Study on Cap Closure Mechanism of Single-Walled Carbon Nanotubes by Molecular Dynamics

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The closing mechanism of zigzag single-walled carbon nanotubes (SWCNT) was investigated using the molecular dynamics (MD) simulation at the experimental arc discharge temperature of 3000 K. The (10,0) SWCNT with a diameter of 0.78 nm showed a dome-shape tip which evolved into a saddle-shaped cap that was caused by double heptagon-octagon pairs. In the case of (18,0) SWCNT with a diameter of 1.404 nm, a zipper-like closing mechanism was observed and the flat cap was obtained.

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1. Introduction

Carbon nanotubes have received much attention because of their unique properties since their discovery by Iijima. CNTs with symmetric caps, for example, can be used as tips for scanning tunneling microscope. Although they have many attractive features, it is difficult to control them and the closing mechanism has not been investigated in detail. The formation and growth still remain controversial. The structure of a CNT must remain open-ended for growth, but carbon atoms at the tip of the tube have highly reactive dangling bonds, which results in a thermodynamically unstable state. Thus it is very important to study the cap closing mechanism in order to understand the growth condition.

Several experimental and theoretical works have been made on the cap closing mechanism of CNTs. Ajayan et al. explained that the conical surface of the tube corresponds to the presence of five pentagons at the tip surface and the presence of six pentagons at the end results in a cylindrical shape. Iijima reported that among many tube-tip shapes, pentagonal defects cause a positive curvature of the tube, whilst the negative curvature is imposed by heptagonal defects. However, most works reported on the closing mechanisms of multi-walled CNTs while the growth of SWCNTs was studied by the group at the North Carolina State University. For practical application it is necessary to synthesize CNT in a single-walled structure which is more difficult to control and observe.

The pioneering theoretical work on the cap closing mechanism has been published by the Car group. They performed first-principles calculations at 3500 K on the (10,0) zigzag SWCNT terminated on one side by an open end and on the other side by hydrogen atoms that complete bonding to the twofold-coordinated carbon atoms. What they observed up to 5 ps (pico sec) was the curved or hemispherical cap morphology composed of seven hexagons, five pentagons, one heptagon, one octagon and two squares. However, as they mentioned, the study of the further evolution of the tip geometry was not performed due to the limited time scale of the first-principles simulations. Additionally, several experimenters observed the rather flat cap geometry and the cylindrical shape of CNT. As a result, it is of great interest to explore atomistically the closing mechanism of the zigzag (10,0) or similarly indexed SWCNTs through the classical MD, which is capable of observing the dynamical behavior of atoms during an extended period of time.

2. Computational Details

Classical MD simulations were used with a time step of 1.0 fs (femto sec). The forces on the carbon atoms are calculated using a covalent bonding potential derived by Tersoff. This potential that was originally developed for silicon has been widely used to describe diamond, graphite, carbon nanotubes, fullerenes and hydrocarbon complexes, and the results are in good agreement with those obtained from experiments and quantum chemical calculations.

The growth of CNT has been reported by Maiti et al. to be energetically favorable only for tubes with a diameter wider than a critical value, estimated to be around 3 nm. For tubes narrower than the critical diameter a large number of well distributed nonhexagons at the tube tip gives rise to a curved geometry in which any additional deposited atom leads to the formation of a new ring rather than inserting into an existing ring. Moreover, according to the histogram showing frequency of diameters of SWCNTs, two peaks were dominant at 0.8 and 1.35 nm. Therefore, two kinds of SWCNTs, (10,0) and (18,0), were considered in this study because both diameters are smaller than 3 nm and (10,0) has a diameter of 0.78 nm and (18,0) has a diameter of 1.404 nm, consistent with dominant peaks in the work of Iijima and Ichihashi. A nanotube with 61 atomic layers was used in all the simulations, which resembles the rather long CNT. The effect of increased length on the closing kinetics or the cap morphology was found insignificant in this study. The bond length between two carbon atoms is 0.142 nm. The Car group and Oh and Lee studied the (5,5) armchair SWCNT as well as the (9,0) or...
(10,0) zigzag SWCNT. Results concerning armchair SWCNT will be published elsewhere.

