Molecular dynamics study of carbon nanotube oscillators revisited

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We performed molecular dynamics simulation of double walled carbon nanotube (DWCNT) oscillators under constant energy and constant temperatures with various commensurations and nanotube lengths. We clarify and resolve questions and differences raised by previous simulation results of similar systems. At constant energy, sustained oscillation is available for a wide range of initial temperatures. But low initial temperature is advantageous for DWCNTs to sustain oscillation under constant energy. We observed sustained oscillation at constant energy for both commensurate and incommensurate DWCNTs. On the other hand, under constant temperatures, both high and low temperatures are disadvantageous to sustain DWCNT oscillations. At constant low temperature, neither commensurate nor incommensurate DWCNTs can maintain oscillation. At appropriate constant temperatures, the oscillatory behavior of incommensurate nanotubes is much more sustained than that of commensurate tubes. The oscillatory frequency of DWCNTs depends significantly on the length of tubes. The initial oscillatory frequency is inversely proportional to the DWCNT lengths. The oscillation frequency of DWCNTs is insensitive to the initial temperatures at constant energy, but slightly dependent on the temperature at constant temperatures. © 2006 American Institute of Physics. [DOI: 10.1063/1.2185623]

I. INTRODUCTION

Carbon nanotubes\textsuperscript{1,2} attracted numerous experimental and theoretical investigations in recent decades due to their many unique properties.\textsuperscript{3} Recently there has been interest in the nanotechnology community in the use of multiwalled carbon nanotubes (MWCNTs) as gigahertz oscillators. Cummings and Zettl\textsuperscript{4} reported the experimental observation of oscillatory properties of concentric MWCNT. This was followed by theoretical works by Kolmogorov and Crespi,\textsuperscript{5} and Zheng \textit{et al.}\textsuperscript{6,7} Kolmogorov and Crespi analyzed the tribological properties of MWCNT and predicted that incommensurate tubes would have extremely small shear strengths. Zheng \textit{et al.} confirmed the possibility that the MWCNT device could be a potential oscillator with natural frequencies in the gigahertz range. While the experimental investigation of such nanoscale systems is limited by the available techniques, the theoretical study on the MWCNT oscillators is relatively straightforward. The interaction between the MWCNT shells is dominated by physical van der Waals force, which makes the MWCNT oscillators ideal systems that can be studied by molecular dynamics (MD) simulations.

Several groups have performed simulation studies of the oscillatory behavior of MWCNT.\textsuperscript{8–14} These simulations were all able to repeat qualitatively the oscillatory phenomena predicted by Zheng \textit{et al.} They agree with each other in that oscillation can be realized under idealized condition (for example, no contamination present between the MWCNT shells) when the inner nanotube is pulled out and released at a certain point. However, these works disagree with each other quantitatively. In addition, some of the simulations have contradictory conclusions in terms of the dependence of oscillation on commensurations, energy dissipation, source of friction, etc.

Leggos \textit{et al.} performed microcanonical ensemble (constant NVE) MD simulations of MWCNT oscillator using the UFF-Valbond 1.1 potential.\textsuperscript{15} The systems they studied were capped single walled carbon nanotube (SWCNT) inside a fixed longer open-end SWCNT. They found that sustained oscillations are possible only when the radii difference between inner and outer double walled carbon nanotubes (DWCNTs) is $\sim$0.34 nm. They also pointed out that the oscillation is possible for a wide range of temperatures (up to 400 K). As examples, they showed the sustained oscillatory movement of $(9,0)/(18,0)$ (perfect radius fitting) DWCNT, and the nonsustained oscillation of an imperfect fitting of $(5,5)/(18,0)$ DWCNT. Their reported frequency of oscillation of DWCNT is up to 87 GHz.

