Effect of chirality on buckling behavior of single-walled carbon nanotubes

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(Received 7 January 2006; accepted 8 July 2006; published online 4 October 2006)

In this paper, molecular dynamics simulations (MDS) are performed on single-walled carbon nanotubes (SWCNTs) in order to study the effects of chirality on their buckling behavior under axial compression. In the MDS, the Tersoff-Brenner potential is used to describe the interaction of carbon atoms in the SWCNTs. The sensitivity of the buckling strains and buckling modes with respect to the chirality of SWCNT is investigated by modeling SWCNTs with different chiral angles, varying from 0° to 30°, but keeping the length-to-diameter ratio constant. The carbon nanotubes are analyzed using a continuum cylindrical shell model based on the theory of nonlocal elasticity so as to assess its validity in predicting the buckling strains when compared with the results that are obtained by MDS. The differences between the buckling strains at the continuum scale and that at the nanoscale are also studied. The present analysis and results are helpful in understanding the buckling behaviors of axially compressed carbon nanotubes. This knowledge is important for the application of carbon nanotubes as building blocks of nanomechanical devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2355433]

I. INTRODUCTION

Ever since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,1 CNTs have attracted considerable attention due to their unique electronic and mechanical properties. Recent studies have indicated that CNTs possess exceptionally high elastic modulus2–8 and can sustain large elastic and failure strains.9–14 Therefore, CNTs have been identified as one of the most promising superfibers for nanotube-composite materials.

In the open literature, considerable effort has been devoted to the exploration of the mechanical behaviors of CNTs under bending,9,15,16 buckling,8,9,17–28 and vibration.29–31 In particular, buckling of CNTs under axial compression has become a topic of great interest because their long and hollow tubelike structure makes them susceptible to buckling. Numerous studies on the buckling of CNTs have been made by using molecular dynamics simulation7–9,17–20 (MDS) as well as continuum mechanics models such as elastic shell and beam models,21–27 nonlocal beam,25,31 and shell models.28 Molecular dynamics simulation is by far the most accepted tool for investigating the mechanical properties of CNTs. For example, Yakobson et al.9 investigated axially compressed armchair single-walled carbon nanotubes (SWCNTs) using molecular dynamics simulations and compared the solutions with those obtained by a simple continuum thin shell model. They observed that the continuum shell models could predict the buckling properties of SWCNT satisfactorily provided that the mechanical parameters, such as Young’s modulus and the effective wall thickness, are judiciously adopted. Cornwell and Wille17 carried out MDS to study the response of a set of armchair SWCNTs and calculated the Young’s modulus of the tubes. Srivastava et al.18 performed MDS to examine the nanoplasticity of a zigzag CNT under compression. Recently, Liew et al.20 studied the buckling behavior of armchair and zigzag SWCNTs and multiwalled CNTs composed of multiple armchair SWCNTs with different diameters. Wang et al.8 applied MDS to study the elastic response and the buckling modes of SWCNTs under axial compression. The SWCNTs simulated were armchair and zigzag CNTs of various length and diameters.

It is worth noting that in the literature, most MDS are performed on the armchair and zigzag CNTs, and rarely on other chiral angles ranging from 0° to 30°. Lu32 investigated elastic properties of nanotubes and nanoropes using an empirical force constant model and showed that the elastic properties of SWCNTs and multi-walled carbon nanotubes (MWNTs) are insensitive to chirality, radius, and number of walls. The energetics and elastic properties were investigated for carbon nanotubes of different chiral angles and radii less than 9 Å. These CNTs were simulated by MDS based on both empirical potentials and first principles total energy methods.33 Shintani and Narita34 adopted MDS for CNTs analysis to check the dependency of Poisson’s ratio on the chirality and the imposed strain. They found that the strain dependence is predominant while the chirality dependence is negligible.

In this work, we carry out molecular dynamics simulations on axially compressed SWCNTs of different chiral angles. The MDS is based on the second generation reactive empirical bond-order35 (REBO) potential. The effect of chirality on the buckling strains and modes are studied. The
results are also compared with those obtained from using classical cylindrical shell model based on the theory of non-local elasticity.

II. MOLECULAR DYNAMICS SIMULATION

Molecular dynamics simulation is a powerful tool for the analysis of nanoscale systems. The basic concept of an MDS is to simulate the time evolution of a system. The atoms in the system are treated as pointlike masses that interact with one another according to a given potential energy \( E(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \) where \( \mathbf{r}_i \) is the vector position of the \( i \)th atom. The evolution is computed at every time step. The instantaneous location and velocity of each atom are determined by solving the Newton dynamics function,

\[
\mathbf{F}_i = m_i \times \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i E(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N),
\]

where \( m_i \) is the mass of the atom, \( \nabla \) is the gradient, and the subscript \( i \) refers to the \( i \)th atom in the system.

