An investigation into the cap deformation of carbon nanotube tips using tight-binding molecular dynamics simulation

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This article employs a tight-binding molecular dynamics simulation approach to investigate the cap deformation of a carbon nanotube tip when used as a probe in a tapping mode measurement process. The simulation results indicate that the deformation behavior of the cap during its interaction with a rigid graphite surface obeys Hooke’s law until a critical repulsive force is attained. At this point, a radial deformation of the cap occurs as the bond orientations and lengths change. This deformation causes a reduction in the magnitude of the repulsive force, and is accompanied by an increase in the axial compression. Consequently, the cap deformation no longer conforms to Hooke’s law. It is observed that when the capped carbon nanotube is withdrawn from the graphite surface, the cap recovers its original shape. By considering the deformation within the Hookean region, this study derives the spring constants of caps of different radii. It is shown that the spring constant decreases as the radius of the carbon nanotube increases toward that of an (8,8) carbon nanotube. Thereafter, there is no significant change in the spring constant as the radius of the nanotube continues to increase. Specifically, the results indicate that the spring constant of a (4,4) armchair carbon nanotube is approximately 1.4 nN/Å, and that this value reduces to 0.4 nN/Å for carbon nanotubes of radii greater than that of an (8,8) carbon nanotube. © 2004 American Institute of Physics.

I. INTRODUCTION

The unique material properties of carbon nanotubes render them particularly suitable for use as microscopy probe tips. Not only can they increase the degree of measurement resolution, but they also tend to cause less sample surface damage than conventional probes. While the use of a carbon nanotube with a high aspect ratio and a small radius of curvature permits their access to narrow sharp recesses, and allows the features of these recesses to be probed, the tip size and features of a conventional pyramid tip probe prevent their application in similar situations.

One of the most sophisticated probing measurement techniques is the so-called tapping mode, in which the cap of a carbon nanotube attached to a cantilever taps the sample surface at regular time intervals. This action causes the cantilever to exhibit a frequency response, whose amplitude of oscillation can then be interpreted so as to derive a corresponding topographic surface image. Using a carbon nanotube in the tapping mode measurement process is advantageous since its inherent flexibility prevents the probe tip from crashing into the measured surface and causes only marginal surface damage to softer samples. During the measurement process, the cap directly impacts the surface of the sample, and consequently, the mechanical properties of the cap significantly affect the derived topographic image. The high frequency response of the cantilever upon which the tip is mounted poses problems when attempting to measure the cap deformation directly using experimental methods. Therefore, researchers generally adopt numerical simulation methods to analyze the deformation process and to determine the material properties. Of these methods, molecular dynamics (MD) simulation provides a reliable means of investigating the material properties of the carbon nanotube cap at an atomistic scale.

A review of the published literature shows that several researchers have successfully applied this method in investigating the deformation properties of capped carbon nanotubes. For example, Harrison et al.5 used MD simulation to investigate nanoindentations formed using hemispherically capped (10,10) armchair nanotubes. Their results showed that the curve relating the applied force to the indentation depth was not smooth at a certain indentation depth. It was suggested that this phenomenon was the result of a cap inversion, in which an increasing repulsive force caused the morphology of the extreme end of the cap to change from an original concave form to a convex form, and the carbon rings of the hexagonal structures to pop into the interior of the carbon nanotube. Garg et al.7 utilized the empirical bond-order potential model to investigate the indentation of diamond and graphene surfaces by a carbon nanotube tip. In their study, it was concluded that the cap deformation mecha-
nisms are strongly influenced by the properties of the indented surface. Furthermore, it was observed that compared to the indentation of a hard surface, a softer surface prevented the carbon cap from slipping during the indentation process, and hence resulted in a greater buckling force. In a later study, the same authors presented the deformation mechanisms of a multiwall carbon nanotube cap during the indentation of hydrogen-terminated diamond and graphene surfaces. Their results suggested that there was no significant interaction between the shells of the multiwall carbon nanotube during the indentation process, i.e., bonds were not formed between the individual walls during the deformation of the carbon nanotube. A review of the related literature reveals comparatively little use of MD simulation to address the issue of the springlike behavior of the carbon nanotube cap under deformation conditions. Yao and Lordi adopted the universal force field (UFF) method to determine the spring constants of carbon nanotubes of different diameters, and concluded that the spring constant was independent of the nanotube diameter for deformation within the Hookean region. However, it is generally believed that the UFF potential model does not accurately reflect the quantum nature of the carbon atoms when the covalent bond orientations and lengths of the cap undergo a violent change. Furthermore, the study by Yao and Lordi did not consider the restoration mechanisms of the cap when it was withdrawn from the indented surface.

