



Molecular dynamics study of multi-walled carbon nanotubes under uniaxial loading

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ABSTRACT

The mechanical behavior of multi-walled carbon nanotubes (MWNTs), being fixed at both ends under uniaxial tensile loading, is investigated via the molecular dynamics (MD) simulation with the Tersoff interatomic potential. It is found that Young's modulus of the MWNTs is in the range between 0.85 and 1.16 TPa via the curvature method based on strain energy density calculations. Anharmonicity in the energy curves is observed, and it may be responsible for the time-dependent properties of the nanotubes. Moreover, the number of atomic layers that is fixed at the boundaries of the MWNTs will affect the critical strain for jumps in strain energy density vs. strain curves. In addition, the boundary conditions may affect "yielding" strength in tension. The van der Waals interaction of the double-walled carbon nanotube (DWNT) is studied to quantify its effects in terms of the chosen potential.

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1. Introduction

The discovery of a carbon nanotube (CNT) has sprung enormous fundamental and applied researches in nanomechanics since 1991 [1]. A single-walled nanotube (SWNT) is a one-atom thick sheet of graphite curved up into a round cylinder with diameter in the order of a nanometer. The high hardness, modulus and toughness of the CNT attract researchers worldwide to study its mechanical properties. It is known that the intensity of CNTs is 100 times higher than steels with the same volume, and the weight of CNTs is only 1/6 to 1/7 of steels [2]. Therefore, the CNTs are also known as super fibers.

In the literature, many MD simulation results about MWNT have been reported. For example, Hwang et al. [3] report the buckling behavior of SWNT, and Lu et al. [4] study the DWNT with the MD simulation method. Sears and Batra study the buckling of DWNT with continuum finite element truss models and MD simulations with the MM3 interatomic potential [5,6]. Liew et al. [7] investigate four-walled carbon nanotubes with the Brenner potential [8]. Hsieh et al. [9] use the MD simulation to investigate Young's modulus of CNT under the different temperatures and radii. Haskins et al. [10] calculate Young's modulus of SWNT via MD simulation with the tight-binding potential. Verma et al. [11] use the same potential as

adopted in the present paper to calculate Young's modulus of SWNT.

In this paper, we perform MD simulation to study the behavior of double- and triple-walled carbon nanotubes under uniaxial tensile displacement loading, and study their strain energy density with respect to strain. We use the curvature method, through the second derivation of the energy curve, to determine Young's modulus of the nanotubes under uniaxial loading. Due to the discrete nature of the nanotubes, Young's moduli determined from tension or bending tests may be different. Several nanotubes are studied here, including the (5,5)@(10,10), and (10,10)@(15,15) double-walled nanotubes (DWNTs) and (5,5)@(10,10)@(15,15) triple-walled carbon nanotubes (TWNTs). After calculating the strain energy density of the CNT with various lengths and diameters, we perform a correlation study to identify the effects of length and diameter on Young's modulus. Further, we discuss the changes in Young's modulus in relation to the number of fixed boundary layers of the nanotubes, and investigate the effects of the intermolecular force between shells compared with the van der Waals interactions.

2. MD simulation

The physical configurations of the double- and triple-walled carbon nanotubes in our MD simulations are depicted in Fig. 1. The CNT has a diameter of D , which is twice its radius (R), and unconstrained length L_u . On the top and bottom of the tubes,

