

Carbon Nanotubes under Bending Strain

M. Huhtala, A. Kuronen, and K. Kaski

Helsinki University of Technology, Laboratory of Computational Engineering
P.O.Box 9400, FIN-02015 HUT, FINLAND

ABSTRACT

Bending induced deformations in single walled carbon nanotubes with zigzag and armchair chirality have been studied computationally using a classical molecular dynamics simulation method. In this the interatomic forces have been described with Brenner's empirical model potential. The results given by this classical model have been assessed by letting the most critical, *i.e.* the most deformed part, of the nanotube further relax by using a dynamical tight binding simulation method. We find that the empirical potential based approach and the tight binding method reproduce similar deformation patterns when the deformation remains relatively small but at higher levels of deformation the results differ significantly. These comparative simulations indicate that graphene interlayer interaction is an important factor in the behavior of deformed nanotubes.

INTRODUCTION

Carbon nanotubes are thin molecular wires that exhibit interesting physical properties [1]. Thus they have recently roused a lot of interest in the materials research community. The dimensions of these tubes which are at nanometer scale have ensured that much of this interest can be concretized as computational research. In the computational approach the bottleneck is the model of interactions between constituent atoms of the system – a too simple model might not be able to reproduce the behavior of the system accurately, while a more complicated model might be computationally unachievable.

In this work we compare two interaction models of different complexity in the context of simulating the bending of carbon nanotubes of different chirality. This we have done by using an empirical interaction model between carbon atoms [2] in the Molecular Dynamics (MD) simulation scheme and compare the results with those obtained by employing a dynamical Tight Binding (TB) scheme [3] on the most critical parts of the bent structure. Nanotube bending was chosen as the topic for the work because structural distortions of different magnitude, and thus of different complexity for the interaction model, can be expected [4–6]. Induced deformations, like local bends, have also been demonstrated to be a way to produce nanoelectronic devices [7–9]. This is due to changes in the conductivity properties of the tube under bending [5, 6, 9–11].

SIMULATION METHODS

In this work we have employed two different simulation methods. Large scale bending has been performed using a classical molecular dynamics method, where the atomic interactions are described with the potential energy function of the form of a reactive empirical bond-order hydro-carbon potential formulated by Brenner [2]. The second simulation method, a tight binding method by Frauenheim *et al.*, is described in Ref. [3]. The tight binding method is used to evaluate the performance of the classical method by focusing on a smaller section of the simulated structure.

In the classical molecular dynamics simulation we have used the second potential parametrization presented in Ref. [2]. This is considered better in reproducing force constants than the first one but with somewhat too long bond lengths. In these simulations we have employed a simple and fast relaxation and cooling method. In it the velocity components of each atom are manipulated depending on the components of the gradient of the potential, *i.e.* the particle acceleration. In this method the directions of the components of the acceleration and the velocity of the particle are checked at each time step. If the components are in the same direction, the velocities are left intact but if they are in the opposite directions, the velocity is scaled down by a factor α . In practice, for each component a check whether $v_i \cdot a_i < 0$ is true is performed. The closer the value of α is to zero the faster the cooling process is, but if the cooling is too fast, the particles get easily stuck into a local energy minimum. In the simulations we chose $\alpha = 0.8$ based on test runs and as a compromise between convergence speed and accuracy. The cooling method is used both in simulating a local heat bath, that is, maintaining the simulation temperature at a wanted value, and in the preparation of the samples for the tight binding simulations. In the tight binding simulations a conjugate gradient cooling method has been used. In this scheme the structure is considered sufficiently relaxed when the maximum force acting on the system is less than 10^{-6} in a.u.

SIMULATION RESULTS

Here we report the results of bending two nanotubes of different chirality, an armchair (8, 8)-tube and a zigzag (14, 0)-tube, which are of almost equal diameters differing only 1% in favour of the (14, 0)-tube. The classical molecular dynamics simulations with Brenner's second parametrization potential were performed for system sizes of 2592 and 2632 atoms for the (8, 8)-tube and the (14, 0)-tube, respectively. The corresponding tube lengths are 19.9 nm and 20.0 nm, where the difference in the length is due to difference in the size of the unit cell. Description of the nanotube chirality indexing and unit cells can be found in Ref. [1].