The reliability of the MDS depends on the use of an appropriate potential. For CNTs, interactions between carbon atoms are commonly described by the well-known REBO potential,\(^{35}\) which is able to describe exactly the bonding structure and properties of graphite, diamond, and hydrocarbon molecules. Moreover, the REBO potential correctly reflects the bond formation and breakage between the atoms. This potential has been used to study the mechanical properties of CNTs, such as Young’s modulus,\(^{7,8,17,33}\) and has shown to furnish reliable results when compared to the more accurate tight-binding\(^{11,36}\) or \( \textit{ab initio} \) density functional theory methods.\(^{37,58}\)

The REBO potential is given by a sum of energy over the bonds, i.e.,

\[
E_b = \sum_{i>j} \left[ V_b(\mathbf{r}_{ij}) - \tilde{b}_{ij} V_A(\mathbf{r}_{ij}) \right],
\]

where \( V_b \) denotes the interatomic repulsion (core-core, etc.), \( V_A \) the attraction from the valence electrons, \( \mathbf{r}_{ij} \) is the distance between pairs of nearest-neighboring atoms \( i \) and \( j \), \( \tilde{b}_{ij} \) is a bond order between atoms \( i \) and \( j \) and it is given by the sum of the following terms:

\[
\tilde{b}_{ij} = \frac{1}{2} (b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}) + \Pi_{ij}^{\text{RC}} + b_{ij}^{\text{DH}}.
\]

The values for the functions \( b_{ij}^{\sigma-\pi} \) and \( b_{ji}^{\sigma-\pi} \) depend on the local coordination and bond angles for atoms \( i \) and \( j \), respectively. The value of \( \Pi_{ij}^{\text{RC}} \) depends on whether a bond between atoms \( i \) and \( j \) has a radical character and is part of a conjugated system. The value of the last term \( b_{ij}^{\text{DH}} \) depends on the dihedral angle for carbon-carbon double bonds.

The attractive and repulsive pair terms in Eq. (2) are given by

\[
V_A(\mathbf{r}_{ij}) = f'(\mathbf{r}_{ij}) \sum_{n=1,3} B_{n} e^{-\beta_{n} \mathbf{r}_{ij}}
\]

and

\[
V_b(\mathbf{r}_{ij}) = f'(\mathbf{r}_{ij}) \sum_{n=1,3} B_{n} e^{-\beta_{n} \mathbf{r}_{ij}}
\]

in which the function \( f'(\mathbf{r}_{ij}) \) is the cutoff function that restricts the pair interaction to the nearest neighbors and it is defined by a switching function of the form

\[
f'(\mathbf{r}_{ij}) = \begin{cases} 
1, & \text{for } r_{ij} < D_{ij}^{\text{min}} \\
\frac{1}{2} \left( 1 + \cos \left[ \frac{\pi(r_{ij} - D_{ij}^{\text{min}})}{D_{ij}^{\text{max}} - D_{ij}^{\text{min}}} \right] \right), & \text{for } D_{ij}^{\text{min}} < r_{ij} < D_{ij}^{\text{max}} \\
0, & \text{for } r_{ij} > D_{ij}^{\text{max}}.
\end{cases}
\]

Table I. Parameters of SWCNT models.

<table>
<thead>
<tr>
<th>Chiral indices ((n_1, n_2))</th>
<th>Chiral angle ((\text{degree}))</th>
<th>Length (Å)</th>
<th>Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(17,0)</td>
<td>0</td>
<td>69.064</td>
<td>13.31</td>
</tr>
<tr>
<td>(16,2)</td>
<td>5.82</td>
<td>69.049</td>
<td>13.38</td>
</tr>
<tr>
<td>(15,4)</td>
<td>11.52</td>
<td>69.662</td>
<td>13.58</td>
</tr>
<tr>
<td>(14,5)</td>
<td>14.70</td>
<td>69.244</td>
<td>13.35</td>
</tr>
<tr>
<td>(13,6)</td>
<td>17.99</td>
<td>67.388</td>
<td>13.17</td>
</tr>
<tr>
<td>(12,8)</td>
<td>23.41</td>
<td>69.811</td>
<td>13.65</td>
</tr>
<tr>
<td>(11,9)</td>
<td>26.70</td>
<td>69.722</td>
<td>13.58</td>
</tr>
<tr>
<td>(10,10)</td>
<td>30.00</td>
<td>70.381</td>
<td>13.56</td>
</tr>
</tbody>
</table>

In Eqs. (4)–(6), the parameters \( Q, A, B_n, \beta_n (n=1,2,3) \), \( \alpha \), \( D^{\text{min}}_{ij} \), and \( D^{\text{max}}_{ij} \) are experimentally fitted and their values are given in Table II.\(^{35}\)

In this study, the REBO potential is used for C-C interactions. The fifth-order Gear’s predictor-corrector algorithm is adopted for solving the equation of motion in Eq. (1). During the simulation, the temperature is controlled by scaling the velocities of all atoms. The process in this MDS on the axial compression of CNTs can be summarized in the following steps: relaxing the initial configuration to obtain the minimum energy configuration; compressing the CNT by applying external displacement at the atoms at the top end, then relaxing the CNT while keeping both ends fixed to reach a new equilibrium state and a new configuration.\(^{8}\)

In order to examine the effects of chirality on buckling behavior of SWCNT, eight SWCNTs with chiral angles \( 0^\circ < \theta < 30^\circ \) are simulated. The eight chiral indices are chosen so that the nanotubes have approximately the same diameter and tube length. There will be no doubt slight differences in the lengths, which cannot completely be eliminated due to the different lengths of their corresponding unit cells. The parameters of the eight SWCNTs are shown in Table I.