The SWCNTs were maintained at a relatively high temperature of 3000 K, in order to simulate the high experimental temperature of the cathode in the arc-discharge apparatus. It is not desirable to reach 3000 K in one step of MD because the temperature change is so abrupt that the desired temperature was reached by simulation after tens of steps. This simulation has been performed in the canonical ensemble condition which means that the system temperature, \( T \), the total number of atoms \( N \) and the total volume \( V \) are conserved. In order to achieve a constant temperature the system is conceptually coupled to a heat bath which introduces energy variations needed to keep the temperature fixed. The kinetic energy of the system determined its temperature by the following equation:

\[
\frac{1}{2N} \sum_{i=1}^{N} m_i v_i^2 = \frac{3}{2} k_B T
\]

where \( m_i \) is the mass of the atom \( i \), \( v_i \) is its velocity and \( k_B \) is the Boltzmann constant.

Starting with an unrelaxed configuration, the potential energy first decreases and if the energy was preserved the kinetic energy would increase and hence the temperature. This increase must be compensated by the removal of the kinetic energy, leading to a decrease of the total energy. In order to preserve the kinetic energy, scaling of velocities was accomplished by multiplying velocity component of each atom by a factor, \( \lambda \)

\[
\lambda = \left( \frac{3Nk_B T}{\sum_{i=1}^{N} m_i v_i^2} \right)^{1/2}
\]

The initial SWCNT used in this study is terminated on both sides by open ends. The edge of the front cap side consisted of 10 single coordinated carbon atoms, while the carbon atoms at the other bottom side have twofold-coordinations. Several bottom layers were kept static and thus fixed in position during simulation assuming that they were saturated by something like the electrode or the template so that the cap closing may occur on one side only.

### 3. Results and Discussion

#### 3.1 Case of (10,0) SWCNT

The total energy, equal to the sum of the potential and the kinetic energy, averaged per atom in the (10,0) tube is shown as a function of simulation time in Fig. 1. The total energy decreased abruptly in early steps but still fluctuated up to about 20 ps. The reason for the abrupt decrease in the total energy is that the initial dangling atoms at the end of the tube are very unstable and therefore, with increased time, they tend to bond with neighboring atoms and an increasingly thermodynamically stable structure is obtained. After 20 ps, only a small change is observed, which means that this system has reached a steady state as will be confirmed by the total energy calculations.

Figure 2 describes in detail the snapshots of (10,0) SWCNT taken with simulation time. In this simulation, an octagon-nonagon pair and another heptagon-octagon pair are formed at 10 ps as shown in Fig. 2(b), which is similar to a previous first principles MD study\(^{11,12}\). The octagon-nonagon pair is dissociated into one hexagon and a pair of heptagon-octagon in Fig. 2(c) at 20 ps. In general, MD simulations do not describe bonding and debonding processes and thus the dissociation seems to have occurred by bond switching mechanism as suggested by Maiti et al.\(^{15}\). Or, the SWCNT is ovalized for small diameters because the terminal carbon atoms are in interaction range while this
would be less likely for larger diameters. After 20 ps, the cap morphology of the SWCNT does not change significantly. By 20 ps, all atoms except double heptagon-octagon pairs maintain a hexagonal network near the tip of the tube as shown in Fig. 2(c). The atomistic configuration at 100 ps is almost the same as that observed at 20 ps, which means that they maintain a stationary state after 20 ps. This result is consistent with the total energy calculation. The side view, Fig. 2(e), in the steady state shows that it is symmetric and saddle-shaped, which is caused by double heptagon-octagon pairs.

Figure 2(b) is very similar to the hemi-spherical or dome-closure morphology of the Car group. Recalling that their simulation was performed at 3500 K for 5 ps while this study was done at 3000 K for 10 ps, it is highly likely that the cap geometry did not reach the thermodynamic equilibrium state yet in their case. The morphology of the closed-end tip of a (10,0) SWCNT continues to evolve with time at high temperatures and thus, the initially transformed hemi-sphere or curved structure changes to saddle-shape.

The schematic formation mechanism on how the saddle-shaped cap is being formed is illustrated in Fig. 3. Bonding between terminal carbon atoms occurs because they are in interaction range, less than about 0.2 nm, while this would be less likely for larger diameters. Iijima reported that the defects in the hexagonal network responsible for the negative curvature are rings composed of more than six atoms. The saddle-shaped cap must have been created due to the negative curvature. In this simulation, double heptagon-octagon pairs were created and resulted in the formation of the saddle-shape cap. Thus, our simulation results are in good agreement with the reasoning of Iijima.