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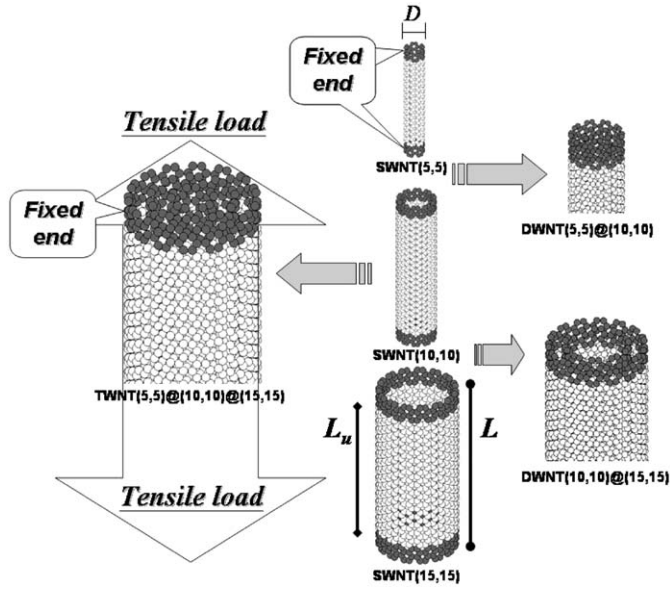


Fig. 1. Schematics of the carbon nanotubes under tension via the displacement control at the top and bottom ends. On both boundaries, four atomic layers of carbon are held in space to simulate the clamped–clamped boundary condition. The carbon nanotube has a diameter of D , twice its radius (R), and unconstrained length L_u . The DWNT is composed of two different chiral types of SWNTs, and the TWNT is composed of three SWNTs.

there are four atomic layers of carbon fixed each to simulate the clamped–clamped boundary condition in the context of continuum mechanics. Effects of boundary layers are to be discussed later through the buckling of the SWNT (3,3), as shown in Fig. 5. The tensile test simulation is performed via moving the displacement of the top end upwards and the bottom end downwards. We adopted a displacement rate of 0.1 m/s, and define the unconstrained length (L_u) of the CNT to be the total length (L) minus the fixed length.

The most important part of MD simulations is to choose a suitable potential to describe the interaction among atoms. We utilize the empirical Tersoff three-body potential [12–14] to study the carbon nanotubes. In the literature, the three-body potential is usually chosen to simulate the atomic structure containing covalent bonds, and the Tersoff potential was further employed to derive interatomic forces among the carbon atoms for force calculation. The form of the Tersoff potential is as follows:

$$E = \sum_i E_i = \frac{1}{2} \sum_i \sum_{j>i} V_{ij} \quad (1)$$

where E is the total energy of all the covalently bonded carbon atoms, E_i the energy for atom i , the interaction energy between atoms i and j . The potential energy V_{ij} is the total bond energy between the atoms i and j , which can be written as follows:

$$V_{ij} = f_c(r_{ij})[V_R(r_{ij}) + b_{ij}V_A(r_{ij})] \quad (2)$$

where r_{ij} is the distance between the two atoms, $V_R(r_{ij})$ the repulsive energy, and $V_A(r_{ij})$ the energy of attraction. They are in the form of Morse potential, which is defined as follows:

$$V_R(r_{ij}) = A_{ij}e^{-\lambda_{ij}r_{ij}} \quad (3)$$

$$V_A(r_{ij}) = -B_{ij}e^{-\mu_{ij}r_{ij}} \quad (4)$$

In Eq. (2), $f_c(r_{ij})$ is the cut-off function. The cut-off distance between a pair of atoms is denoted by S_{ij} , for $R_{ij} < r_{ij} < S_{ij}$, as

follows:

$$f_c(r_{ij}) = \frac{1}{2} + \frac{1}{2} \cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right) \quad (5)$$

For $R_{ij} > r_{ij}$, $f_c = 1$, and for $r_{ij} > S_{ij}$, $f_c = 0$. The symbol b_{ij} in Eq. (2) plays an interesting role in the Tersoff potential. It represents the bond order between the atoms i and j , which can be written as follows:

$$b_{ij} = \chi_{ij}(1 + \beta_i^{n_i} \zeta_{ij}^{n_i})^{-\frac{1}{2n_i}} \quad (6)$$

where $\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik})\omega_{ij}g(\theta_{ijk})$, and $\omega_{ij} = 1$ and $g(\theta_{ijk}) = 1 + \frac{c_{ij}^2}{d_{ij}^2 + (h_{ij} - \cos\theta_{ijk})^2}$.