During the simulation, we adopted a constant compression strain rate of \( 7 \times 10^{-4} / \text{ps} \), which is applied via displacement of the atoms at the top end of the SWCNTs. During the relaxation period (taken as 1 ps) the atoms at both ends of the SWCNTs are fixed in position. It is important to adopt a constant strain rate for all the tubes simulated since the strain...
rate would play a significant role in the MDS results.\textsuperscript{13} When the strain rate was halved, the buckling modes of the SWCNTs remained unchanged. The environmental temperature of the simulations is maintained at 0.01 K so as to avoid thermal kinetic effect.\textsuperscript{8}

III. NONLOCAL SHELL MODEL

Cylindrical shell models based on the Donnell shell theory\textsuperscript{39} have been commonly applied for the analysis of CNTs. But their validity is rarely confirmed by MDS results or experimental tests. In the few instances, Yakobson et al.\textsuperscript{9} conducted MDS on an armchair SWCNT (7, 7) under compression and they found that the critical strain obtained using the classical thin shell model is close to the MDS result. In the work of Ru\textsuperscript{21} and Kitipornchai et al.\textsuperscript{27} the validity of their shell models are confirmed by only one or two available MDS results. The general applicability of the shell models is, however, an area of active research. Efforts have been made by Wang et al.\textsuperscript{8} to check the applicability of the beam and shell models for the buckling problem of carbon nanotubes. Their comparison study showed that the conventional continuum mechanics theory is not very suitable for analyzing the deformation of carbon nanotubes. In the continuum shell model, the discrete CNTs are treated as homogeneous and continuum structures. The material microstructure, such as the lattice spacing between individual carbon atoms, is ignored. At the nanometer scale, however, the material microstructure becomes important and thus the small scale effect cannot be neglected. The existence of small length scale in nanomaterials makes the applicability of classical or local continuum models questionable. Therefore, continuum models have to be refined to incorporate the small scale effect. This has led to the application of nonlocal elasticity theory which was developed by Eringen.\textsuperscript{40,41}

The theory of nonlocal continuum mechanics was initially proposed\textsuperscript{40,41} to account for the small scale effect. In nonlocal elasticity, it is assumed that the stress at a given point is dependent not only on the strain state at that same point (as in the classical continuum mechanics), but also on the strain states of all points in the body. In other words, the stress at a given point is a function of strain states at every point in the body. Thus, the internal length scale could be simply incorporated in the constitutive equations as a material parameter. So far, the continuum mechanics beam and shell models, based on the theory of nonlocal elasticity, have been developed to analyze the mechanical behaviors of CNTs such as buckling,\textsuperscript{25,28} vibration,\textsuperscript{31} and wave propagation.\textsuperscript{42,43} The nonlocal models account for small length scale (microstructure) effect and thus they provide better theoretical results.

In this study, we adopt the theory of nonlocal continuum mechanics for the shell model and check its validity against the newly obtained MDS results. This nonlocal shell model for the buckling of MWCNTs is developed by Zhang et al.\textsuperscript{28} By simplifying the buckling strain expression for double-walled carbon nanotubes of Zhang et al., the buckling strain for SWCNT can be expressed as

\[ \varepsilon_{cr} = \frac{DR^2\lambda^4 + h\eta^4}{hR^2\lambda^2\eta^2(1 + \lambda e_0^2d^2)}, \]  

(7)

where

\[ D = \frac{h^3}{12(1-v^2)}, \quad \lambda = \left( \frac{m\pi}{L} \right)^2 + \left( \frac{n}{R} \right)^2, \quad \eta = \frac{m\pi}{L}. \]

\( h \) is the effective thickness of SWCNT and is taken as 0.066 nm, \( R \) the radius, \( L \) the length, \( a \) is a small scale parameter which is taken as the C–C bond length of 0.142 nm, \( e_0 \) is a constant to be determined, and \( m \) and \( n \) are the number of half waves in axial and circumferential directions, respectively.

By neglecting the small length scale effect (i.e., setting \( a=0 \)), the above equation reduces to the classical local result based on the Donnell shell theory,\textsuperscript{39}

\[ \varepsilon_{cr} = \frac{DR^2\lambda^4 + h\eta^4}{hR^2\lambda^2\eta^2}. \]

(8)

It can be observed that Eq. (7) gives a smaller axial buckling strain than the classical local shell model results given by Eq. (8). In other words, the classical shell model overpredicts the axial buckling strain.

The critical axial buckling strain can be determined by minimizing the right-hand side of Eq. (7) with respect to the integers \( m \) and \( n \). The theoretical results incorporating the microstructure effect can then be used to check the validity of the continuum shell model by comparing with those obtained by MDS.

IV. SIMULATION RESULTS

A. Buckling modes of SWCNTs

We first discuss the buckling modes of SWCNTs (its properties defined in Table I) as obtained from MDS. Figure 1 shows the morphological changes for the armchair SWCNT (10, 10) at different strain levels. During the MDS, the SWCNT retains its cylindrical symmetry until the critical strain is reached at which point the tube begins to buckle. The critical strain is determined from the strain versus strain energy curve.\textsuperscript{8,9,13,20} On further compression, the CNTs can still sustain deformation without any deflection until the structure buckles severely.

The buckling modes of SWCNTs with different chiralities are depicted in Fig. 2. It is interesting to observe that the buckling modes of chiral CNTs are similar to that of the armchair where two flattenings (referred to as “fins” by Yakobson et al.\textsuperscript{9}), that are perpendicular to each other, are formed as shown in Fig. 2. However, the chiral angles affect the positioning of the fins, albeit slightly. But in the zigzag CNT, a three-fin pattern is observed instead at the critical strain value. Since all the tubes have similar length-to-diameter ratios, the difference in buckling modes can only be attributed to the chiral angles. In sum, the chiral angles affect slightly the buckling mode except for the zigzag configuration, which yields a completely different buckling mode.

