Molecular-Dynamic Investigation of Buckling of Double-Walled Carbon Nanotubes under Uniaxial Compression

Jian-Ming Lu1,2, Yun-Che Wang3, Jee-Gong Chang2, Ming-Horng Su1, and Chi-Chuan Huang1*

1Department of Engineering Science, National Cheng Kung University, Tainan 70101, Taiwan
2National Center for High-Performance Computing, National Applied Research Laboratories, No. 28, Nanke 3rd Rd., Sinshih Township, Tainan County 74147, Taiwan
3Engineering Materials Program, Department of Civil Engineering, National Cheng Kung University, Tainan 70101, Taiwan
4Department of Fire Science, WuFeng Institute of Technology, Chiayi 621, Taiwan

(Received June 19, 2007; accepted February 14, 2008; published April 10, 2008)

This paper studies the buckling phenomena and mechanical behavior of single-walled carbon nanotubes (SWNTs) and double-walled carbon nanotubes (DWNTs) via molecular dynamics simulations. The Tersoff interatomic C–C potential is adopted. Using a dimensionless parameter, slenderness ratio \( S_R \), the ratio of length to diameter, we investigate the mechanical behavior of long and short nanotubes under compression through their buckling modes, total strain energy and strain energy density, as well as post-buckling. The curvatures of strain energy provide a means to measure the Young’s modulus of the nanotubes. Moreover, jumps in either the strain energy or strain energy density indicate identical mechanical buckling strains, and are studied in relation to buckling modes. In our simulations, a transition time is observed for short nanotubes to reach stable vane-like buckling mode, indicating a time-dependent property of nanotubes. Furthermore, nanotubes with small \( S_R \) can bear higher compressive load after their first buckling. In addition, nanotubes with same chirality exhibit roughly the same elastic modulus, regardless of their lengths, when applied compressive strains are less than 5% strain. However, long nanotubes show smaller buckling strength. Effects of temperature at 300 K on buckling strength for SWNT are also discussed in connection to our present study at 1 K.

KEYWORDS: molecular dynamics simulation, carbon nanotube, buckling, slenderness ratio

DOI: 10.1143/JPSJ.77.044603

1. Introduction

The discovery of carbon nanotubes (CNTs) has stimulated enormous fundamental and applied researches on carbon nano-mechanics in the last 15 years.1,2 It is now well known that single- and multi-walled CNTs have very high strength and stiffness along their axial direction, but are very flexible in the transverse direction.3–5 For single-walled CNTs (SWNTs), their Young’s modulus under axial deformation may be greater than 1 TPa; an ideal candidate as inclusions for fiber-reinforced composites.6,7 For real-world applications, it is therefore important to fully characterize the mechanical aspects of carbon nanotubes, in particular, instabilities beyond linear responses for the CNT under axial compressions. This has been studied quite extensively, and some works are mentioned, as follows.8–12

After the determination of the Young’s modulus of SWNTs by Yakobson et al., Treacy performed molecular dynamics (MD) simulations to study the morphological patterns of SWNTs subjected to large deformations.8,13 They observed local buckling in nanotubes, and compared their simulation results with a continuum shell model. Instead of classical MD simulations, Srivastava et al. used quantum generalized tight-binding MD models to investigate the nanoplasticity of SWNTs under axial compressions.14 They showed that the nanoplasticity arises from the bonding geometry collapse that is driven by a graphite (sp²) to a localized diamond-like (sp³) reconstruction transition. Wei et al. pointed out the classical MD method, though fails at 0 K, can be used to successfully explain the nanoplasticity of CNTs under axial compression at finite system temperatures.10 Ozaki et al. performed O(N) tight-binding MD simulations to show that the buckling shape of SWNTs depends greatly on the temperature of the system and that the 0 K stress under large strain insensitive to helicity or chirality.11 It was found that a zigzag nanotube and an armchair nanotube are the stiffest under elongation and compression regimes, respectively.12 For SWNTs, temperature effects on their buckling have been discussed and the effects of van der Waals interactions can be neglected when the nano tubes are under uniaxial compression.13 Continuum mechanics approaches to analyze the mechanical properties have been reported, and reasonable agreements between MD simulations and continuum modeling are achieved.15,16 Experimentally, Louie et al. observed the buckling of CNT’s embedded in polymeric films with transmission electron microscopy, and found that multi-walled CNTs (MWNTs) may have a compressive strength of 60 GPa.9 Moreover, the axial compressive strengths of thin- and thick-walled CNTs are about 2 orders of magnitude higher than those of any known fibers. Recently, Cao et al. demonstrate that CNT films may be used as energy-absorbing coatings.17