In the simulations we fixed $2.5a_0$ portions from both ends of the tube, where a_0 is the graphite lattice constant 2.46 \AA , and forced one of these ends to move on a semi-circular path, with radius of a half of the tube length. This was done in order to eliminate stretching

the tube as much as possible. The rate of this bending was such that the the end of the tube moved a distance of a_0 in 3000 fs and after a simulation time of 45000 fs it was held in place for 20000 fs in order to let the structure relax. The total simulation time was approximately 400000 fs. During the simulations the system temperature was kept at 300 K with the method described above.

During this bending procedure different types of deformations and bending induced structural changes were observed. These are depicted in Figs. 1 and 2. Fig. 1 presents the total potential energy of the simulated structures as a function of the amount of bending. Fig. 2 shows snapshots of various bending stages for both the (14, 0)- and the (8, 8)-tube. First for small amount of bending both the tubes show oval deformation of the cross section and then, when the local strain overcame some critical value, buckling was observed. This occurs slightly after points b and i in Figs. 1 and 2, respectively, and can be observed as a potential energy decrease in the bent structure. As the bending angle becomes larger the buckle becomes steeper and steeper and also may relocate itself along the tube length, if energetically favored. Labels c and j correspond to the structure after the first relaxation period, which can be seen as a decrease in the potential energy curve. The steep rise in potential energy for the (14, 0)-tube at point d corresponds to a bond breakage at the buckle. In contrast the (8, 8)-tube suffers much less of this kind of damage. At point f a second buckle is formed on the (14, 0)-tube. The potential energy rise is accounted for by bond breakage, which occurs when the buckle is formed. In our simulations we have observed that the armchair (8, 8)-tube bends more smoothly than the zigzag (14, 0)-tube, and without significant structural damage. It is, however, too early to say how and how much the chirality plays a role in the occurrence of damage in the bent tube. Obviously further work is needed to determine this more conclusively.

The set shown in Fig. 2 is a sample of the set chosen as the basis for studying the stability of the structure with the dynamical tight binding simulations. Of each bending stage (a) – (n) in Fig. 2 a slice of approximately 300 particles was chosen such that the slice in each case contain the critical part of the bent structure, *i.e.*, the buckle. With a layer of atoms fixed in both ends the slice was first let to relax using the classical molecular dynamics method with the Brenner empirical potential model. Then the resulting configuration of atoms in this small portion of the system was used as the input configuration for the tight binding program. The relaxation was continued with the dynamical tight binding model and the occurring differences to the relaxed structure obtained with the classical molecular dynamics approach were examined. Figure 3 shows some of these results.

As a result of the tight binding simulations the equilibrium distance between carbon atoms turned out to be slightly shorter than that obtained with the classical molecular dynamics approach using Brenner's second parametrization of the potential. The difference is approximately 2%. Because of the shorter equilibrium distance, the tight binding simulation shows some distortion inwards which is due to its desire for shorter bonding. This should be taken into account when interpreting the results.

Our simulations also indicate that there is a difference in the relaxed configurations that

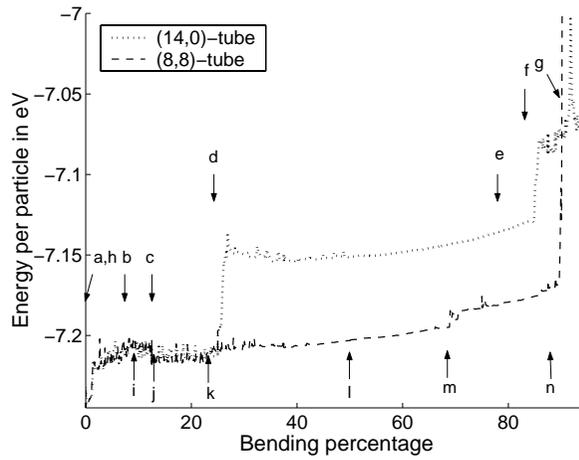


Figure 1: Potential energy development of the (14, 0)- and the (8, 8)-tube under bending. A rising trend in the potential energy is observed as the tube is bent. Abrupt rises correspond to bond breakages and local decreases to buckle formation and buckle relocation. Labels $a - n$ refer to Fig. 2. On the horizontal axis 100% corresponds to the system being bent the full semicircle.