The CNTs simulated above are of a moderate length, about 7 nm. In order to study the effect of the CNT length on the buckling mode, three more sets of CNTs with small and
large lengths (5, 11, and 17.6 nm, respectively) are analyzed. It is found that the same conclusion still holds, that is, the chiral CNTs display similar buckling modes to that of armchair CNT but the zigzag CNT buckles in a different way. The buckling modes of the slender tubes with a relatively long length of 17.6 nm are shown in Fig. 3. From Fig. 3, it is interesting to observe that the armchair and chiral CNTs buckle locally at the upper parts of the tubes since the compressive load is applied on the upper ends of the tubes. In this range of chirality, the compressive load fails to distribute evenly downward along the length of the carbon nanotube. Therefore, the lower part of the tube length remains almost straight (or unchanged). However, for the zigzag CNT with the chiral angle of 0°, the compressive force appears to be transmitted more uniformly through the tube and thus the buckling mode display a more even distribution of bulges. The zigzag CNT appears to make full use of its material under compression when compared to the CNTs of other chiral angles. This enables the zigzag CNT to yield a higher buckling load which will be further discussed in the following section on the buckling strain values. Similar buckling modes for the slender armchair (10,10) CNT are also observed by Liew et al.\textsuperscript{44} But the buckling morphology of the tube is symmetric with one bulge at each end because they applied the axial compressive force on both ends of the tubes\textsuperscript{44} as opposed to applying the compressive force at one end in this study. Although the chiral and armchair CNTs show similar buckling configurations, the positions of the flattening move downward with decreasing chiral angles. The example of a long and slender CNT clearly demonstrates the dependence of the load transmissibility on the chirality.

B. Critical buckling strains

The critical strains of the eight SWCNTs in Table I obtained by the MDS against chiral angles are plotted in Fig. 4. It is observed that the critical strains decrease as the chiral angle increases except for the chiral angle of 30°. At \( \theta = 30° \), the critical strain is increased slightly for the armchair CNT. It is shown in Fig. 4 that the zigzag SWCNT preserves high buckling capability, which was also noted by Robertson \textit{et al.}\textsuperscript{33} It is also clear from Fig. 4 that the critical strain decreases abruptly with increasing chiral angles until the chiral angle reaches 15°. For example, the critical strain drops rapidly from a value of 0.0894 for zigzag CNT with \( \theta = 0° \) to 0.054 for chiral CNT (14,5) with \( \theta = 14.7° \). Beyond this chiral angle, the critical strain decreases slowly until it converges to a particular value. The relationship between buckling load and chiral angle is also plotted as an inset in Fig. 4. It is found that the trend of the buckling load is similar to that of the critical strain. The zigzag CNT can sustain the highest buckling load and the buckling loads of chiral CNTs decreases as the chiral angle increases. The disparity between zigzag CNT and other CNTs may result from different bond configurations due to the different chiralities. In an armchair CNT, for example, one-third of the bonds are perpendicular to the axial direction. During axial compression, these bonds are stretched. In a zigzag CNT, however, one-third of the bonds are aligned along the loading direction.
During axial compression, all of the bonds are in compression, providing a stronger resistance to the lateral deformation than that of armchair CNT. As a consequence, the buckling capability of the zigzag CNT is superior to the armchair and other chiral CNTs. Interestingly, in nature, the honeybee hive is of a zigzag configuration rather than that of the armchair configuration!

To make use of Eq. (7) on the basis of nonlocal elasticity for the theoretical critical strains, it is important to determine the magnitude of parameter $e_0$ first. Although the value of the parameter for CNTs is not available at present, it may be estimated by curve fitting theoretical results obtained by Eq. (7) to those from molecular dynamics simulations. Since the MDS results of all tubes are varied, it is believed that the parameters $e_0$ are different for different tubes. As an example, we describe the use of the critical strain of the armchair (10,10) SWCNT for the prediction of the value of $e_0$. In the present MDS, it is found that the armchair CNT began to buckle locally at the critical strain of 0.0526 with the axial half wave number $m=2$ and the circumferential wave number $n=2$ while the axis remains straight, as shown in the first snapshot in Fig. 2. The classical result for the critical buckling strain of this tube can be determined by solving Eq. (8) and the result is about 0.0606 with $m=n=2$. The ratio of the classical result to that obtained by MDS is about 1.152. It is known that the ratio of the classical result to nonlocal result for the axial buckling strain of SWCNT can be derived by use of Eqs. (7) and (8) as

$$\chi = 1 + \left[ \pi^2 m^2 + n^2 \left( \frac{L}{R} \right)^2 \right] \left( \frac{e_0}{L} \right)^2. \quad (9)$$

For the ratio $\chi = 1.152$, from Eq. (9), the value of parameter $e_0$ for the armchair CNT is found to be $e_0 = 0.89$. All the parameters of $e_0$ of the other tubes can be determined except for zigzag (17,0) and chiral (16,2) CNTs, the tubes with the first two smallest chiral angles. The parameters calculated by the foregoing procedure for the two CNTs are complex numbers, which are not reasonable. Hence, we use the classical local results determined by Eq. (8) instead of nonlocal ones for the two CNTs when comparing with their corresponding MDS results. The magnitudes of $e_0$ for the other six CNTs are listed in Table II. By applying the values of $e_0$ into Eq. (7), the theoretical critical strains based on nonlocal elasticity for the SWCNTs can be obtained. The results are compared with those from MDS in Fig. 4. In this study, the effective thickness of all the carbon nanotubes is assumed to be 0.066 nm as suggested by Yakobson et al. 9