MD simulations on MWNTs have been reported. Sears and Batra study the buckling of double- and three-walled CNTs with continuum finite element truss models and MD simulations with the MM3 interatomic potential.18–20 Liew et al. investigate up to four-walled CNTs with the Brenner potential. The aforementioned authors did not study the effects of temperature and slenderness ratio \( S_R \) on the buckling modes and corresponding energy landscapes.21 In this paper, we perform MD simulations with the Tersoff interatomic potential to study the buckling problem of SWNTs and double-walled CNTs (DWNTs) at temperature \( T = 1 \) K. A particular focus is placed on the comparisons of

*E-mail: chchwang@mail.ncku.edu.tw
buckling modes for long and short CNTs. The rationale for simulation at $T = 1\, \text{K}$, albeit not realistic, is to obtain basic understandings of the nanotube mechanics under minute thermal-noise influences for future buildup. Effects of temperature on SWNT at $T = 300\, \text{K}$ are also studied for comparison.

2. Methodology

Although the applications of Tersoff potential in MD studies of CNTs are well known, we briefly recapitulate and summarize our MD scheme in this section.\textsuperscript{22–25} The empirical Tersoff potential is employed to derive the interatomic forces among the carbon atoms of the SWNTs and DWNTs. This particular potential model is chosen since it provides rapid insights into the thermo-mechanical behavior of the CNTs without the need to consider chemical reactions. Furthermore, Raravikar \textit{et al.} have reported that the Tersoff potential model provides a suitable means of investigating the temperature dependence of the radial breathing mode Raman frequency of SWNTs in the case where the formation or breakage of carbon–carbon bonds does not take place.\textsuperscript{26} 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 parameters used in the Tersoff potential for the carbon–carbon binding are reported.\textsuperscript{20} The usual Leap–Frog algorithm is employed to derive the new position and velocity of each atom based on the data obtained in the previous step.\textsuperscript{27} Our simulation time step was $\Delta t = 1\, \text{fs}$, and during simulations an equilibrium configuration was searched with a verlet list. This time step is less than the period of the CNT’s atomic thermal vibrations (about 41s), and through extensive simulation works we found that it does not cause excessive computational rounding errors. Finally, the tube is maintained at the specified temperature using a rescaling method.\textsuperscript{28}

We used the Tersoff potential to simulate the sp$^3$ covalent bonds among the carbon atoms of the SWNT and DWNT. The Tersoff potential is a function of the interactive distance of atoms or molecules and has strong repulsive force below 2.1 Å to prevent carbon atoms from being too close. Even though it has no interactive force beyond 2.1 Å on account of the cutoff function $f_c(r_{ij})$, but it is reasonable and negligible in comparison with the compressive force in the buckling process. It is noted that the cut-off radius in the Tersoff potential may over-estimate the number of interacting atoms inside the cut-off sphere, resulting possibly slightly higher calculated energy. Remark that for either SWNTs or DWNTs no additional van der Waals force fields were used in our present simulations. We consider the van der Waals interactions beyond the Tersoff potential as a second-order effect, not discussed in the present study.

Figure 1 shows the schematic of the buckling problem of the CNTs. The top and bottom ends of the tube are held to be fixed laterally throughout our simulations. Axial strains are applied along the longitudinal direction of the tubes to simulate compression. We define the unsupported length ($L_u$) of the CNTs to be the length of their unconstrained part, in contrast to $L$ (the total length of the tube). At the both top and bottom of the tube, several layers of carbon atoms are assumed to have zero displacements along all lateral directions to simulate the clamped–clamped boundary condition. Note for DWNTs both inner and outer tubes are
clamped in the same manner. Before performing any buckling simulations, we run 50000 time steps to reach equilibration. The condition for minimum surface tractions would be met when the structure is relaxed and equilibrated. Buckling simulations were performed by controlling the displacement of the top clamped layers of carbon atoms to move downward uniformly with a rate of $10^{-12}$ nm/fs. The free length, i.e., the length of the CNT between the two displacement boundary conditions, was about 7 nm for long nanotubes, and 4 nm for short ones. The diameter of a CNT can be computed as $D = a\sqrt{3(m^2 + n^2 + mn)}/\pi$, where $(m, n)$ is the chirality of the CNT and the symbol $a = 1.44$ Å, as often used, denotes the interatomic C–C bond length.\(^{29}\)

3. Results and Discussion

We organize our results and discussion as the following. First, the buckling modes of long and short SWNTs are discussed, and then we discuss the buckling modes of DWNTs with different lengths. Lastly, we compare the long, short SWNTs and DWNTs through their strain energy with respect to applied compressive strain.