The symbol θ_{ijk} is the bond angle between atoms ij and jk , and f_c is the cut-off function to restrict the range of the potential. The values of all the constants, used in the present analysis, are as follows: $A = 1393.6$ eV, $B = 346.7$ eV, $\lambda = 3.4879$ 1/Å, $\mu = 2.2119$ 1/Å, $\beta = 1.5724 \times 10^{-7}$, $n = 0.7275$, $c = 38049$, $d = 4.384$, $h = -0.57058$, $R = 1.8$ Å, and $S = 2.1$ Å. Subscripts are dropped for clarity. It is noted that the cut-off radius in the Tersoff potential may overestimate the number of interacting atoms inside the cut-off sphere, resulting possibly in slightly higher calculated energy. In a sense, this overestimation can be considered as an inclusion of van der Waals interaction, which is not directly included in the present simulations.

The Tersoff potential model is chosen since it provides quick estimates and significant insights into the thermo-mechanical behavior of the CNT without the need to consider chemical reactions. The tube is maintained at the specified temperature using a rescaling method [15]. The motion of each carbon atom is governed by Newton's laws of motion, in which the resultant force acting on each atom is deduced from the energy potential related to its interactions with neighboring atoms within a prescribed cut-off radius. The conventional Leap-Frog algorithm [16] was employed to derive the new position and velocity of each atom based on the data obtained in the previous step. Our simulation time step was 0.1 fs, and during simulations an equilibrium configuration was searched with a verlet list. This time step is far less than the period of the CNT atomic thermal vibrations.

3. Results and discussion

Three different chiral vector types (5,5), (10,10), and (15,15) of SWNTs were adopted to construct the MWNTs, and their radii are 3.44, 6.88, and 10.31 Å, respectively. It is assumed that the interatomic distance between nearest-neighboring two carbon atoms of the MWNT was 1.44 Å [17]. From an equilibrium MD run, it was found that the system energy was not at minimum based on the distance choice. Hence, the equilibrium interatomic distance was found to be deviated from that reported in the literature. Through tension and compression tests, the energy vs. strain curves were obtained. We utilize the curvature of the energy curves near zero strain to calculate Young's modulus of nanotubes, and the strain range was chosen to be 0.75% around the strain zero [18]. The formula calculated is as follows:

$$Y = \frac{1}{V_0} \frac{\partial^2 E}{\partial \epsilon^2} \quad (7)$$

where Y is Young's modulus, E the strain energy, ϵ the uniaxial strain, V the volume of the MWNT, and $\partial^2 E / \partial \epsilon^2$ the curvature of the strain energy curve near zero strain. We defined the strain as engineering strain, $\Delta \ell / \ell_0$, where $\Delta \ell$ is the change in length and ℓ_0 the unconstrained length. Because the CNT is