It is observed in Fig. 4 that both sets of results are in excellent agreement. As for the zigzag (17,0) and chiral (16,2) CNTs, the classical shell results furnished by Eq. (8) are smaller than those of MDS. The difference in percentage between the theoretical and MDS results is up to 30.5% for the zigzag CNT. The percentage difference for the chiral (16,2) CNT is about 3.57%. Therefore, it seems that the continuum mechanics models cannot be applied to the zigzag CNT. With suitably determined parameters $e_0$ for the CNTs with larger chiral angles, the theoretical shell model based on the theory of nonlocal elasticity can estimate the buckling strains of CNTs rather well. It is expected that the parameters $e_0$ can be obtained from experiments for CNTs with different chiral angles in order to examine the applicability of the theoretical continuum models.

![FIG. 3. Snapshots of slender tubes ($L/D = 13.1$) at their critical strains.](image)

![FIG. 4. Critical buckling strains from MDS and nonlocal shell models.](image)

**TABLE II. Magnitudes of parameters $e_0$ for SWCNTs.**

<table>
<thead>
<tr>
<th>Chiral indices $(n_1, n_2)$</th>
<th>$e_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(17,0)</td>
<td>NA</td>
</tr>
<tr>
<td>(16,2)</td>
<td>NA</td>
</tr>
<tr>
<td>(15,4)</td>
<td>0.546</td>
</tr>
<tr>
<td>(14,5)</td>
<td>0.854</td>
</tr>
<tr>
<td>(13,6)</td>
<td>1.023</td>
</tr>
<tr>
<td>(12,8)</td>
<td>0.995</td>
</tr>
<tr>
<td>(11,9)</td>
<td>1.043</td>
</tr>
<tr>
<td>(10,10)</td>
<td>0.890</td>
</tr>
</tbody>
</table>
V. CONCLUSION

The effect of chirality on the buckling behaviors of single-walled carbon nanotubes (SWCNTs) is examined by means of molecular dynamics simulations. It is found from the simulation results that all SWCNTs display similar buckling modes except for the zigzag SWCNT. The buckling strains of SWCNTs decrease with increasing chiral angles. The chirality independent tubes can be simulated by the continuum shell model based on the theory of nonlocal elasticity and the critical strains are in excellent agreement with those obtained by MDS. However, the continuum shell model fails to capture the buckling strains for the SWCNTs with small chiral angle such as the zigzag CNT.

In summary, chirality plays a significant role in the buckling behaviors of SWCNT with small chiral angles and cannot be ignored. However, the effect can be neglected for SWCNT with relative larger chiral angles and the buckling behavior of such tubes can be represented by armchair CNTs.

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Ever since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,1 CNTs have attracted considerable attention due to their unique electronic and mechanical properties. Recent studies have indicated that CNTs possess exceptionally high elastic modulus2–4 and can sustain large elastic and failure strains.5–9 Therefore, CNTs have been identified as one of the most promising superfibers for nanotube-composite materials.

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II. MOLECULAR DYNAMICS SIMULATION

Molecular dynamics simulation is a powerful tool for the analysis of nanoscale systems. The basic concept of an MDS is to simulate the time evolution of a system. The atoms in the system are treated as pointlike masses that interact with one another according to a given potential energy $E(r_1, r_2, \ldots, r_n)$ where $r_i$ is the vector position of the $i$th atom. The evolution is computed at every time step. The instantaneous location and velocity of each atom are determined by solving the Newton dynamics function,

$$\mathbf{F}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i E(r_1, r_2, \ldots, r_n),$$  \hspace{1cm} (1)

where $m_i$ is the mass of the atom, $\nabla_i$ is the gradient, and the subscript $i$ refers to the $i$th atom in the system.

The reliability of the MDS depends on the use of an appropriate potential. For CNTs, interactions between carbon atoms are commonly described by the well-known REBO potential,\textsuperscript{35} which is able to describe exactly the bonding structure and properties of graphite, diamond, and hydrocarbon molecules. Moreover, the REBO potential correctly reflects the bond formation and breakage between the atoms. This potential has been used to study the mechanical properties of CNTs, such as Young’s modulus,\textsuperscript{7,8,17,33} and has shown to furnish reliable results when compared to the more accurate tight-binding\textsuperscript{11,36} or ab initio density functional theory methods.\textsuperscript{37,38}

The REBO potential is given by a sum of energy over the bonds, i.e.,

$$E_b = \sum_i \sum_{j>i} [V_p(r_{ij}) - \bar{b}_{ij} V_A(r_{ij})],$$  \hspace{1cm} (2)

where $V_p$ denotes the interatomic repulsion (core-core, etc.), $V_A$ the attraction from the valence electrons, $r_{ij}$ is the distance between pairs of nearest-neighboring atoms $i$ and $j$, $\bar{b}_{ij}$ is a bond order between atoms $i$ and $j$ and it is given by the sum of the following terms:

$$\bar{b}_{ij} = \frac{1}{2} (b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}) + \Pi_{ij}^{RC} + b_{ij}^{DH}. $$  \hspace{1cm} (3)

The values for the functions $b_{ij}^{\sigma-\pi}$ and $b_{ji}^{\sigma-\pi}$ depend on the local coordination and bond angles for atoms $i$ and $j$, respectively. The value of $\Pi_{ij}^{RC}$ depends on whether a bond between atoms $i$ and $j$ has a radical character and is part of a conjugated system. The value of the last term $b_{ij}^{DH}$ depends on the dihedral angle for carbon-carbon double bonds.