Figure 2 shows the buckling evolution of a long (5,5) SWNT in the order of increasing compressive strains. The total length of the SWNT was chosen to be 7.86 nm; its unconstrained length was 7.5 nm ($S_R = 5.9$). Global buckling of the SWNTs can be understood and envisaged as the Euler buckling behavior, as shown in Fig. 2(a), which can be modeled as

$$\varepsilon_{cr} = \frac{4\pi^2 I}{L_o^2 A} = \frac{\pi^2 (r_o^2 + r_l^2)}{L_o^2},$$

(1)

Here $\varepsilon_{cr}$ is the critical strain for the first buckling mode, $L_o$ the unconstrained length of the tube, $A$ the cross-sectional area, and $I$ the area moment of inertia of the cross-section. The symbols $r_o$ and $r_l$ indicate the radius of outer and inner surfaces of the tube, respectively. It can be seen that the critical strain depends on geometry only. For the (5,5) SWNT, tube radius $R = 0.344$ nm. Assuming $r_o^2 + r_l^2 = 2R^2$, one obtains $\varepsilon_{cr} = 0.04$, which is in agreement with our strain energy analysis in Fig. 8. Note that eq. (1) only applies to the Euler buckling; not for kinks or other local buckling modes, which may require mathematical formulations for membrane-type objects and finite element analysis.\(^{15}\) We emphasize that the critical strains identified through the jumps in strain energy in MD are quite different from those from quasi-static experiment due to high strain rates in MD simulations (about 133 s\(^{-1}\)).

When applied strain increases, a local buckling phenomenon occurs. In other words, formation of a kink at the center portion of the buckled tube can be observed in Fig. 2(c). The angle of the kink in its vicinity is approximately about 100\(^\circ\). The stored energy in the locally buckled tube is related to this angle, and detailed studies of kink angles and system energy will be reported in a later paper.\(^{30,31}\) Figure 2(d) shows that, when continuing to increase applied strain, two other kinks are formed near the displacement boundaries. This may be due to the local stress concentration between constrained and unconstrained displacement boundaries. The compressibility of the tube at the kinks can be easily seen through these deformed images, which show a factor of two reductions on the tube radius. Due to the fin-like deformed shape of the kinks, the reduction of the fin width implies increases in the in-plane dimension of the fin (out-of-paper dimension, not shown). This specific simulation shows that global lateral displacement of the tube after buckled was about 1.6 nm. Compared with the total original length (7.5 nm), this amount of lateral displacement can be experimentally observable.

In this work, we use strain to measure the onset of buckling, instead of stress since estimation of buckling loads may depend on the choice of interatomic potentials. Remark that buckling occurs not exactly at the middle of the length of the tube. This may be due to our displacement boundary conditions in that two layer of atoms at the bottom are confined, but three at the top. Even if the boundary conditions are symmetric, due to no defects are introduced into the nanotube, kink formation may occur in an unsymmetrical manner due to bifurcation, as shown in the short-column case (Fig. 3).

As for the short SWNT (4 nm long, $S_R = 3.6$), our results are shown in Fig. 3. Figure 3(a) shows the short SWNT right before first buckling. Upon this compression, the tube’s length is reduced from 48.64 to 45 Å. This amount of reduction in length follows the conventional axial deformation, defined by the Young’s modulus. In other words, one can estimate the critical stress by $(48.64 - 45)/48.64 \times 10^{12} = 74.83$ GPa for the first buckling mode with the assumption remains to be about 1 TPa upon this compression. When the compressive load reaches a critical value, a local buckling (vase-like buckling pattern) occurs near the center along the axial direction of the tube, but not exactly in the middle, as shown in Fig. 3(b). The kink angle is about 50\(^\circ\). The side view of Fig. 3(b), not shown, indicates that the kink is flattened to become wider along the out-of-paper direction, and the vicinity of the kink is also flattened to become thinner; a fin-like structure. More compressive strain results in a pair of unsymmetrical kinks formed, as shown in
Fig. 4. Buckling modes of the (5,5)@(10,10) long DWNT at different loading stages (\(S_i = 15.2, S_o = 7.6\), where \(S_i\) is the ratio for the inner tube and \(S_o\) is that for the outer tube): (a) compressed right after the first buckling, (b) intermediate buckling stage after the first buckling, and (c) final buckling stage in the simulations. Note compressed figure right before the first buckling is not shown. Total length of the nanotube was 98.52 Å, and the unconstrained length was 96.03 Å. An atomic layer and two atomic layers of carbon were fixed at the top and bottom ends, respectively. Length is in units of Å. Our simulation temperature was 1 K.

