Lip-Lip Interactions and the Growth of Multiwalled Carbon Nanotubes

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Using a realistic many-body potential, we have simulated the properties of double-walled carbon nanotubes with the aim of investigating the role of lip-lip interactions on nanotube growth. Surprisingly, the lip-lip interaction *by itself* does not stabilize open-ended growth, but rather facilitates tube closure by mediating the transfer of atoms between inner and outer shells. A simulation of growth on a wide double-wall nanotube leads to considerable deviations from the ideal structure, in contrast to corresponding simulations for single-wall tubes, which result in nearly perfect structures. [S0031-9007(97)04989-2]

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The discovery of carbon nanotubes [1–3], has revitalized and refocused much of fullerene research. The interest and excitement in carbon nanotubes derives largely from their unusual structural and electronic properties. Experiments and theory indicate that they are superstrong fibers, showing a remarkable resilience to extreme conditions of strain. Simply put, because of the uniqueness of the graphene sp^2 bond, carbon nanotubes may be the ultimate strength fibers produced by nature. Nanotubes also hold considerable promise as composites, catalysts, field emitters, photonic materials, molecular straws, molecular wires, and switches [4–10].

Nanotubes are currently synthesized in a number of different ways: in carbon arc discharges, during catalytic combustion, and following laser vaporization [1–3, 10–16]. Given these different techniques for production, it is likely that a variety of mechanisms play a role in the assembly of nanotubes [13–19]. In this Letter, we discuss the growth of multiwalled carbon nanotubes as formed in an arc discharge, with a primary focus on the so-called "lip-lip" interaction between adjacent tube tips [13]. Such an interaction may arise when atoms or small clusters from the vapor deposit themselves at the tips of the nanotubes. These then form bridges or "spot-welds" between the tubes, which are thereby kept open for continued growth. Lip-lip interactions are also conjectured to be particularly important in stopping the unraveling of carbon nanotubes under field-emission conditions [9]. To investigate the importance of lip-lip interactions, we have carried out extensive molecular dynamics (MD) simulations and find, surprisingly, that the double-walled tubes are more prone to closure than the single-walled ones. Further, simulations of atom deposition on double-walled tubes have led to fairly disordered structures at the tip, in contrast to corresponding simulations of open-ended growth of single-walled tubes [17], which resulted in defect-free tubes.

Typically, bundles of multiwalled nanotubes, with diameters in the 2–20 nm range, are formed at the negative electrode of a carbon arc. While it was initially believed that nanotube growth takes place via the incorporation of adatoms at the tips of closed tubes, experiments show that the tubes actually remain open during growth [3]. This is surprising, because energetic considerations definitely favor a closed-tube geometry with no dangling bonds. A number of reasons have been proposed to explain this. Among these, the idea that it is the high electric fields ($\sim$1 V/Å) present at the tube tips that keeps the tubes open is the most appealing [20]. However, detailed *ab initio* investigations of this effect show that the high electric field alone cannot stabilize the open-tube geometry, even for very narrow tubes [17,21]. Similarly, other reasons such as a temporary saturation of the dangling bonds with hydrogen, or the presence of large thermal gradients, can likewise be eliminated [20].

However, there are strong indications from theory that tube closure is associated with the formation of curvature-inducing defects, such as adjacent pentagon pairs and related structures [17]. This suggests that nanotube growth may indeed proceed in an open-ended fashion, provided that the formation of such defects is somehow suppressed. Energetically, the formation of curvature-inducing defects is favored only for narrow nanotubes, so that tubes with diameters greater than $\sim$3 nm should remain open. Under conditions of catalytic growth, it is believed that either the presence of small metal particles [17,22], a root growth mechanism [18], or the catalytic action of Co or Ni atoms on the tube tips (the "scooter" mechanism [19]) prevents the nucleation of defects and leads to the formation of single-walled carbon nanotubes with relatively narrow diameters. However, it has also been pointed out that multiwalled carbon nanotubes, which are the dominant species formed in arc discharges, have another important kinetic alternative available to them in the form of the lip-lip interaction [13]. This idea appears to be particularly interesting and natural, and is the subject of our investigations.

Carbon atoms were modeled with a classical three-body Tersoff potential [23], using a parametrization due to Brenner [24]. Our experience with this potential shows that it is able to adequately reproduce the important

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features of the bonding in carbon nanotubes, even under extreme conditions of stresses and bending [4]. In a typical simulation, the bottom atomic layer of the tubes was kept fixed. A standard fifth-order Beeman-Verlet algorithm was used to integrate the equations of motion with a basic time step of 0.5 fs.

To study the formation of the lip-lip interaction, we first constructed a $(10,0)@(18,0)$ multiwalled tube having a height of 12 atomic layers [25], which was then uniformly heated up from 0 to 3000 K over a 40 ps period of time. Although there was no initial interaction between the tube tips, bridging bonds were first observed to form at $\sim$900 K, when the amplitudes of the radial distortions were large enough to bring the carbon atoms of the tips within interaction range. Such bonds continued to form as the temperature was increased, until a complete network of bridging bonds was formed; see Fig. 1(a). The bonds between the lips are of a fluctuating character: on a time scale of several picoseconds the bonds bridging the tube tips break and reform into similar configurations. Similar results were also obtained with different initial conditions. For example, allowing the tubes to rotate with respect to each other did not suppress the formation of the lip-lip bonds. Eventually, a fluctuation always formed a bond across the lips, and a network formed. Likewise, the impact of depositing carbon atoms did not disrupt the lip-lip bonds; atoms, directed towards the rims of the nanotubes with energies in the 1–8 eV range, were always captured by the tips, and incorporated into the network structure. These results are in complete agreement with similar simulations based on the more accurate *ab initio* methods [25].