The attractive and repulsive pair terms in Eq. (2) are given by

$$V_A(r_{ij}) = f^*(r_{ij}) \sum_{n=1,3} B_n e^{-B_n r_{ij}}$$  \hspace{1cm} (4)

and

$$V_p(r_{ij}) = f^*(r_{ij}) \left[ 1 + \frac{\pi}{D_{ij}^{\max} - D_{ij}^{\min}} \right](1 + Q(r_{ij}) \Delta e^{-\alpha r_{ij}})$$  \hspace{1cm} (5)

in which the function $f^*(r_{ij})$ is the cutoff function that restricts the pair interaction to the nearest neighbors and it is defined by a switching function of the form

$$f^*(r_{ij}) = \begin{cases} 
1, & r_{ij} < D_{ij}^{\min} \\
\frac{1}{2} \left[ 1 + \cos \left( \frac{\pi (r_{ij} - D_{ij}^{\min})}{D_{ij}^{\max} - D_{ij}^{\min}} \right) \right], & D_{ij}^{\min} < r_{ij} < D_{ij}^{\max} \\
0, & r_{ij} > D_{ij}^{\max}.
\end{cases}$$  \hspace{1cm} (6)

In Eqs. (4)–(6), the parameters $Q$, $A$, $B_n$, $\beta_n$ ($n=1,2,3$), $\alpha$, $D_{ij}^{\min}$, and $D_{ij}^{\max}$ are experimentally fitted and their values are given in Table II.\textsuperscript{35}

In this study, the REBO potential is used for C–C interactions. The fifth-order Gear’s predictor-corrector algorithm is adopted for solving the equation of motion in Eq. (1). During the simulation, the temperature is controlled by scaling the velocities of all atoms. The process in this MDS on the axial compression of CNTs can be summarized in the following steps: relaxing the initial configuration to obtain the minimum energy configuration; compressing the CNT by applying external displacement at the atoms at the top end, then relaxing the CNT while keeping both ends fixed to reach a new equilibrium state and a new configuration.\textsuperscript{8}

In order to examine the effects of chirality on buckling behavior of SWCNT, eight SWCNTs with chiral angles $0^\circ < \theta < 30^\circ$ are simulated. The eight chiral indices are chosen so that the nanotubes have approximately the same diameter and tube length. There will be no doubt slight differences in the lengths, which cannot completely be eliminated due to the different lengths of their corresponding unit cells. The parameters of the eight SWCNTs are shown in Table I.

During the simulation, we adopted a constant compression strain rate of $7 \times 10^{-4}$/ps, which is applied via displacement of the atoms at the top end of the SWCNTs. During the relaxation period (taken as 1 ps) the atoms at both ends of the SWCNTs are fixed in position. It is important to adopt a constant strain rate for all the tubes simulated since the strain

<table>
<thead>
<tr>
<th>Chiral indices $(n_1, n_2)$</th>
<th>Chiral angle (degree)</th>
<th>Length (Å)</th>
<th>Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(17,0)</td>
<td>0</td>
<td>69.064</td>
<td>13.31</td>
</tr>
<tr>
<td>(16,2)</td>
<td>5.82</td>
<td>69.049</td>
<td>13.38</td>
</tr>
<tr>
<td>(15,4)</td>
<td>11.52</td>
<td>69.662</td>
<td>13.58</td>
</tr>
<tr>
<td>(14,5)</td>
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<td>13.35</td>
</tr>
<tr>
<td>(13,6)</td>
<td>17.99</td>
<td>67.388</td>
<td>13.17</td>
</tr>
<tr>
<td>(12,8)</td>
<td>23.41</td>
<td>69.811</td>
<td>13.65</td>
</tr>
<tr>
<td>(11,9)</td>
<td>26.70</td>
<td>69.722</td>
<td>13.58</td>
</tr>
<tr>
<td>(10,10)</td>
<td>30.00</td>
<td>70.381</td>
<td>13.56</td>
</tr>
</tbody>
</table>
rate would play a significant role in the MDS results. When the strain rate was halved, the buckling modes of the SWCNTs remained unchanged. The environmental temperature of the simulations is maintained at 0.01 K so as to avoid thermal kinetic effect.

III. NONLOCAL SHELL MODEL

Cylindrical shell models based on the Donnell shell theory have been commonly applied for the analysis of CNTs. But their validity is rarely confirmed by MDS results or experimental tests. In the few instances, Yakobson et al. conducted MDS on an armchair SWCNT under compression and they found that the critical strain obtained using the classical thin shell model is close to the MDS result. In the work of Ru and Kitipornchai, the validity of their shell models are confirmed by only one or two available MDS results. The general applicability of the shell models is, however, an area of active research. Efforts have been made by Wang et al. to check the applicability of the beam and shell models for the buckling problem of carbon nanotubes. Their comparison study showed that the conventional continuum mechanics theory is not very suitable for analyzing the deformation of carbon nanotubes. In the continuum shell model, the discrete CNTs are treated as homogeneous and continuum structures. The material microstructure, such as the lattice spacing between individual carbon atoms, is ignored. At the nanometer scale, however, the material microstructure becomes important and thus the small scale effect cannot be neglected. The existence of small length scale in nanomaterials makes the applicability of classical or local continuum models questionable. Therefore, continuum models have to be refined to incorporate the small scale effect. This has led to the application of nonlocal elasticity theory which was developed by Eringen.