As for short DWNT, Fig. 5(a) shows the DWNT model right before first buckling. The short DWNT was 33.67 Å long (\(L_o = 23.69\), \(S_i = 2\), \(S_o = 1\)), and its four atomic layers both at the top and bottom ends were fixed, including the inner tube. Hence, \(L_o = 23.69\) Å. In the buckling evolution, we observe that right after the first buckling the outer shell wrinkles, as shown in Fig. 5(b). Similar waviness features on the outer shell of MWNTs have been observed in DWNTs under compression. Upon increasing compressive strains, a vase-like buckling pattern is formed [Fig. 5(c)]. This feature is close to that occurred in the short SWNT case [Fig. 3(b)], but less symmetry, due to the interplay between the inner and outer nanotubes. A distorted vase-like buckling mode can be observed in Fig. 5(d) when further compressed. At this stage, the total length of the DWNT was about 29.5 Å, including the fixed ends. During the buckling process, the nanotube was shortened about 4 Å.

Since a DWNT can be viewed as a composite consisting of a long and a relatively short SWNT, we compare their strain energies with respect to applied compressive strain in Fig. 6 to understand their buckling behavior quantitatively. We define the units of strain to be 10 microstrains. The labels on the figure along the curves correspond to the figure.
numbering in this paper, i.e., “2a” indicates the buckling pattern shown in Fig. 2(a). The positions of the labels indicate the correspondent strains that are applied to obtain the buckling patterns. Strain energy discontinuities indicate the occurrence of buckling. For the (5, 5)@(10, 10) DWNT, the discontinuity in strain energy occurs between the buckling morphologies of Figs. 4(a) and 4(b). For the (5, 5) SWNT, the strain discontinuity occurs from buckling pattern Figs. 2(a) to 2(b). Further compression beyond the strain discontinuities results in accumulation of deformation energy. By direct observation in our MD simulations, we identify the buckling patterns, labeled as 5c, 3c, and 3d along the strain energy curve. We remark that a delicate action between a long- and short-column effect. 30,31) It can be envisaged that the confinement from the outer tube may significantly influence the buckling of the inner tubes. In addition, during our simulations of short CNTs, we observed that the neck of the vase-like buckling pattern would move along the tube in a transition from a straight-column configuration to a stable vase-like buckling pattern. It is found that the transition time is proportional to the radius of the nanotubes, based on our direct simulation observations.

All of aforementioned simulations were carried out at temperature of 1 K. To understand the effects of temperature, Fig. 7 shows the results of strain energy vs compressive strain at Fig. 7(a) 300 K and Fig. 7(b) 1 K. First, when $T = 300$ K, the noisy result from our MD simulations is due to thermal fluctuations. Second, for the same length and chirality, the buckling strengths of SWNTs are reduced as temperature increases. This observation for SWNTs has also been reported. 11) Study of temperature effects on the buckling of DWNTs is to be reported. 30,31) When $T = 1$ K, the 5-nm case is identical with that studied in Fig. 3, and the 7.5-nm case is identical with that discussed in Fig. 2. In our simulations with the chosen interatomic potential, the 5-nm ($S_R = 3.6$) and 7.5-nm ($S_R = 5.9$) long SWNT reduce their $\varepsilon_{ct}$ from 4.2 to 3% and from 2.85 to 2.6%, respectively. The boundaries of the 5-nm case were two atomic layers being fixed, and the boundaries for the 7.5-nm case were three atomic layers fixed at the top and two fixed at the bottom. The 10-nm long SWNT ($S_R = 15.2$) shows a critical $\varepsilon_{ct}$ at 3% at 1 K, but no clear buckling strain at 300 K due to critical strain for buckling is at about $\varepsilon_{ct} = 2.5$, and hence it appears that the DWNT could only bear smaller buckling strain. However, the reduction of the buckling strain in the DWNT is due to its large $S_R$ ratio. A systematic and quantitative study of the effects of the interplay between the shells of MWNTs is currently underway. 30,31) It can be seen that the SWNT appears to have higher $\varepsilon_{ct}$ than that of the (5, 5) SWNT is due to the difference in buckling mode between them, i.e., short vs long tube buckling. For all the cases here, our simulation temperature was 1 K.
thermal fluctuations induced bending from the beginning of compression. The boundaries of the 10-nm case were an atomic layer fixed at the top and two atomic layers fixed at the bottom. In the lower panel of Fig. 7, from the total strain energy the curvatures of the SWNTs coincide with each other for small strains up to 7% compressive strain, indicating the Young’s modulus of the nanotubes is independent on the tube length, consistent with earlier experimental and theoretical studies.\(^{32,33}\) In the latter reference, it has been revealed that with suitable normalization on the strain energy with respect to the number of atoms in the systems, the difference in curvatures between \((5,5)\) and \((10,10)\) SWNT may result from the Young’s modulus dependence on the radius of the carbon nanotubes. We remark that the curvature of the total strain energy is not equal to the Young’s modulus, but the curvature of the strain energy density is. Therefore, the valid deformation range for identical Young’s modulus in the case of \((5,5)\) SWNT with different lengths is more than 7% compressive strain. It is worth-noting that although the total strain energy does not provide correct Young’s modulus, it does provide correct buckling strains, as does the strain energy density, due to the occurrence of jumps in strain energy along the horizontal (strain) axis is not affected by division of the total number of atoms in the system.