The resolution of the tapping mode measurement process can be improved by specifying an appropriate diameter for the carbon nanotube tip. Consequently, the present study adopts a tight-binding molecular dynamics simulation approach to perform a detailed investigation into the deformation mechanisms of capped carbon nanotubes of different radii when used as probes in the tapping mode measurement process. This study specifically adopts the tight-binding method since it reflects the quantum nature of the covalent bonding of the carbon atoms, and hence assures the reliability of the identified deformation mechanisms. This study determines the spring constants of caps of various radii. The present results provide a valuable reference for those seeking to select an appropriate carbon nanotube tip radius for use in a variety of different applications.

II. SIMULATION MODEL

Figure 1 presents a schematic representation of the simulation model adopted in the present investigation. To prevent any interaction from taking place between the atoms of the capped carbon nanotube and those of the surface, the nanotube is initially positioned at a distance of 1 nm from the graphite surface. Furthermore, the simulation assumes that all of the carbon atoms within the graphite layer are fixed. Once the atoms of the carbon nanotube have attained a Maxwell–Boltzmann distribution at 300 K, motion of the carbon nanotube toward the graphite surface is simulated at a mass velocity of 300 m/s. Since MD simulation is limited to a femto-second time scale, the simulated velocity is actually several orders larger than that which is generally employed in the physical tapping mode measurement process. Consequently, the simulation applies the scaling method at each time step in order to maintain the temperature of the capped carbon nanotube at a constant value of 300 K. In this way, the simulation accurately reflects the deformation behavior, which occurs at a constant temperature of 300 K in the physical probing process. In the scaling method, the capped carbon nanotube is assumed to be the thermostat, and all the carbon atoms of the capped carbon nanotube are rescaled to maintain a constant temperature of 300 K. Hence, the capped carbon nanotube deformation behavior at a constant temperature of 300 K can be obtained. If this step were not taken, the higher driving velocity would result in a significant accumulation of energy within the cap, and would hence result in cap damage. This would degrade the validity of the simulation results since this phenomenon is not observed in experimental investigations into the indentation of graphite surfaces by capped carbon nanotubes. Additionally, the deformation mechanism of a capped carbon nanotube depends on its length. Specifically, cap inversion occurs for shorter nanotubes, whereas slipping of the cap with the contact surface takes place for longer carbon nanotubes. Obtaining the cap spring constants of the carbon nanotubes of different diameters considered in the present study requires a prior knowledge of the axial cap compression arising from cap inversion. Accordingly, this study deliberately specifies capped carbon nanotubes with lengths of approximately 2.5 nm such that only cap inversion occurs and cap slipping is avoided.

Molecular dynamics simulation of a deformation process requires the use of an interatomic model to describe the interactions between the various atoms of the simulation system such that the corresponding mechanical behaviors and thermal dynamic properties can be predicted accurately. As the precision of the simulation is largely dependent upon the accuracy of the adopted interatomic model, this study employs the tight-binding potential model for carbon since it is known to provide accurate results. With its concern for the minimal basis set and the two-center integrals of carbon atoms, tight-binding molecular dynamics is more computationally efficient than the local density approximation approach, while yielding similarly precise results for the material properties. Additionally, the transferable character of the
tight-binding potential reflects the quantum nature of the \(sp\), \(sp^2\), and \(sp^3\) bonding of the carbon atoms. Consequently, various researchers have used this potential model to investigate the material properties, growth mechanisms, and structural stability of different carbon materials, including carbon nanotubes,\(^{15-18}\) carbon fullerenes,\(^{19}\) diamond,\(^{13}\) graphite,\(^{13}\) linear chains,\(^{13}\) and liquid carbon.\(^{20,21}\) In this model, the total energy of the atoms within the simulation system can be separated into two parts, i.e.,

\[
E_{\text{tot}} = E_{\text{bs}} + E_{\text{rep}}.
\]