Rivera \textit{et al.}\textsuperscript{14} have carried out MD simulations of DWCNTs at constant temperatures using the Dreiding model.\textsuperscript{16,17} They studied systems of open-end SWCNT inside an open SWCNT of the same length, with both incommensurate $(7,0)/(9,9)$ and commensurate $(5,5)/(10,10)$ pairs at 298.15 K. They found that the oscillations are in the range of

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gigahertz, and the damping of the oscillation is inversely dependent on the length of the DWCNTs, in agreement with the theoretical prediction of Zheng et al. For the commensurate system, the damping is faster than that of incommensurate systems. They noticed that increasing the temperature will accelerate the damping, because the intershell frictional forces in DWCNT were presumed to be as being primarily from thermal fluctuations.

Guo et al. studied the energy dissipation of DWCNT oscillator via constant energy MD, using both assisted model building with energy refinement and Tersoff-Brenner potentials. They performed simulations at initial temperatures as low as 8 K, yielding a sustained oscillation up to 60 ns. They found that the decay of oscillation amplitude of commensurate DWCNT [for example, (9,0)/(18,0)] is orders of magnitude faster than that of incommensurate DWCNT [for example, (5,5)/(18,0)]. They also found that the energy dissipation rate sharply increases as temperature rises. The frequency of oscillation they reported was up to 100 GHz.

Zhao et al. studied the energy dissipation mechanism of DWCNT oscillator using MD simulations. The potential model they used was chemistry at Harvard molecular mechanics (CHARMM) force field. They simulated short DWCNTs ranging from 1.5 to 7.0 nm and found that the energy dissipation mechanism depends on the overlap length of the DWCNTs. In turn, the dynamical frictional force between the DWCNT shells is also dependent on the overlap area. In addition, by comparing simulations with the outer tube fixed or not, they found the deformation of the outer tube plays an important role in the damping of the oscillation.

Tangney et al. reported another NVE MD simulation of DWCNT oscillators at initial temperature of 300 K. The potential model they used was the extended Tersoff-Brenner coupled with Lennard-Jones model. They compared commensurate and incommensurate oscillators of equal dimensions. In contrast to the results from previous work reported above, their simulations indicate that commensuration has little effect on the rate of energy dissipation. They found that the friction force is due to the end effects of DWCNT and virtually independent of the overlap area between tubes.

There are a few very important disagreements in the simulation results listed above. The first important open question is how the commensuration affects the oscillation behavior of the DWCNT oscillators. Most of the simulations presume or show that incommensurate DWCNTs have a much smoother oscillation than commensurate DWCNTs, while the results of Tangney et al. suggest that the degree of commensuration barely affects the oscillation. Even for results that agree qualitatively on these points, the impact significance of commensuration on oscillation seems quite different. For example, the simulations of Rivera et al. indicate that the oscillation of commensurate DWCNTs damps faster than that of incommensurate DWCNTs do, but much slower than that seen in the result of Guo et al.

Discrepancies are also evident in the dependence of the damping feature, or friction force, on the length of the DWCNT. It is typical to assume that the nanoscale friction between surfaces is proportional to the contact area. Most of the previous simulation works on DWCNT oscillator appear to support this hypothesis, while the results by Tangney et al. contradict with it. In addition, the simulation of short DWCNT by Zhao et al. indicates a strong dependence of energy dissipation on the deformation of the outer tube, which was not found in other longer tube simulations.

It is hard to reconcile these available simulation results since they were performed under various conditions. The results are from simulations under different ensembles (constant energy or constant temperature), using a variety of potential models [united force field (UFF), Dreiding, AMBER, Tersoff-Brenner, and CHARMM], with different DWCNT lengths (from 1.5 to 100 nm), different DWCNT conformations (capped or open), different relative sizes (length ratio of inner tube to outer tube from $\frac{1}{2}$ to 1), different settings (prepulled inner tube, pulling both tubes in opposite directions, and outer tube fixed), at different temperatures (from 8 to 300 K), etc. The disagreements in the results from these works could stem from any of these factors. There are no reliable experimental data available to resolve these discrepancies observed in simulations.

In this paper, we perform a series of simulations under different ensembles, different system sizes, different commensurations, and different temperatures to investigate the impacts of these factors on the oscillation behavior of DWCNTs. For comparison purposes, we employ a consistent potential model and DWCNTs with the same initial relative positions in all the simulations. On this basis we attempt to clarify some of the disagreements mentioned above through a series of comparative simulations.