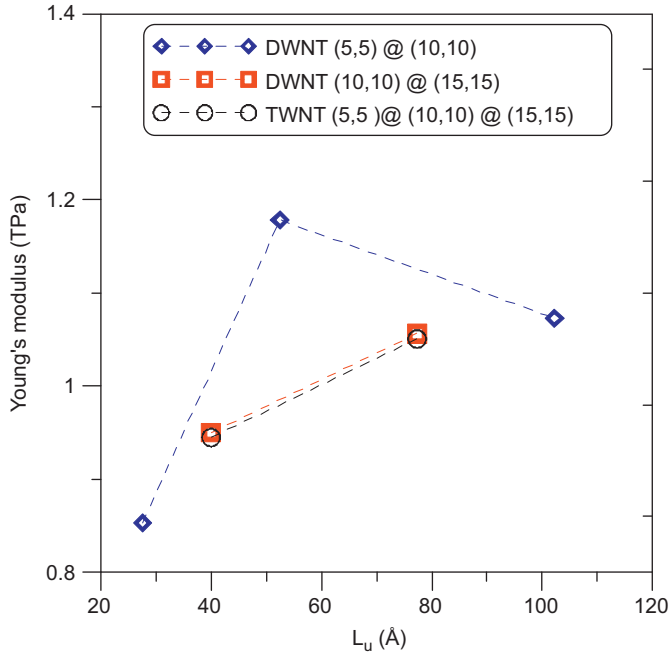


Fig. 2. Young's modulus vs. unconstrained length for different chiral types of DWNTs and TWNTs. Using the curvature of strain energy density vs. strain, we calculate Young's modulus of every CNT, and the range is about from 0.85 to 1.16 TPa. Moreover, Young's modulus of DWNT(5,5)@(10,10) and TWNT(5,5)@(10,10)@(15,15) is located at the same point, due to the same outermost SWNT(15,15). These results indicate that Young's modulus of the multi-walled nanotubes is length independent in the studied length region.

very thin in tube thickness, the method to calculate the volume was to multiply its surface area and thickness directly, $V_0 = 2\pi Rl_0\delta$, where R is the radius of CNT and δ the thickness of CNT, $\delta = 3.4$ Å.

Fig. 2 shows the relationships between Young's modulus and length for various nanotubes. It can be seen that the range of Young's modulus is from 0.85 to 1.16 TPa (1 TPa=1000 GPa). Furthermore, the results of the DWNT (10,10)@(15,15) and the TWNT (5,5)@(10,10)@(15,15) are identical. In Lu et al. [19] it is proposed that the buckling strain of MWNT is dominated by its outermost shell, and it appears that Young's modulus of MWNT is also influenced by the chiral vector type of the outer-most shell. Single-walled nanotubes were calculated for comparison purposes. From previous studies, Young's modulus of the nanotubes can be compared as shown in Fig. 3. Peralta-Inga et al. [20] investigate the CNT with small pipe diameter with density functional tight binding (DFTB) method, and Young's modulus is found in the range 2.2–2.75 TPa. Krishnan et al. [21] obtained Young's modulus of CNT 1.25 TPa experimentally. Coze et al. [22] have calculated CNT with different chiral vectors, and found that the Young's moduli are from 1.22 to 1.25 TPa. Cai et al. [23] utilize tight-binding methods and find CNT's Young's modulus to be 0.95 TPa. van Lier et al. [24] adopted *ab initio* assumptions, and found Young's modulus to be 0.75–1.18 TPa for (5,5) SWNT. Moreover, Robertson et al. [25] obtain CNT's Young's modulus with the Tersoff potential to be 1.06 TPa, similar to the present results. Our results show variations in Young's modulus at a given radius and length due to the anharmonicity of the calculated energy curves. The consistency in Young's modulus for the DWNT and TWNT indicates that the outermost shell may dominate the overall Young's modulus of multi-walled nanotubes. Further verifications may be required.

Fig. 4 shows the total potential energy required to pull out the inner tube of the DWNT. The required energies at the two