In this expression, \(E_{\text{bs}}\) represents the summation of the ground electronic states occupied by the outer shell electrons. These ground states correspond to the eigenvalues of the empirical tight-binding Hamiltonian model, which is constructed from a set of hopping integral parameters for carbon atoms, i.e., \(V_{\text{ss} \sigma}\), \(V_{\text{sp} \sigma}\), \(V_{\text{pp} \sigma}\), and \(V_{\text{pp} \pi}\) using the two-center approximation method.\(^{22}\) The corresponding values of these parameters are listed in Table I. Meanwhile, \(E_{\text{rep}}\) denotes the repulsive energy, and is expressed as

\[
E_{\text{rep}} = \sum_i \left( \sum_j \Phi(r_{ij}) \right),
\]

where \(\Phi(r_{ij})\) is the interatomic potential induced between two atoms \(i\) and \(j\), which are separated by a distance of less than the cutoff distance, 2.6 Å. The complete form of \(\Phi(r_{ij})\) is given below in Eq. (3). Furthermore, as shown in Eq. (4), \(f(x)\) can be expressed in the form of a fourth-order polynomial.\(^{13}\)

\[
\Phi(r) = \Phi_0 \left( d/r \right)^n \exp\left[ m \left( -r/d_c \right)^{m_c} + \left( d/d_c \right)^{m_c} \right],
\]

\[
f(x) = \sum_{n=0}^{4} c_n x^n.
\]

The function \(s(r)\) used for scaling \(E_{\text{tot}}\) is given as follows:\(^{13}\)

\[
s(r) = \left( r/r_c \right)^n \exp\left[ n \left( -r/r_c \right)^{n_c} - \left( r/r_c \right)^{n_c} \right].
\]

The parameters for the functions \(\Phi(r)\) and \(s(r)\) are presented in Table II, while those of \(f(x)\) are listed in Table III. It is noted that the present simulation uses the Verlet velocity method to calculate the trajectories of the carbon atoms.\(^{23}\)

### Table I. Hopping integral parameters for carbon atom.

<table>
<thead>
<tr>
<th>Hopping integral parameters</th>
<th>(V_{\text{ss} \sigma}) (eV)</th>
<th>(V_{\text{sp} \sigma}) (eV)</th>
<th>(V_{\text{pp} \sigma}) (eV)</th>
<th>(V_{\text{pp} \pi}) (eV)</th>
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</thead>
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<td>(E_{\text{rep}})</td>
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<td>4.7</td>
<td>5.5</td>
<td>-1.55</td>
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</table>

### Table II. Parameters for \(S(r)\) and \(\phi(r)\).

<table>
<thead>
<tr>
<th>(S(r))</th>
<th>(n)</th>
<th>(n_c)</th>
<th>(r_c(\text{Å}))</th>
<th>(r_0(\text{Å}))</th>
<th>(r_1(\text{Å}))</th>
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<td>(m)</td>
<td>(m_c)</td>
<td>(d_1(\text{Å}))</td>
<td>(d_0(\text{Å}))</td>
</tr>
<tr>
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<tr>
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<td>3.30304</td>
<td>8.66555</td>
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### Table III. Parameters for \(f(x)\).

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<th>(c_1)</th>
<th>(c_2)</th>
<th>(c_3)</th>
<th>(c_4)</th>
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<td>-2.5909765 118 191</td>
<td>0.5721 151 498 619</td>
<td>-1.7896 349 903 996 \times 10^{-3}</td>
<td>2.3539 221 516 757 \times 10^{-5}</td>
<td>-1.2425 169 551 587 \times 10^{-7}</td>
</tr>
</tbody>
</table>

### III. RESULTS AND DISCUSSION

In order to observe the detailed deformation behaviors of capped carbon nanotubes of different radii, simulations were performed for three different forms of nanotubes, namely, (4,4), (7,7), and (11,11) armchair capped nanotubes. In each case, the deformation mechanisms were deduced from the magnitude of the repulsive force exerted by the graphite surface on the cap, and by the magnitude of the corresponding axial compression within the cap. The magnitude of the repulsive force was calculated by aggregating the \(z\)-directional forces of the capped nanotube atoms, while the magnitude of the axial compression was determined from the difference in the length measured from the top of the cap to the cap/nanotube interface before and after the cap interacted with the graphite surface.