II. POTENTIALS AND SIMULATION METHODOLOGY

The oscillation of DWCNTs is driven by the van der Waals interaction between the inner and outer tubes. Therefore, the choice of a potential model for the interaction between each pair of $sp^2$ carbon atoms is prominent because the energy dissipation during oscillation is dependent on the potential model employed. In turn, it may affect the oscillatory behavior of DWCNTs such as frequency and damping speed. A variety of potential models had been used to model carbon nanotubes. However, it is not yet conclusive about which of these models is best for modeling DWCNTs. A recent simulation study compared the application of registry-independent and registry-dependent van der Waals potentials in modeling DWCNT oscillators. They pointed out that different van der Waals potentials mainly affect the frequency of nanotube oscillators but not the normalized decay rate of the oscillations. In this study, we focus on the effects of simulation ensembles, commensurations, and dimensional sizes of DWCNTs on the oscillation behavior. So we chose arbitrarily one of the parametrizations of the van der Waals model that had been used to model SWCNTs and DWCNTs. We realize that quantitative energetic information would be beneficial in understanding DWCNT systems. However, such information is strictly dependent on the particular potential model used in the simulation. The energetics from one potential could be very different from that...
TABLE I. Dimensions of the incommensurate and commensurate DWCNT systems studied in this work.

<table>
<thead>
<tr>
<th>Chirality</th>
<th>Inner tube radius, $R_i$ (nm)</th>
<th>Outer tube radius, $R_o$ (nm)</th>
<th>$R_o - R_i$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10,0)/(19,0)</td>
<td>0.386</td>
<td>0.733</td>
<td>0.347</td>
</tr>
<tr>
<td>(10,0)/(11,11)</td>
<td>0.386</td>
<td>0.735</td>
<td>0.349</td>
</tr>
<tr>
<td>(10,0)/(16,5)</td>
<td>0.386</td>
<td>0.733</td>
<td>0.347</td>
</tr>
</tbody>
</table>

The radius of a $(n,m)$ carbon nanotube is given by $R = (a/2)(n/m)n + m + n$, where $a$ is the C–C bond length. In this work, $a = 1.4$ Å, which is the C–C bond length of graphite.

obtained using another potential. Therefore, in this paper we have not attempted to discuss the energetics quantitatively.

The potential model used in this work is from the van der Waals model for $sp^2$ carbons in AMBER force field. Carbon atoms were modeled as uncharged Lennard-Jones particles with parameters of $\sigma_{CC} = 0.34$ nm and $\epsilon_{CC} = 0.086$ kcal/mol. The cutoff of the pairwise Lennard-Jones interaction between carbon atoms was 10 Å. The carbon-carbon bond length of 0.14 nm and bond angle of 120° were maintained by harmonic potentials with spring constants of 938 (kcal/mol)/Å² and 126 (kcal/mol)/rad². In addition, a dihedral angle is applied to bonded carbon atoms. This model had been used widely to model $sp^2$ carbons in organic and biological systems and also graphene carbons in nanotubes. Detailed potential expressions and additional parameters can be found in Refs. 18 and 32.

The coordinates of carbon nanotubes with different chiralities were generated using the schemes in literature. The inner and outer tubes have identical lengths. The ends of the tubes were uncapped and the dangling carbon bonds in the ends were not saturated. We studied one commensurate DWCNT and two incommensurate DWCNTs with varied lengths. The diameter difference between the inner and outer tubes is about 0.34 nm, satisfying the optimal condition for sustainable DWCNT oscillators. The detailed dimensional parameters for the systems studied are shown in Table I.