The theory of nonlocal continuum mechanics was initially proposed to account for the small scale effect. In nonlocal elasticity, it is assumed that the stress at a given point is dependent not only on the strain state at that same point (as in the classical continuum mechanics), but also on the strain states of all points in the body. In other words, the stress at a given point is a function of strain states at every point in the body. Thus, the internal length scale could be simply incorporated in the constitutive equations as a material parameter. So far, the continuum mechanics beam and shell models, based on the theory of nonlocal elasticity, have been developed to analyze the mechanical behaviors of CNTs such as buckling, vibration, and wave propagation. The nonlocal models account for small length scale (microstructure) effect and thus they provide better theoretical results.

In this study, we adopt the theory of nonlocal continuum mechanics for the shell model and check its validity against the newly obtained MDS results. This nonlocal shell model for the buckling of MWCNTs is developed by Zhang et al. By simplifying the buckling strain expression for double-walled carbon nanotubes of Zhang et al., the buckling strain for SWCNT can be expressed as

\[ \varepsilon_c = \frac{DR^2\lambda^4 + h\eta^4}{hR^2\lambda^2\eta^2(1 + \lambda e_0^2)\varepsilon_c} , \]  

where

\[ D = \frac{h^3}{12(1 - \nu^2)} , \quad \lambda = \left( \frac{m\pi}{L} \right)^2 + \left( \frac{n}{R} \right)^2 , \quad \eta = \frac{m\pi}{L} . \]

\( h \) is the effective thickness of SWCNT and is taken as 0.066 nm. \( R \) the radius, \( L \) the length, \( a \) is a small scale parameter which is taken as the C–C bond length of 0.142 nm, \( e_0 \) is a constant to be determined, and \( m \) and \( n \) are the number of half waves in axial and circumferential directions, respectively.

By neglecting the small length scale effect (i.e., setting \( a=0 \)), the above equation reduces to the classical local result based on the Donnell shell theory.

\[ \varepsilon_c = \frac{DR^2\lambda^4 + h\eta^4}{hR^2\lambda^2\eta^2} . \]

IV. SIMULATION RESULTS

A. Buckling modes of SWCNTs

We first discuss the buckling modes of SWCNTs (its properties defined in Table I) as obtained from MDS. Figure 1 shows the morphological changes for the armchair SWCNT at different strain levels. During the MDS, the SWCNT retains its cylindrical symmetry until the critical strain is reached at which point the tube begins to buckle. The critical strain is determined from the strain versus strain energy curve. On further compression, the CNTs can still sustain deformation without any deflection until the structure buckles severely.

The buckling modes of SWCNTs with different chiralities are depicted in Fig. 2. It is interesting to observe that the buckling modes of chiral CNTs are similar to that of the armchair where two flattenings (referred to as “fins” by Yakobson et al.), that are perpendicular to each other, are formed as shown in Fig. 2. However, the chiral angles affect the positioning of the fins, albeit slightly. But in the zigzag CNT, a three-fin pattern is observed instead at the critical strain value. Since all the tubes have similar length-to-diameter ratios, the difference in buckling modes can only be attributed to the chiral angles. In sum, the chiral angles affect slightly the buckling mode except for the zigzag configuration, which yields a completely different buckling mode.

The CNTs simulated above are of a moderate length, about 7 nm. In order to study the effect of the CNT length on the buckling mode, three more sets of CNTs with small and
large lengths (5, 11, and 17.6 nm, respectively) are analyzed. It is found that the same conclusion still holds, that is, the chiral CNTs display similar buckling modes to that of armchair CNT but the zigzag CNT buckles in a different way. The buckling modes of the slender tubes with a relatively long length of 17.6 nm are shown in Fig. 3. From Fig. 3, it is interesting to observe that the armchair and chiral CNTs buckle locally at the upper parts of the tubes since the compressive load is applied on the upper ends of the tubes. In this range of chirality, the compressive load fails to distribute evenly downward along the length of the carbon nanotube. Therefore, the lower part of the tube length remains almost straight (or unchanged). However, for the zigzag CNT with the chiral angle of 0°, the compressive force appears to be transmitted more uniformly through the tube and thus the buckling mode display a more even distribution of bulges. The zigzag CNT appears to make full use of its material under compression when compared to the CNTs of other chiral angles. This enables the zigzag CNT to yield a higher buckling load which will be further discussed in the following section on the buckling strain values. Similar buckling modes for the slender armchair (10,10) CNT are also observed by Liew et al. It is also clear from Fig. 4 that the critical strain decreases abruptly with increasing chiral angles until the chiral angle reaches 15°. For example, the critical strain drops rapidly from a value of 0.0894 for zigzag CNT with \( \theta = 0° \) to 0.054 for chiral CNT (14,5) with \( \theta = 14.7° \). Beyond this chiral angle, the critical strain decreases slowly until it converges to a particular value. The relationship between buckling load and chiral angle is also plotted as an inset in Fig. 4. It is found that the trend of the buckling load is similar to that of the critical strain. The zigzag CNT can sustain the highest buckling load and the buckling loads of chiral CNTs decreases as the chiral angle increases. The disparity between zigzag CNT and other CNTs may result from different bond configurations due to the different chiralities. In an armchair CNT, for example, one-third of the bonds are perpendicular to the axial direction. During axial compression, these bonds are stretched. In a zigzag CNT, however, one-third of the bonds are aligned along the loading direction.
During axial compression, all of the bonds are in compression, providing a stronger resistance to the lateral deformation than that of armchair CNT. As a consequence, the buckling capability of the zigzag CNT is superior to the armchair and other chiral CNTs. Interestingly, in nature, the honeybee hive is of a zigzag configuration rather than that of the armchair configuration!