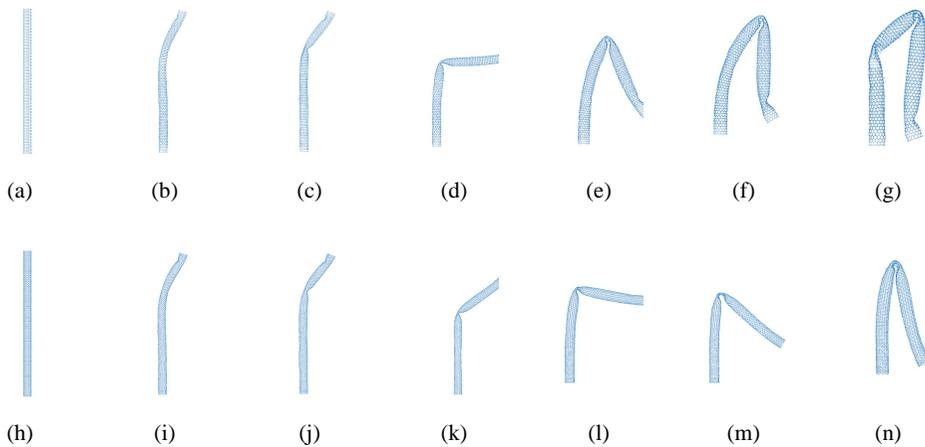


Figure 2: Two series of images depicting the nanotube behavior in the course of increased bending. Images (a)-(g) correspond to the bending of the (14, 0)-tube and images (h)-(n) to the (8, 8)-tube. Image labels correspond to those in Fig. 1.

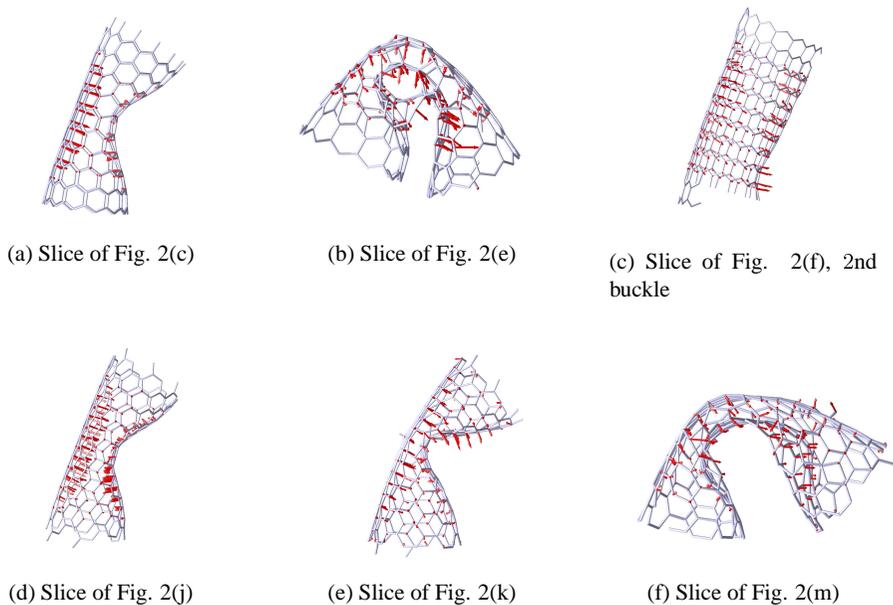


Figure 3: Difference between the empirical molecular dynamics model and the dynamical tight binding model. The carbon framework is the relaxed configuration obtained by using the empirical Brenner model and the arrows indicate the displacement of atoms when relaxed with the tight binding model.

