stochastic PDEs which are first order in time derivatives and have additive noise), we can simply average over η_μ in Eq. (D.128). When the average is performed all terms which have odd power of noise fields will vanish because of Eq. (D.121). Thus, to first order in Δt,

$$P_\psi\Big(\{\psi_\mu(\mathbf{x})\},t+\Delta t\,|\,\{\psi'_\mu(\mathbf{x})\},t\Big) \approx \Bigg[1+\Delta t\int d\mathbf{x}\left(U'_\mu(\mathbf{x})-\Gamma_{\mu\nu}\frac{\delta F[\psi']}{\delta\psi'_\nu(\mathbf{x})}\right)\frac{\delta}{\delta\psi'_\mu(\mathbf{x})} + \Delta t\,T\,\Gamma_{\mu\nu}\int d\mathbf{x}\,\frac{\delta}{\delta\psi'_\mu(\mathbf{x})}\frac{\delta}{\delta\psi'_\nu(\mathbf{x})}\Bigg]\prod_{\mathbf{x}\mu}\delta(\psi'_\mu(\mathbf{x})-\psi_\mu(\mathbf{x}))\ . \tag{D.129}$$

Substitution of this result back into the Smoluchowski equation (D.123) allows us to perform the functional integral immediately thanks to the functional delta function appearing it the previous formula. We obtain

$$P_\psi\Big(\{\psi_\mu(\mathbf{x})\},t+\Delta t\,|\,\{\psi^0_\mu(\mathbf{x})\},t_0\Big) \approx \Bigg[1+\Delta t\int d\mathbf{x}\left(U_\mu(\mathbf{x})-\Gamma_{\mu\nu}\frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x})}\right)\frac{\delta}{\delta\psi_\mu(\mathbf{x})} + \Delta t\,T\Gamma_{\mu\nu}\int d\mathbf{x}\,\frac{\delta}{\delta\psi_\mu(\mathbf{x})}\frac{\delta}{\delta\psi_\nu(\mathbf{x})}\Bigg]P_\psi\Big(\{\psi_\mu(\mathbf{x})\},t\,|\,\{\psi^0_\mu(\mathbf{x})\},t_0\Big)\ . \tag{D.130}$$

Notice that all ψ'_μ dependence has been replaced with ψ_μ which means that U'_μ has become U_μ, and so on. Dividing both sides by Δt it is easy to see that the previous equation gives

$$\partial_t P_\psi = T\int d\mathbf{x}\,\Gamma_{\mu\nu}\frac{\delta}{\delta\psi_\mu(\mathbf{x})}\left[\left(\frac{\delta}{\delta\psi_\nu(\mathbf{x})}+\frac{1}{T}\frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x})}\right)P_\psi\right]-\int d\mathbf{x}\,\frac{\delta}{\delta\psi_\mu(\mathbf{x})}\left[U_\mu(\mathbf{x})P_\psi\right]\ . \tag{D.131}$$

Derivation of this form assumes that when partial integration is performed, the substitution terms $[U_\mu P_\psi]^{\infty}_{-\infty}$ and $[P_\psi\,\delta F/\delta\psi_\mu]^{\infty}_{-\infty}$ vanish.

Let us check now the validity of the Gibbsian equilibrium assumption. Substitution of $P_\psi = P_{eq} \equiv \exp(-F/T)$ clearly renders the first term on the right hand side of Eq. (D.131) zero. What about the second term? It gives

$$\int d\mathbf{x}\,\frac{\delta}{\delta\psi_\mu(\mathbf{x})}\left[U_\mu(\mathbf{x})P_{eq}\right]=\int d\mathbf{x}\left[-\frac{1}{T}\frac{\delta F[\psi]}{\delta\psi_\mu(\mathbf{x})}\,U_\mu+\frac{\delta U_\mu}{\delta\psi_\mu(\mathbf{x})}\right]P_{eq}\neq 0, \tag{D.132}$$

if we substitute the expression for U_μ defined in Eq. (D.119). To fulfil the requirement of Gibbs distribution as the equilibrium distribution, we repeat the analysis from Eq. (D.120) on. First we write

$$\partial_t\psi_\mu(\mathbf{x}) = N_\mu(\mathbf{x})-\Gamma_{\mu\nu}\frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x})}+\eta_\mu(\mathbf{x},t)\ . \tag{D.133}$$

The difference between Eq. (D.120) and Eq. (D.133) is that in the former the expression of N_μ is unknown. We only know that it should make the integral in Eq. (D.132) vanish when U_μ is replaced with N_μ. We can also assume that U_μ forms part of the correct expression N_μ but there is an extra term the form of which is justified below. Substitution of

$$N_\mu = U_\mu + T\int d\mathbf{x}'\,\frac{\delta Q_{\mu\nu}(\mathbf{x},\mathbf{x}')}{\delta\psi_\nu(\mathbf{x}')} \tag{D.134}$$

yields the desired result [5], $\int d\mathbf{x}\, \delta[N_\mu(\mathbf{x})P_{eq}]/\delta\psi_\mu(\mathbf{x}) = 0$. This can be seen in the following way:

$$\begin{aligned}
&\int d\mathbf{x}\, \frac{\delta}{\delta\psi_\mu(\mathbf{x})}\Big[N_\mu(\mathbf{x})P_{eq}[\psi]\Big] = \\
&\int d\mathbf{x} \int d\mathbf{x}' \left\{ \frac{1}{T}\frac{\delta F[\psi]}{\delta\psi_\mu(\mathbf{x})}\left[Q_{\mu\nu}(\mathbf{x},\mathbf{x}')\frac{\delta F}{\delta\psi_\nu(\mathbf{x}')} - T\frac{\delta Q_{\mu\nu}(\mathbf{x},\mathbf{x}')}{\delta\psi_\nu(\mathbf{x}')}\right]\right. \qquad \text{(D.135)} \\
&\left. - \frac{\delta Q_{\mu\nu}(\mathbf{x},\mathbf{x}')}{\delta\psi_\mu(\mathbf{x})}\frac{\delta F[\psi]}{\delta\psi_\nu(\mathbf{x}')} + Q_{\mu\nu}(\mathbf{x},\mathbf{x}')\frac{\delta^2 F[\psi]}{\delta\psi_\mu(\mathbf{x})\delta\psi_\nu(\mathbf{x}')} - T\frac{\delta^2 Q_{\mu\nu}(\mathbf{x},\mathbf{x}')}{\delta\psi_\mu(\mathbf{x})\delta\psi_\nu(\mathbf{x}')}\right\} P_{eq}[\psi]\ .
\end{aligned}$$

Using the symmetry property of the Poisson bracket term, $Q_{\mu\nu}(\mathbf{x},\mathbf{x}') = -Q_{\mu\nu}(\mathbf{x}',\mathbf{x})$ it is easy to show that the last term on the second line and the first of the last line cancel each other out. The remaining terms all vanish individually.

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