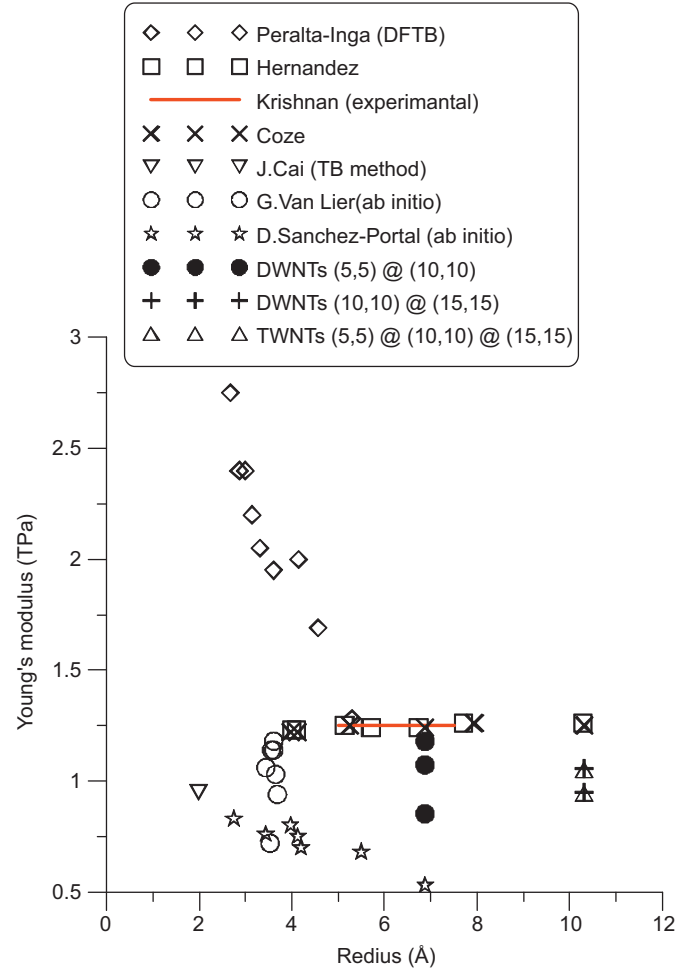


Fig. 3. Young's modulus vs. tube radius for different experimental and computational results of carbon nanotubes. The solid circle, cross, and triangle symbols indicate DWNT(5,5)@(10,10), DWNT(10,10)@(15,1) and TWNT(5,5)@(10,10)@(15,15), respectively. Other symbols are obtained from the literature, and explained in the text.

temperatures are very close to each other. It is reasoned that these energies can be considered as the weak interaction energy due to van der Waals between shells of the nanotubes. The Lennard–Jones (LJ) potential, $U = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6]$, is commonly used for describing the van der Waals interactions. Here $\epsilon = 12$ meV and $\sigma = 3.4$ Å are the van der Waals parameters for carbon nanotubes [26]. From the distance between the inner and outer shell for the DWNT (assumed to be 2.36 Å, considering the finite size of a carbon atom), one can calculate the weak interaction energy due to the LJ potential to be about 3.41 eV, which is in agreement with our MD results (the minus sign in the MD results is due to the choice of the zero potential surface). By this analysis, it is not claimed that one does not need to directly include the LJ potentials in the MD simulations, but it is suggested that by the Tersoff potential alone, some of the weak interaction features can be captured.

Fig. 5 shows the effects of the number of boundary layers in the MD calculations. As can be seen, by fixing 1, 2, 3, and 4 layers, the energy curves and related energy jumps are different. The energy jumps can be interpreted as atomic buckling due to some atoms or a cluster of atoms snap through to a different equilibrium configuration. The detailed differences in the energy curves can be found in the inset of Fig. 5. The physical rationale of the effects of boundary layers lies at the connection between

