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# Irradiation-induced stiffening of carbon nanotube bundles

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## Abstract

Recent experiments have demonstrated that electron irradiation of bundles of single-walled carbon nanotubes resulted in dramatic increase of the bundle bending modulus at moderate irradiation doses, followed by a decrease in mechanical properties at higher doses. To understand such a behavior, we employ molecular dynamics simulations with empirical potentials and analytical approximations to calculate defect production rates and mechanical properties of the irradiated nanotubes. We show that the observed peak in the bending modulus originates from a trade-off between irradiation-induced bundle stiffening via inter-tube covalent bonds and a drop in the Young's modulus of individual nanotubes due to vacancies.

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## 1. Introduction

Single-walled carbon nanotubes (SWNTs) have outstanding mechanical properties with the axial Young's modulus of about 1TPa [1]. This combined with their low weight makes SWNTs ideal candidates for reinforcement of other materials,

e.g. polymers [2–4]. In macroscopic samples, however, the SWNTs frequently clamp into bundles due to weak van der Waals (vdW) interactions. These bundles have very low shear modulus, which is detrimental for the reinforcement effectiveness, as only the outermost tubes connected to the host matrix contribute to the reinforcement.

There is both experimental and theoretical evidence that electron and ion irradiation of nanotubes should give rise to covalent bonds between tubes in bundles, shells of multi-walled nanotubes, and layers in graphite [5–9]. These bonds should

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increase the shear modulus of the sample. Indeed, recent experiments [10] have demonstrated that electron irradiation of SWNT bundles resulted in dramatic increase of the bundle bending modulus which can be associated with the Young's modulus of the whole bundle. However, the dependence of the modulus on the irradiation dose proved to be a nonlinear function: the modulus grew up at moderate irradiation doses, but decreased back at higher doses.

In order to understand such a behavior, we employ analytical approximations to estimate defect production rates and make use of molecular dynamics with empirical potentials to calculate the mechanical properties of irradiated nanotubes. We show that the observed peak in the bundle bending modulus originates from a trade-off between irradiation-induced bundle stiffening via inter-tube covalent bonds and a drop in axial Young's modulus of individual nanotubes due to vacancies.

## 2. Computational methods

In the computational approach of this study we employ molecular dynamics with the Brenner potential model [11]. In tube-tube shear simulations an extension involving long-range vdW interaction is used [12]. Berendsen temperature control method [13] was employed to describe the energy exchange with the heat bath. Other details of simulations can be found in our other publications [14,15].

## 3. Results

The stiffness of a SWNT bundle is characterized by the bending modulus  $Y_B$  of the bundle. Assuming that the bundle can be represented as a cylindrical macroscopic bar the modulus can be written as

$$\frac{1}{Y_B} = \frac{1}{Y} + \frac{10}{3} \frac{D^2}{L^2} \frac{1}{G}, \quad (1)$$

where  $Y$  is the Young's modulus of the SWNTs,  $G$  the shear modulus,  $D$  the bundle diameter and  $L$  the bundle length [10].

Electron irradiation gives rise to formations of vacancies in the atomic network of nanotubes and interstitials inside and between the tubes. One can expect that due to 1D atomic structure of SWNTs vacancies should have a strong impact on the Young's modulus of individual tubes. On the other hand, the axial effects of interstitials should be small. Therefore we concentrate on the effects of vacancies on the Young's modulus.

The Young's modulus  $Y$  of a quasi-one-dimensional body with atomic-scale defects can be computed through

$$Y_0/Y = 1 + n_{\text{def}} a_Y, \quad (2)$$

where  $Y_0$  presents the intact body Young's modulus and  $n_{\text{def}} = N_{\text{def}}/L$  is the linear defect concentration [14]. Fig. 1 presents the simulations results for the Young's modulus of a single (5,5) CNT with a varying vacancy concentration. The slope of the curve fitted to the points corresponds to  $a_Y = 1.2 \text{ \AA}$  in Eq. (2).