Figure 8 shows the comparisons of SWNTs with same chirality \((5,5)\), but different \(S_R\)’s at \(T = 1\) K. For the simulated cases, \(S_R = 1.8, 3.6,\) and \(7.2\), it is found that the corresponding buckling strains are 0.8, 0.65, and 0.55, respectively. Hence, we may conclude that larger \(S_R\) requires smaller applied strain for buckling to occur at \(T = 1\) K. The definition of our axial compression is identical with that of conventional strain. With the same chirality, total strain energy results indicate irregular trends of buckling, but the strain energy density correctly reveals that shorter nanotubes exhibit higher buckling strength. Two atomic layers of carbon were fixed both at the top and bottom ends. Note that axial compression larger than 20% may not reflect reality due to the limitations of the Tersoff potential. Simulation temperature was 1 K.
indicate different Young’s modulus for different \( m \) with the same tube radius. However, after suitable normalization with respect to the number of atoms in the system, we obtain correct relationship between the length of tubes and Young’s modulus, as shown in Fig. 8(b). In other words, the Young’s modulus of a carbon nanotube is independent on the length of the tube. In addition, our study reveals that the amount strain energy density that can be stored in a nanotube (before buckling) depends on \( \delta S \); the smaller \( \delta S \), the higher strain energy density. Because of the same modulus, a SWNTs with a smaller \( \delta S \) has larger buckling load, albeit different buckling modes. We remark that due to the limitation of the Tersoff potential, axial compression greater than 20% may not reflect reality.

We remark that distinctions between pure buckling and plastic deformation in CNTs may require further atomistic analysis including loading–unloading MD simulations and considerations of quantum effects. In the present work, we identify jumps in strain energy to be associated with pure buckling for perfect carbon nanotubes and temperature much less than that of sublimation. Furthermore, we identify post-buckling morphologies with their corresponding strain energy vs strain plots by direct observations during simulations. Buckling strength can be inferred from buckling strain, assuming Young’s modulus of a CNT remains roughly the same during compression. This assumption is valid when one compares nanotubes with the same radius but different lengths. Therefore, larger buckling strains, higher buckling strengths. In addition, qualitative comparisons may be achieved between MD results and dynamic Euler buckling theorem, due to unavoidable high strain rates in MD simulations. However, our MD simulation results of CNT buckling may manifest themselves for comparisons with experimental work. As for the number of fixed atomic layers at boundaries, we ignore its effects in the present work, and a systematic investigation on the effects of boundary layers is underway.

4. Conclusions

MD simulations enable to reveal a variety of buckling and post-buckling behavior of SWNTs and DWNTs to reflect the discrete nature of the nanotubes. Upon compression, global buckling (lateral bending) appears before local buckling (kink formation) for long SWNTs, but reverse for short SWNTs. For DWNTs, long DWNTs exhibit similar buckling patterns as long SWNTs, but with the interplay between the inner and outer shells. Short DWNTs show the wavy buckling feature on the outer shell first, and then buckle with similar features as short SWNTs but with global lateral bending. We find that the transition time to form a stable vase-like buckling mode for short nanotubes depends on the radius of the tubes. Moreover, temperature effects reduce the buckling strength of the nanotubes, and may even make the strain discontinuity disappear for long nanotubes. For SWNT with the same chirality, longer tubes have smaller buckling strength.

Acknowledgements

The authors wish to thank Professor Shin-Pon Ju (NSYSU, Taiwan) for valuable helps. A grant from the Taiwan National Science Council under the contract NSC 96-2221-E-192-007-MY3 is gratefully appreciated.