Figures 2, 3, and 4 present the variations in the repulsive force and the axial compression over the duration of the simulation for the (4,4), (7,7), and (11,11) capped carbon nanotubes, respectively. Meanwhile, Figs. 5, 6, and 7 illustrate the corresponding characteristic morphologies of these three carbon nanotubes. In order to explore the evolution of the nanotube morphology more clearly, each of these figures presents three separate morphologies, i.e., corresponding to the moments of critical repulsive force, maximum axial com-

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**FIG. 2.** Variation in repulsive force and axial compression of cap over duration of simulation for a (4,4) capped carbon nanotube.
pression, and tip withdrawal from the surface. These snapshots are indicated in the figures by the labels (a), (b), and (c), respectively. Meanwhile, these points are indicated in Figs. 2, 3, and 4 by the labels A, B, and C, respectively.

Figure 2 demonstrates that the repulsive force is approximately proportional to the magnitude of the axial compression until the point at which the critical force is attained. Within this region of proportionality, the cap behavior resembles that of a spring with a constant of 1.4 nN/Å (i.e., the ratio of the critical force to the corresponding axial compression magnitude). Beyond the point of critical force, the repulsive force decreases rapidly, while the magnitude of the axial compression continues to rise. Clearly, this behavior does not obey Hooke’s law for a spring. Rather, this phenomenon can be attributed to the radial compression of the cap, during which the bond orientations and lengths change in order to relieve the force acting upon them. Figure 5(b) shows the morphology associated with the maximum axial compression within the (4,4) carbon nanotube. From a comparison with Fig. 5(a), it is clear that the \( sp^2 \) bond orientations which originally existed between the carbon atoms of the cap at the point of critical force have changed such that they lie in one flat plane. From Fig. 2, it can be seen that after the point of maximum axial compression, the magnitudes of the force and the axial compression decrease. As shown in Fig. 5(c), when the tip is withdrawn from the graphite surface, the force approaches a value of zero when the distance between the cap and the surface exceeds the cutoff distance. Under these conditions, the carbon atoms recover their initial arrangement.

Figures 3 and 4 show the variations of the repulsive force and the axial compression of the (7,7) and (11,11) capped carbon nanotubes over the course of the simulation.
It is immediately obvious that the characteristics of the repulsive force in both cases strongly resemble the trend discussed above for the (4,4) capped carbon nanotube. As before, the deformation of the cap conforms to Hooke’s law until the point at which the repulsive force causes radial deformation. Thereafter, the force is relieved, and the axial compression increases accordingly. This process is illustrated more clearly by the morphologies presented in Figs. 6(a) and 6(b) for the (7,7) carbon nanotube, and in Figs. 7(a) and 7(b) for the (11,11) nanotube. In both sets of figures, the bond orientations and lengths are seen to change over the time interval between the point of critical force and the point of maximum axial compression. Finally, as shown in Figs. 6(c) and 7(c), the atomic arrangements of both carbon nanotubes return to their original configurations as the tip moves away from the surface causing the force to fall toward zero. A careful comparison of Figs. 2, 3, and 4 reveals that the principal influence of the nanotube radius is to determine the magnitude of the axial compression of the cap once it is withdrawn from the graphite surface. For a cap of smaller diameter, such as that of the (4,4) nanotube, the cap rapidly recovers its original structure once it exits the surface. This point is represented by label C in Fig. 2, in which it can be seen that both the repulsive force and the axial compression fall to a value of zero at an elapsed simulation time of approximately 1200 fs. However, for the larger radii (7,7) and (11,11) carbon nanotubes, the simulation results indicate that the cap remains in a compressed state shortly after it has been withdrawn from the surface at approximately 1100 fs. Even after an elapsed time of 2000 fs, Figs. 3 and 4 show that the axial compression has not reduced to a value of zero, thus indicating the presence of a residual compressive stress within the nanotube. This result is to be expected since there are a greater number of bond orientations and lengths to be changed in a cap of larger diameter, and hence more time is required for the atomic arrangement to return to its original configuration. Although the axial compressions of the (7,7) and (11,11) carbon nanotube caps are not zero at 2000 fs, plastic deformation does not occur because the covalent bonds of the carbon atoms of the cap are not broken, even at the axial compression associated with the maximum repulsive force [as shown in Figs. 6(a) and 7(a)]. Since no carbon atoms change their covalence bonding with neighboring carbon atoms as its original bonding, the capped carbon nanotubes recover their original shapes after 2000 fs. This is because the original structure with its original bond lengths and orientations represents the most stable structure.