For small deformations, the shear modulus is defined  $G = \tau/\gamma$ , where  $\tau = F/A$  is the shear stress and  $\gamma = \Delta x/\Delta y$  is the shear strain. Here  $F$  is the axial force acting on area  $A$  and  $\Delta x$  and  $\Delta y$  define the shear angle. We compute the shear behavior of the bundle by applying a linearly in time increasing force  $F$  to the inner tube of a bundle consisting of seven tubes. Axial periodic boundary conditions are employed and the bundle length is  $L = 15.6 \text{ nm}$ . The edge atoms in the surrounding tubes were fixed, and the force was applied on the edge atoms of the inner tube. Again, we consider the bundle as bulk medium and obtain an area  $A = 15.76 \text{ nm}^2$  corresponding to the force  $F$ . Fig. 1 shows that  $G = a_G n_{\text{bonds}}$ , where  $a_G = 14.5 \text{ N/m}$  and  $n_{\text{bonds}}$  is the linear intertube bond density.

We then estimated the concentration of vacancies created by electron irradiation. The atomic displacement cross section of light elements, such as carbon, under electron irradiation can be obtained from an approximative formula [9]:

$$\sigma = \frac{4Z^2 E_R^2}{m^2 c^4} \left( \frac{T_{\text{max}}}{T_{\text{thr}}} \right) \pi a_0^2 \left( \frac{1 - \beta^2}{\beta^4} \right) \cdot \left( 1 + 2\pi\alpha\beta \left( \frac{T_{\text{thr}}}{T_{\text{max}}} \right) \right)^{1/2} - \frac{T_{\text{thr}}}{T_{\text{max}}} \left[ 1 + 2\pi\alpha\beta + (\beta^2 + \pi\alpha\beta) \ln \left( \frac{T_{\text{max}}}{T_{\text{thr}}} \right) \right], \quad (3)$$

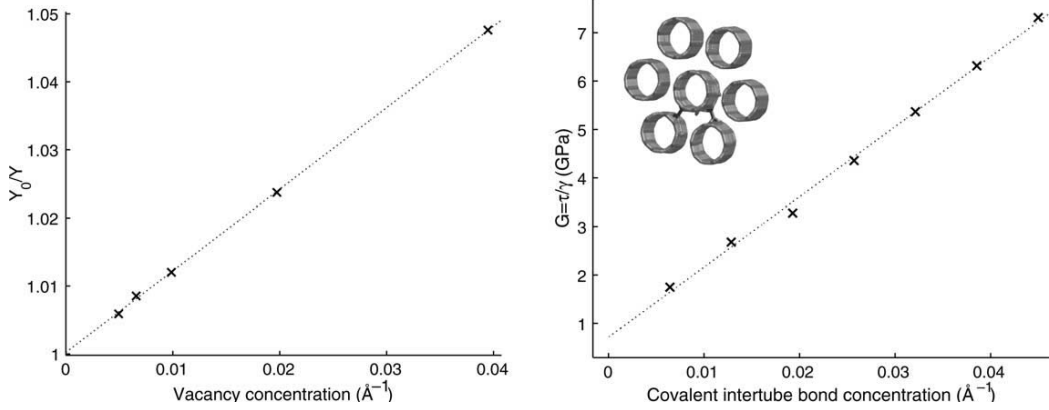


Fig. 1. Left: Inverse of the Young's modulus as a function of vacancy density (slope  $a_Y = 1.2 \text{ \AA}$ ). Right: Shear modulus as a function of inter-tube bond density (slope  $a_G = 14.5 \text{ N/m}$ ). The inset shows a slice of the simulated 7-tube bundle with inter-tube bonds.

where  $T_{\max}$  and  $T_{\text{thr}}$  are the maximum and threshold transferred energies,  $Z = 6$  is the atomic number of the displaced atom,  $E_R = 13.6 \text{ eV}$  refers to the Rydberg energy,  $a_0 = 5.3 \times 10^{-11} \text{ m}$  is the Bohr radius of hydrogen,  $\beta = v/c$  and  $\alpha = Z/137$ . Based on the graphite value  $T_{\text{thr}} = 15\text{--}20 \text{ eV}$  [9] we employ  $T_{\text{thr}} = 15 \text{ eV}$ . Assuming head-on collisions the maximum transferred energy

$$T_{\max} = \frac{2ME(E + 2mc^2)}{(m + M)^2 c^2 + 2ME}, \quad (4)$$

where  $M$  is the mass of the atom to be displaced and  $m$  and  $E$  are the mass and the energy of the incident particle. If the displaced atom is energetic enough, it can knock out more atoms in secondary collisions. For each primary displaced atom, the number secondary cascade atoms can be approximated from the formula