Molecular dynamics simulations were performed using NAMD packages. A typical simulation included 1000 step energy minimization using conjugate gradient and linear search algorithm, 5000 time steps of MD equilibration with outer and inner shells in full contact and no external forces, an appropriate number of MD steps to pull apart the concentric nanotubes, followed by several nanoseconds of simulation after releasing the pulled tubes. We used a time step of 2.0 fs for all the simulations. The pulling of tubes was realized by applying a constant force on each carbon atom of the inner tube along the tube axis direction while applying an identical force on the atoms of the outer tube along the opposite direction. The number of steps in which the tubes are pulled apart varied from system to system. The separation between the centers of mass of the tubes is monitored during the pulling process until it reaches exactly 45% of the tube length. Then the pulling force is removed and velocities of each atom are randomized according the initial interested simulation temperature. Oscillation begins immediately after the force is removed. The potential energy and coordinates information was collected every 0.2 ps for later analysis. For constant temperature simulations, the temperature is calculated from the atom velocities excluding the velocities of the nanotube centers of mass in order to keep the relative motion of the inner and outer tubes out of the thermalization process. The heat bath coupling technique was applied to maintain the target temperature. Analysis was performed using the VMD packages.

III. RESULTS AND DISCUSSIONS

A. Comparison of constant energy and constant temperature simulations

We have performed simulations of DWCNT at constant energy (NVE) and constant temperature (NVT). Constant energy simulations correspond to simulations in a vacuum, where there is no avenue for heat dissipation to the environment. The kinetic energy of a DWCNT is damped only by the friction force between the tube shells. Constant temperature simulations correspond to the situation when the nanotubes are in contact with a heat bath. The damping of oscillation is partly due to the kinetic energy lost to the environment. In order to compare the difference between constant energy and constant temperature simulations, we used identical initial DWCNT configurations as the starting point of simulations. In addition, the overlapping percentage between the inner and outer shells at the beginning of oscillation is consistently 45% of the tube lengths. For constant energy simulations, the initial temperatures were set to 20, 100, and 300 K respectively. For constant temperature simulations, the temperatures were kept at 20, 100, and 300 K throughout simulations, respectively. Then we collect the oscillation data for both a commensurate (10,0)/(19,0) DWCNT and two incommensurate (10,0)/(11,11) and (10,0)/(16,5) DWCNTs for comparison.

For constant energy simulations, we found that a low initial temperature is advantageous for the DWCNT oscillators to sustain the oscillation amplitudes. Increasing the initial temperature results in a faster damping in oscillation. This behavior is illustrated in Fig. 1, the oscillation behavior of a (10,0)/(19,0) DWCNT. We can see that damping on the DWCNT oscillator is much faster for the initial temperature of 300 K than for 20 K, although the frequencies of oscillations under different initial temperatures are comparable. This observation is consistent with the conclusion by Rivera et al., and Guo et al., in that a higher temperature would accelerate the damping. This is explained by the source of intershell frictional forces in DWCNT being primarily from the thermal fluctuation affecting the diameters of DWCNTs.

Under constant temperatures, we found that both high and low temperatures could result in damping of the oscillations. This is shown in Fig. 2, the oscillation behavior of a (10,0)/(19,0) DWCNT under constant temperatures of 20, 100, and 300 K. If the temperature is too low, for example, 20 K, the oscillation is very rapidly damped. If the temperature is too high, for example, 300 K, the oscillation is also damped. The DWCNT at 100 K maintains the longest oscillation behavior under the three temperatures investigated. Apparently a high constant temperature is disadvantageous...
for the oscillation due to the high friction force from interlayer thermal fluctuations. It is possible that an optimal temperature exists at which oscillations are sustained for the longest time. However, the question remains to be open and subject to further studies.

For the two incommensurate DWCNT oscillators studied we observed similar phenomena. The oscillation data for them under constant energy and temperature environments can be found in a later section. The phenomenon is also present in DWCNTs with different lengths. We also noticed that oscillatory frequencies of the same DWCNT under constant energy and constant temperature are comparable to each other. But the oscillatory envelope functions are not strictly consistent in time dependence (for example, see Fig. 1).

B. Results from commensurate/incommensurate DWCNTs

For any DWCNT \((n,m)/(n',m')\), typically they are axially incommensurate if \(n/m \neq n'/m'\) (but not always), and commensurate if \(n/m = n'/m'\) (and other special cases).\(^{3,41}\) Superlubricity is present for the case of incommensurate DWCNT systems.\(^{5,42}\) In order to study the effects of commensuration on the oscillation of DWCNT, one needs to compare an incommensurate DWCNT with a commensurate one of exactly the same size. Such exact comparable systems are not available with DWCNTs of different type of chiralities, but we can model incommensurate and commensurate DWCNT oscillators with nearly the same dimensions. The DWCNT systems used in this study are shown in Table I. These systems have different commensuration features but almost identical dimensions. They serve as good comparison systems for studying the impact of commensurability on the oscillation behavior of DWCNTs.