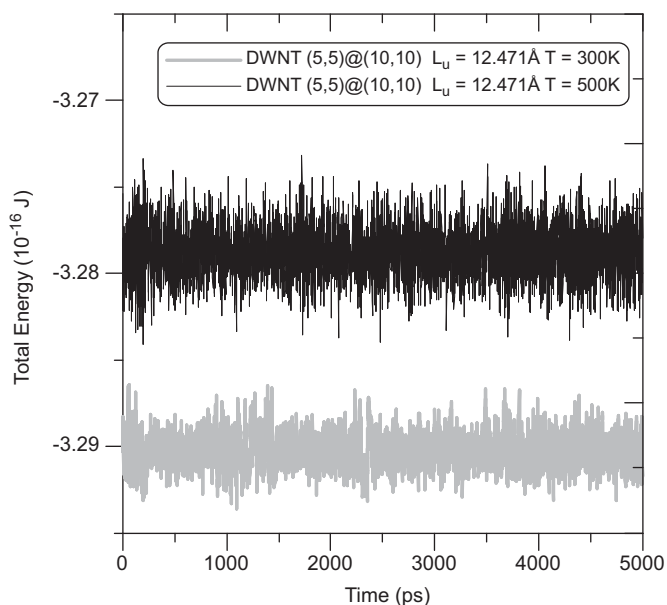


Fig. 4. The weak interactions between the inner shell SWNT(5,5) and the outer shell SWNT(10,10) of the DWNT(5,5)@(10,10) with different temperatures. The gray line indicates the temperature at 300 K, and the black one is for the case at 500 K. During the pull-out of the inner shell, the outer shell is also pulled toward the opposite direction. The van der Waals interactions between shells are observed through the potential-energy calculations in terms of the Tersoff interatomic potential with a suitable cutoff. The mean values of the total energies at 300 K and 500 K are -3.290 and -3.27 eV, respectively and the standard deviations are 0.96 and 1.52 . It shows that the thermal noise level at 500 K is larger than that at 300 K.

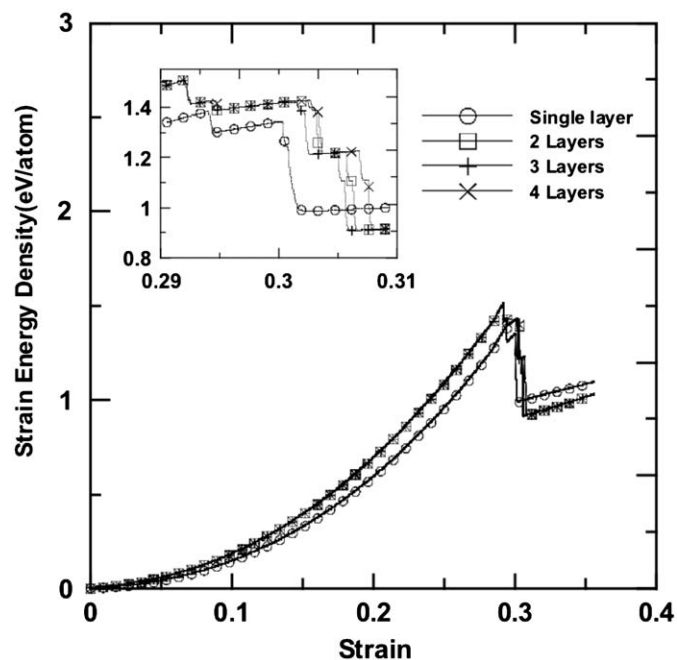


Fig. 5. Effects of boundary layers on the buckling of the SWNT(3,3). The inset shows an expanded figure around the strain energy jumps. Constraining 2, 3, and 4 layers of carbon atom on both ends of the tube shows consistent results on buckling strain. However, the buckling strain obtained from single-layer constraints on both ends underestimates the buckling strength. Also, the curvatures of the strain energy density before the jumps are different, indicating the choice of the number of fixed layers may affect the estimation of Young's modulus of the CNT. Multiple jumps in the SWNT(3,3) demonstrate the highly discrete nature of the system.

atomic and continuum assumptions. To construct a clamped-clamped boundary condition in the continuum sense, one needs to verify the rotational degrees of freedom at the boundaries. Without enough boundary layers being fixed, one allows certain rotation freedom, and hence the energy curves and jumps from the MD simulations are different.

4. Conclusions

Through the MD calculations, Young's modulus of multi-walled carbon nanotubes was found to be in the range 0.85 – 1.16 TPa. The variations in the modulus may be due to different radii and lengths of the tubes. By changing the number of boundary layers, it is found that the calculated mechanical properties remain consistent when the more fixed layers are adopted, indicating the role of mechanical boundary conditions in the MD simulations. In addition, the anharmonic behaviors, as observed in the energy curves, show possible mechanisms for time-dependent properties of carbon nanotubes.

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