Figure 8 shows the relationship between the spring constant and the carbon nanotube diameter for eight nanotubes in the range of (4,4) to (11,11). In general, it is noted that the spring constant initially decreases as the radius of the nanotube increases, but then assumes a stable value as the radius continues to increase. The (4,4) nanotube has the highest spring constant value of approximately 1.4 nN/Å, while the radius of the (8,8) armchair carbon nanotube represents the radius at which the spring constant attains a stable value of approximately 0.4 nN/Å. The smaller the spring constant value, the softer the end of the cap will be. This result can be attributed to the different strain energies of the carbon atoms in carbon nanotubes of different diameters. This strain en-
energy represents the energy required to remove the carbon atom from the carbon nanotube. Previous tight-binding molecular dynamics simulation reveals that the strain energy decreases significantly as the diameter changes from that of a (4,4) carbon nanotube to that of a (8,8) carbon nanotube, but exhibits little further change as the diameter continues to increase. Therefore, carbon nanotubes with smaller radii will be stiffer than those with larger radii. Furthermore, the strain energies of the (4,4) and (8,8) carbon nanotubes are approximately 0.32 and 0.09 eV/atom, respectively, which corresponds to a ratio of approximately 3.5. The results of the present study yield spring constants for the (4,4) and (8,8) nanotubes of 1.4 and 0.4 nN/Å, respectively, which also corresponds to a ratio of 3.5. The fact that these two ratios have a common value confirms that the strength or stiffness of a carbon nanotube depends on its diameter. Consequently, the results of Fig. 8 demonstrate that the caps of carbon nanotubes with radii larger than that of the (8,8) armchair carbon nanotube are more flexible, and will therefore provide better shock absorption properties. As a result, these particular nanotubes are more suitable for the probing of soft surfaces since they are less likely to cause surface damage.

In the Yao and Lordi study, the spring constant of the (10,10) carbon nanotube was found to be 9.35 nN/Å, which is approximately 20 times greater than the value obtained in the current study. This discrepancy can be attributed to the limitation of the UFF potential model. The UFF potential model employs the harmonic form of the bond stretching energy. This model is only reasonable when the variation of the specific bond length from the reference bond length is small since the parabolic curve of the relationship between the bonding energy and the bond length is only accurate when this condition is satisfied. If the specific bond length is much larger or smaller than the reference bond length, the modeled variation of the bonding energy with the bond length is much sharper than the actual variation of the bonding energy. This implies that the repulsive or attractive force obtained from the harmonic form is much larger than the actual value when the specific bond length is much larger or smaller than the reference bond length. In the current study, the bond lengths of the carbon atoms in the cap are changed from their reference bond lengths as the cap interacts with the graphite surface. With the same compression magnitude, the repulsive force calculated by the UFF potential model is larger than that predicted by the tight-binding scheme. Consequently, a larger spring constant is obtained if the UFF potential model is employed.

IV. CONCLUSIONS

This article has presented a tight-binding molecular dynamics simulation investigation into the complex deformation mechanisms of capped carbon nanotubes during the indentation of a graphite surface. The results have shown that the cap initially behaves like a spring in that it obeys Hooke’s law until a certain critical repulsive force causes radial deformation of the cap. This deformation occurs as the bond orientations and lengths of the atoms within the cap are rearranged in order to relieve forces in the cap. It has been shown that following deformation, the cap behavior no longer conforms to Hooke’s law, and that the reduction in repulsive force is accompanied by an increase in the magnitude of the axial compression. The axial compression increases to a maximum value and then reduces toward a value of zero. The simulation results have also shown that since more covalent bonds participate in relieving the force exerted on the cap of a nanotube of larger diameter, more time is required for the atomic arrangement to return to its original configuration. Finally, this study has explored the relationship between the spring constant and the carbon nanotube radius. It has been shown that the (4,4) carbon nanotube has the highest spring constant (approximately 1.4 nN/Å), and that the spring constant assumes a stable value of approximately 0.4 nN/Å when the radius of the nanotube exceeds that of the (8,8) carbon nanotube.

Since an increasing number of applications are being proposed for capped carbon nanotubes, there is an urgent requirement to determine the material properties of nanotubes of different radii. It is the current authors’ belief that the present molecular dynamics simulation results provide a valuable insight into the deformation mechanisms, which occur at the atomistic scale in the tip of a capped carbon nanotube when used in the tapping mode measurement process.

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2. Y. Nakayama, Ultramicroscopy 91, 49 (2002).