To make use of Eq. (7) on the basis of nonlocal elasticity for the theoretical critical strains, it is important to determine the magnitude of parameter \( e_0 \) first. Although the value of the parameter for CNTs is not available at present, it may be estimated by curve fitting theoretical results obtained by Eq. (7) to those from molecular dynamics simulations. Since the MDS results of all tubes are varied, it is believed that the parameters \( e_0 \) are different for different tubes. As an example, we describe the use of the critical strain of the armchair (10,10) SWCNT for the prediction of the value of \( e_0 \). In the present MDS, it is found that the armchair CNT began to buckle locally at the critical strain of 0.0526 with the axial half wave number \( m=2 \) and the circumferential wave number \( n=2 \) while the axis remains straight, as shown in the first snapshot in Fig. 2. The classical result for the critical buckling strain of this tube can be determined by solving Eq. (8) and the result is about 0.0606 with \( m=n=2 \). The ratio of the classical result to that obtained by MDS is about 1.152. It is known that the ratio of the classical result to nonlocal result for the axial buckling strain of SWCNT can be derived by use of Eqs. (7) and (8) as

\[
\chi = 1 + \left[ \pi^2 m^2 + n^2 \left( \frac{L}{R} \right)^2 \right] \left( \frac{e_0 a}{L} \right)^2.
\]

For the ratio \( \chi = 1.152 \), from Eq. (9), the value of parameter \( e_0 \) for the armchair CNT is found to be \( e_0 \approx 0.89 \). All the parameters of \( e_0 \) of the other tubes can be determined except for zigzag (17,0) and chiral (16,2) CNTs, the tubes with the first two smallest chiral angles. The parameters calculated by the foregoing procedure for the two CNTs are complex numbers, which are not reasonable. Hence, we use the classical local results determined by Eq. (8) instead of nonlocal ones for the two CNTs when comparing with their corresponding MDS results. The magnitudes of \( e_0 \) for the other six CNTs are listed in Table II. By applying the values of \( e_0 \) into Eq. (7), the theoretical critical strains based on nonlocal elasticity for the SWCNTs can be obtained. The results are compared with those from MDS in Fig. 4. In this study, the effective thickness of all the carbon nanotubes is assumed to be 0.066 nm as suggested by Yakobson et al.\(^9\)

It is observed in Fig. 4 that both sets of results are in excellent agreement. As for the zigzag (17,0) and chiral (16,2) CNTs, the classical shell results furnished by Eq. (8) are smaller than those of MDS. The difference in percentage between the theoretical and MDS results is up to 30.5% for the zigzag CNT. The percentage difference for the chiral (16,2) CNT is about 3.57%. Therefore, it seems that the continuum mechanics models cannot be applied to the zigzag CNT. With suitably determined parameters \( e_0 \) for the CNTs with larger chiral angles, the theoretical shell model based on the theory of nonlocal elasticity can estimate the buckling strains of CNTs rather well. It is expected that the parameters \( e_0 \) can be obtained from experiments for CNTs with different chiral angles in order to examine the applicability of the theoretical continuum models.

<table>
<thead>
<tr>
<th>Chiral indices ((n_1,n_2))</th>
<th>(e_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((17,0))</td>
<td>NA</td>
</tr>
<tr>
<td>((16,2))</td>
<td>NA</td>
</tr>
<tr>
<td>((15,4))</td>
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</tr>
<tr>
<td>((14,5))</td>
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<td>((13,6))</td>
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</tr>
<tr>
<td>((12,8))</td>
<td>0.995</td>
</tr>
<tr>
<td>((11,9))</td>
<td>1.043</td>
</tr>
<tr>
<td>((10,10))</td>
<td>0.890</td>
</tr>
</tbody>
</table>

TABLE II. Magnitudes of parameters \(e_0\) for SWCNTs.
V. CONCLUSION

The effect of chirality on the buckling behaviors of single-walled carbon nanotubes (SWCNTs) is examined by means of molecular dynamics simulations. It is found from the simulation results that all SWCNTs display similar buckling modes except for the zigzag SWCNT. The buckling strains of SWCNTs decrease with increasing chiral angles. The chirality independent tubes can be simulated by the continuum shell model based on the theory of nonlocal elasticity and the critical strains are in excellent agreement with those obtained by MDS. However, the continuum shell model fails to capture the buckling strains for the SWCNTs with small chiral angle such as the zigzag CNT.

In summary, chirality plays a significant role in the buckling behaviors of SWCNT with small chiral angles and cannot be ignored. However, the effect can be neglected for SWCNT with relative larger chiral angles and the buckling behavior of such tubes can be represented by armchair CNTs.