$$N_c = 1 + \ln(T_{\max}/2T_{\text{thr}}). \quad (5)$$

Assuming that the irradiation time and displacement rate are so small that practically no particles are displaced twice, the number and probability of displacements, i.e. vacancies, can be approximated

$$N_{\text{vac}} = \sigma j t N_{\text{atoms}} (1 + N_c), \quad (6)$$

$$p_{\text{vac}} \approx N_{\text{vac}}/N_{\text{atoms}} = \sigma j t (1 + N_c),$$

where  $j$  is the current density of the incident beam, irradiation time is marked by  $t$  and  $N_{\text{atoms}}$  is the total number of particles.

The combined probability of having a vacancy and another in a neighboring tube close enough to form an intertube bond results in an estimate for the number of intertube bonds in each tube:

$$N_{\text{bond}} = N_{\text{atoms}} M_{\text{sites}} (N_{\text{vac}}/N_{\text{atoms}})^2, \quad (7)$$

where  $M_{\text{sites}}$  is the number of potential vacancy sites for bond formation in a neighboring tube and  $N_{\text{atoms}}$  is the number of atoms in the tube. We use  $M_{\text{sites}} = 8$ . This value is obtained by assuming that the areas spanned by opposing dangling bonds should overlap on graphite layers and then taking into account that curvature reduces the number of potential sites.

The inverse of the bending modulus of the bundle (Eq. (1)) can be presented as a function of linear vacancy density  $n_{\text{vac}} = N_{\text{vac}}/L$  (Eq. (6)) and inter-tube covalent bond density  $n_{\text{bond}} = N_{\text{bond}}/L$  (Eq. (7)):

$$\frac{1}{Y_B} = \frac{1 + a_Y n_{\text{vac}}}{Y_0} + \frac{10}{3} \frac{D^2}{L^2} \frac{1}{a_G n_{\text{bond}}}. \quad (8)$$

Fig. 2 shows the bending modulus calculated through Eq. (8) as a function of irradiation dose for various beam energies. A  $D^2/L^2 = 10^{-4}$  ratio has been used in computing the plot. Note that we consider the electron energies above the threshold for defect production. An increase in the bending modulus has also been reported for energies below the threshold [10], but in this case the links

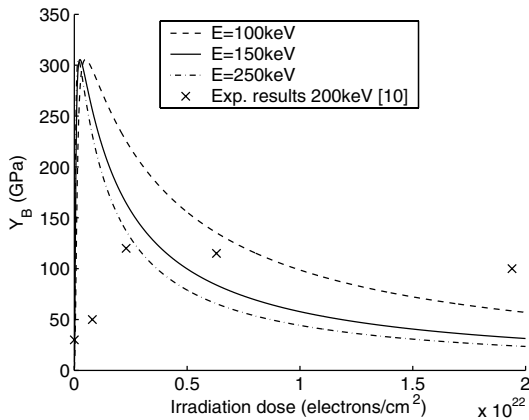


Fig. 2. Bending modulus as a function of irradiation beam dose for varying energies. The experimental results are from [10].

might originate from amorphous carbon and hydro-carbon species in the sample, which is beyond the scope of this work. We treated here the bundle as bulk medium and used  $Y_0 = 370$  GPa.

The results of Fig. 2 are in qualitative agreement with the experimental results of Kis et al. [10]. The plot shows a steeply increasing bending modulus behavior for small irradiation doses because the shear modulus of the bundle increases enormously as a result of the induced defects. When the irradiation dose increases, the counter effect, that is, the structural weakening of the tubes starts to show and the bending modulus decreases from the maximum value. The decay is relatively slow and becomes significant only at very high doses. The absolute values of  $Y_B$  we obtain are higher than the experimental results because we likely overestimated the Young's modulus for the bundle as we did not take into account nonuniform load distribution.

#### 4. Summary

We showed that the steeply increasing and then decreasing bending modulus value observed in electron irradiation measurements of [10] originates from trade-off between bundle stiffening due to inter-tube covalent bonds and a drop in

Young's modulus of the individual nanotubes due to the irradiation induced defects. Therefore, irradiation is a good tool to enhance the mechanical properties of nanotube bundles when they are used as reinforcement agents.

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