We found that both commensurate and incommensurate DWCNTs can show sustained oscillation to some degree under constant energy, but the oscillation difference between the two types of DWCNT depends on the initial temperature. The oscillation behaviors of two incommensurate DWCNTs \((10,0)/(11,11)\) and \((10,0)/(16,5)\) are shown in Figs. 3 and 4 for comparison with Fig. 1. For these two systems, the length of DWCNTs and the starting overlap distance between inner and outer tubes are the same as that of Fig. 1. We can see that the oscillatory behavior in Figs. 1, 3, and 4 are very much alike at high initial temperatures. This is in agreement with the observation by Tangney et al.\(^{13}\) However, under lower initial temperatures, the two incommensurate DWCNTs show much better sustained oscillation amplitudes than the commensurate tubes. This is also in agreement with the previous simulations under low temperatures. Therefore, the results of Tangney et al. and others (such as Guo et al.) about the impact of commensuration on the oscillation are not in conflict when the impact of temperature is taken into account.
However, the oscillatory behavior of commensurate and that of incommensurate DWCNTs under high constant temperatures vary from each other more significantly than under constant energy. For commensurate DWCNTs, the oscillation could not be sustained for more than 1.4 ns. For incommensurate DWCNTs, the oscillation is sustained much longer, especially at 100 K (compare Figs. 5 and 6, with Fig. 2).

Despite the difference in damping speeds, the commensurate and incommensurate DWCNTs studied have roughly the same initial oscillatory frequencies.

Comparing the two incommensurate DWCNTs, the (10,0)/(16,5) system seems to have a slightly more sustained oscillation than the (10,0)/(11,11) system. Under constant energy, the decaying pattern of (10,0)/(11,11) is roughly linear, which is faster than the decay of the (10,0)/(16,5) which has an obvious bottleneck (compare Figs. 3 and 4). At constant temperatures, the oscillation of (10,0)/(11,11) DWCNTs is quickly damped when the temperature is low (20 K), while the oscillation of (10,0)/(16,5) DWCNTs is sustained with a very small amplitude (see Figs. 5 and 6) at 20 K.

The differences in the oscillatory behavior between commensurate and incommensurate DWCNTs come from the corrugation effects between the inner and outer tube shell interaction. The driving force for the oscillation is the potential energy between the tubes. For commensurate and incommensurate systems, the details in the potential energy fluctuations are quite different. In Fig. 7 we present the potential energy curves as a function of time for three types of DWCNTs.
DWCNTs with the same dimensions and simulation conditions. We focus on a short section of the potential energy curves. We can see that clear local minimums exist in the commensurate DWCNT potential energy while the potential energy curves for incommensurate DWCNTs are much smoother. These local energy minimums can significantly increase the friction force between the inner and outer tubes and result in a faster decay in the oscillation of commensurate DWCNTs.

C. Comparison of DWCNTs with different lengths

We have performed simulations for DWCNTs with two different lengths. Note that the inner and outer SWCNTs remain equal in lengths; what varied is the length of DWCNTs. The short DWCNTs studied have a length of 8 nm, and the longer ones have a length of 24 nm. The simulations were performed under both constant energy and constant temperatures, with various commensurabilities. The goal was to study the impact of nanotube length on the frequencies and also the decaying patterns of the oscillators.