goes beyond the the change caused by the bond length difference in equilibrium. In case of small deformations this difference is also small and can for most part be accounted for by the equilibrium distance difference just as the slightly earlier onset of buckling observed in the tight binding simulations. The difference between the two models becomes significant as the buckling takes place. The tight binding model enhances the buckle distortion from the one predicted by the classical molecular dynamics approach using Brenner’s empirical model potential as can be seen in Figs. 3(a) and 3(d). These figures also show that the backside of the buckle deforms inwards due to bond formation between the opposite tube walls. This phenomenon is not predicted by the empirical potential based model because it can not account for such interlayer bond formation because of the short cut-off distance. The deformation may also be displaced from the Brenner model predicted location (for example Figs. 3(c) and 3(e)). This predicts that if the whole bending procedure were computationally feasible with the tight binding model the behavior might differ from that observed in Fig. 2. However, qualitative behavior, that is, buckle formation, similar distortion form and such, appear when using both the models. With the tight binding model

we have also investigated highly deformed nanotube structures, like in Figs. 3(b) and 3(f). These structures turned out to be stable but similar interlayer bonding as discussed before can be observed.

CONCLUSIONS

In this work we have concentrated to study structural properties of nanotubes under different bending conditions by using classical molecular dynamics with an empirical interaction model by Brenner [2] and dynamical tight binding model by Frauenheim *et al.* [3]. We report that although the models predict similar behavior when the nanotube structure is only slightly deformed, the results differ significantly when buckling occurs. An important feature in the tight binding model appears to be its capability to form graphene interlayer bonds. Our conclusion is that although qualitatively the tight binding and the empirical models predict similar behavior, the latter is not sufficient if exact structural information of the deformations is required.

ACKNOWLEDGMENTS

This work is supported by the Academy of Finland, Research Centre for Computational Science and Engineering, project no. 44897 (Finnish Centre of Excellence Programme 2000-2005).

REFERENCES

1. R. Saito, G. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press (1998).
2. D.W. Brenner, *Phys. Rev. B* **42** 9458 (1990); D.W. Brenner, *Phys. Rev. B* **46** 1948 (1992).
3. D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, *Phys. Rev. B* **51** 12947 (1995); T. Frauenheim, F. Weich, T. Köhler, S. Uhlmann, D. Porezag, and G. Seifert, *Phys. Rev. B* **52** 11492 (1995); G. Seifert, D. Porezag, and T. Frauenheim, *Int. J. Quantum Chemistry* **58**, 185 (1996); M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, and G. Seifert, *Phys. Rev. B* **58** 7260 (1998); T. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, and R. Scholz, *phys. stat. sol.* **217/1** 41 (2000).
4. B. I. Yakobson, C. J. Brabec, and J. Bernholc, *Phys. Rev. Lett.* **76** , 2511 (1996).
5. A. Rochefort, D. R. Salahub, and P. Avouris, *Chem. Phys. Lett.* **297**, 45 (1998).
6. A. Rochefort, P. Avouris, F. Lesage, and D. R. Salahub, *Phys. Rev. B* **60**, 13824 (1999).
7. T. W. Tomblar, C. W. Zhou, L. Alekseyev, J. Kong, H. J. Dai, L. Lei, C. S. Jayanthi, M. J. Tang, and S. Y. Wu, *Nature* **405**, 769 (2000).
8. H. W. Ch. Postma, M. de Jonge, Z. Yao, and C. Dekker, *Phys. Rev. B* **62** , 10653 (2000).
9. D. Bozovic, M. Bockrath, J. H. Hafner, C. M. Lieber, H. Park, and M. Tinkham, *Appl. Phys. Lett.* **78**, 3693 (2001).
10. M. S. C. Mazzoni and H. Chacham, *Phys. Rev. B* **61**, 7312 (2000).
11. A. Hansson, M. Paulsson, and S. Stafström, *Phys. Rev. B* **62**, 7639 (2000).