### 3.2 Case of (18,0) SWCNT

In Fig. 4, the total energy per atom in (18,0) SWCNT has been calculated and shown. The total energy decreases abruptly with time but it does not converge and its value increases after 900 ps, which means that it did not reach a steady state within 1000 ps. Figure 5 shows the snapshots of a (18,0) SWCNT with simulation time. A perfect cap has not been formed yet and the defects such as combinations of pentagons, hexagons, heptagons and octagons are created and they continue to change in different combinations. Because the diameter of a (18,0) SWCNT, 1.404 nm, is relatively large, the dangling atoms do not adjust themselves toward the tube axis along the radial direction, but they prefer to bond with each other along the circumferential direction of the tube. The atomic configurations continue to change and the interaction between defects through mostly bond switching is accelerated as suggested by Maiti et al.

The closing process of this tube goes slowly compared with the previous case of (10,0) SWCNT and the closing is not complete until 1000 ps of Fig. 5(e). At the stage of 1000 ps that is depicted in Fig. 5(e), the tube is more distorted and more closed. However, this SWCNT is still not completely closed. Therefore, additional tens of carbon atoms were deposited randomly near the incompletely closed cap in a gas phase right after 1000 ps in order to complete the closing. The gaseous carbon atoms were constrained to stay within a sphere with a diameter of about 2.8 nm (twice the diameter of the original tube) centered at the tube axis separated by about 1.4 nm from the open tip. Except for 9 carbon atoms the rest of them did not take part in the closing process and they remained separate from the tube.

The deposition rate of carbon atoms is experimentally estimated about one per 10–100 ps and the annealing of defect structures takes place on time scales of about 100–1000 ps. Therefore this type of additional deposition of carbon atoms is reasonable and realistic, not manipulative. If the simulation time scale is much longer than the experimental deposition rate, then the simulation may be interrupted by the deposition of atoms, however, the experimental deposition rate was quite comparable with the simulation time scale in this study. The atomistic behavior near the tip of this SWCNT after the addition of 9 atoms is shown in Figs. 5(f)–5(i). The closing process becomes more accelerated and it is complete by 2000 ps. Overall, a zipper-like closing mechanism is also observed in which the closing of the tube starts from both ends of the cap and finishes at the center of the cap, which is indicated by arrows in Figs. 5(f) through 5(h). The cap morphology of the stable (18,0) SWCNT is flat as seen in the side view of Fig. 6. When these CNTs take on a multi-walled structure, then they would show the flat top morphology and this has already been experimentally
Fig. 5 Snapshots of the (18,0) SWCNT with 61 atomic layers taken with simulation time of (a) 0 ps, (b) 100 ps, (c) 300 ps, (d) 700 ps, (e) 1000 ps, (f) 1010 ps, (g) 1050 ps, (h) 1100 ps and (i) 2000 ps. The atoms with bright contrast are illustrated to show the non-hexagonal defects.
observed by Ajayan et al.\textsuperscript{7)}

As shown in this study, the SWCNT with a diameter smaller than a critical size has a strong tendency of self closure with or without deposition of additional carbon atoms and therefore they do not grow in long tubes. This is the reason why it is difficult to observe SWCNTs in arc-discharge experiments without the use of catalytic metal elements. Finally, it is notable again that the cap morphology of the zigzag SWCNT that is similar to the work of Charlier et al.\textsuperscript{11,12)} was obtained in Fig. 2(b). Remembering that their simulation was performed at 3500 K for 5 ps while this morphology was attained at 3000 K for 10 ps, the cap geometry did not reach the equilibrium state in their case. The morphology of the open-end edge can continue to evolve with time at high temperatures and thus, the initially transformed hemi-sphere or dome-closure structure may change to saddle-shape or flat cap. This is probably why the carbon nanotubes are capped in shapes of polyhedrons, cones, semi-toroidal type and sometimes flat morphology.

4. Summary

During growth of the (10,0) SWCNT with 61 atomic layers, defects such as double heptagon-octagon pairs were created and they resulted in the formation of the saddleshape cap. The closing behavior of (18,0) SWCNT was different. It was not completely closed by itself and the closing was completed only after deposition of additional carbon atoms. The cap of the closed (18,0) tube was flat and the zipper-like closing mechanism was observed.

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REFERENCES