We found that the frequency of the DWCNT oscillators significantly depends on the length of tubes. In Fig. 8 we present one of the simulation results for (10,0)/(11,11) DWCNTs with a length of 24 nm under constant energy. By comparing Fig. 8 with Fig. 3, we can see that frequency of the 8 nm DWCNT oscillators is about 35 GHz while that of the 24 nm DWCNTs is three times lower, about 12 GHz. For all the simulations (either under constant energy or temperature, commensurate or incommensurate) of the 24 nm DWCNTs, the oscillation frequencies are very similar to each other, just like that exhibited in the 8 nm DWCNT simulations discussed in previous sections. The dependence relationship between the frequency and tube length found in this work agree qualitatively with the results reported by Rivera et al. It is also in agreement with the theoretical prediction of Zheng et al. for DWCNTs composed of equal-length SWCNTs. However, it is difficult to have a fair quantitative comparison and evaluation of all the frequencies reported from various groups mentioned in Sec. I because of the variance in the potentials and the nanotube dimensions studied by different authors.

We found that the oscillation is better sustained in longer nanotubes although the longer DWCNTs have a lower frequency than the shorter nanotubes. This is illustrated in Fig. 8, which should be compared with Fig. 3. However, under constant temperature simulations, the oscillation of the longer nanotubes is also quickly damped when the temperature is 20 K. (see Fig. 9).

![Oscillation of (10,0)/(11,11) nanotubes at constant energy. The length of the DWCNTs is 24 nm.](image1)

![Oscillation of (10,0)/(19,0) nanotubes at constant temperatures. The length of the DWCNTs is 24 nm.](image2)

![Oscillation of (10,0)/(11,11) nanotubes at constant temperatures. The length of the DWCNTs is 24 nm.](image3)
D. Temperature effects

At constant energy, oscillation is observed for a wide range of initial temperature, in agreement with Refs. 8 and 12. However, at constant temperatures, the sustainable oscillation is only observed for temperatures high enough. We assume that a threshold temperature exists. But the threshold temperature would depend on many factors such as the potential models used, tube commensuration, etc. We did not attempt to determine this value.

Unlike the sustainability, the oscillation frequency of DWCNTs is insensitive to temperatures. Under constant energy, the oscillation frequencies are almost unaffected by initial temperatures as long as the length of the tubes are the same. This can be seen from Figs. 1, 3, 4, and 8. The difference in the frequencies of DWCNTs at 20 and 300 K within the first 500 ps oscillation is essentially negligible. This is consistent with the results reported by Guo et al. At constant temperatures, the frequency of DWCNT is slightly dependent on the temperature, but far less significantly than on the nanotube length. Higher temperatures result in a slightly higher frequency. This is illustrated in Figs. 2, 5, 6, 9, and 10. For example, for (10,0)/(19,0) and (10,0)/(11,11) DWCNTs of 24 nm length, the frequencies of oscillation at 100 K are about 10%–15% smaller than those at 300 K (see Fig. 9).

IV. CONCLUSIONS

We studied the damped oscillatory properties of DWCNTs with various lengths and chiralities under different environments by molecular dynamics simulations. For constant energy simulations, sustained oscillation is available for a wide range of initial temperature, but low initial temperature is more advantageous than high initial temperature. At constant temperatures, the sustainable oscillation is only available if the temperature is higher than some threshold value. In addition, high and low temperatures would result in fast damping of the oscillations. There appears to be an optimal temperature for the best sustaining of the oscillations.

We observed sustained oscillation under constant energy for both commensurate and incommensurate DWCNTs. However, the oscillation difference between these two types of DWCNTs depends on the initial temperature. At low initial temperatures, oscillations of commensurate and incommensurate DWCNTs are similar. At high initial temperatures, the oscillation of incommensurate DWCNTs is more sustained than that of commensurate ones. At constant low temperature, neither commensurate nor incommensurate DWCNTs sustain oscillation. But under high constant temperature, the oscillatory behavior of incommensurate nanotubes is better conserved than that of commensurate tubes.

We found that the frequency of the DWCNTs significantly depends on the length of tubes. Longer tubes have a smaller oscillation frequency. The initial frequency is roughly inversely proportional to the DWCNT lengths. The oscillation frequency of DWCNTs is insensitive to the temperatures.

To summarize, we have resolved some of the differences outlined in the Introduction, finding that most of the published differences are the result of the different MD ensembles used (NVE versus NVT), different commensurabilities, and different temperatures (either initial temperatures for NVE or maintained temperatures for NVT).

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