To test the efficacy of the lip-lip interaction in keeping multiwalled tubes open, we continued annealing the $(10,0)@(18,0)$ tube. Surprisingly, we find that the double-wall tube closes spontaneously on a hundreds of picoseconds time scale. The lip-lip interaction by itself simply cannot keep narrow, multiwalled tubes open for growth. This is one of the main results of our study.

Top views of sample configurations showing the closing of the $(10,0)@(18,0)$ tube and of the corresponding single-walled tubes are shown in Fig. 1, while details of the $(18,0)@(26,0)$ double-wall closing are shown in Fig. 2. The figures show that the lip-lip interaction actually facilitates the closing of the tubes. Because of the fluctuating nature of the lip-lip interaction, bonds that bind atoms of the lip-lip network break, leading to the transfer of atoms to the inner tube. Within a time scale of picoseconds, the lip-lip bonds reform near those spots, but now the lips of the outer tubes are curved compared to their initial state, as shown in the side views on Fig. 2. At the same time, curvature inducing defects such as adjacent pentagons readily form on the inner tube, so that it begins to curve inwards. This, of course, bends the outer tube

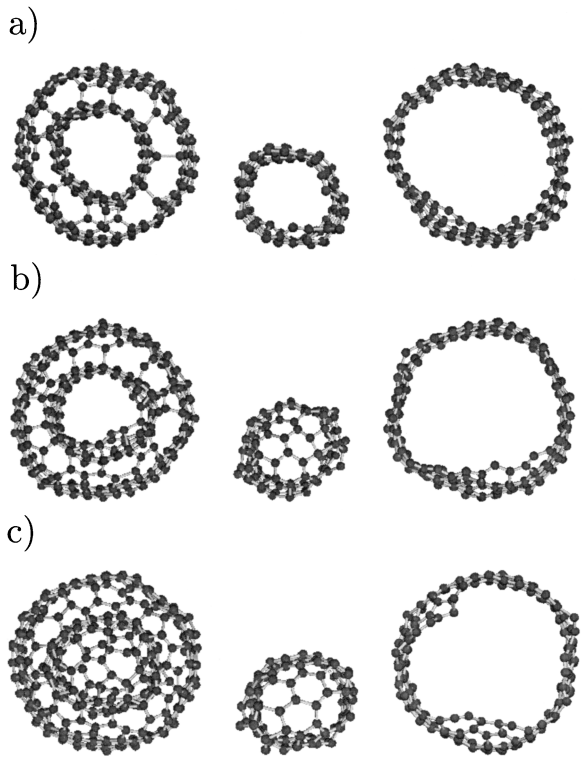

FIG. 1. Top view of a $(10,0)@(18,0)$ double-wall and the corresponding single-wall tubes at different times: (a) 0 ps; (b) 45 ps; and (c) 154 ps. Note the closure of the double-wall tube at 154 ps.

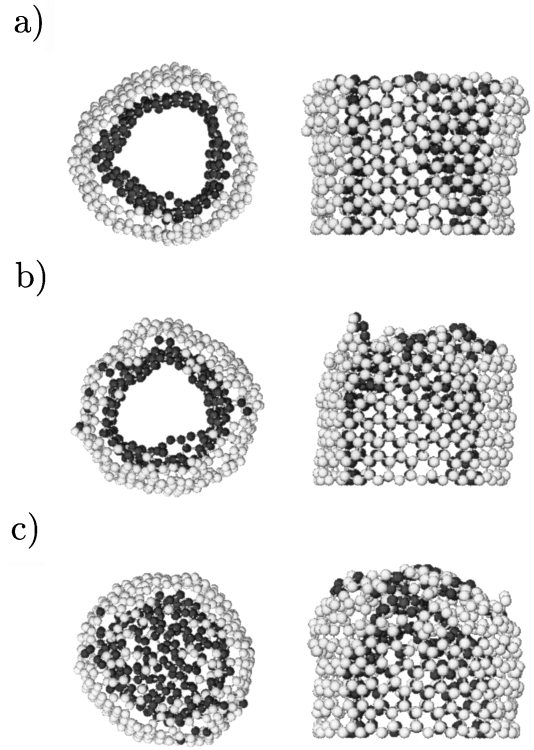

FIG. 2. Top and side views of $(18,0)@(21,0)$ double-wall tubes from the top and side. Lighter (darker) colors are used to represent atoms from the outer (inner) tube: (a) 0 ps; (b) 45 ps; (c) 180 ps. Note that at these high temperatures, a small number of atoms from the inner tube move towards the outer tube.

even more, further enhancing the transfer of atoms from the outer towards the inner tube via the lip-lip network. As this network of atoms moves across the tubes, there is a general collapse of the upper parts of the tubes, which form a two-layer cap closing off the double-walled tube. Again, this is facilitated by the lip-lip network, which helps drag atoms from the tube edges towards the center. Mechanistically, these observations suggest that shells of multiwalled nanotubes close in pairs, and that the driving force for tube closure is set by the curvature (diameter) of the inner tube, where the defects leading to closure first form. Simulations of double-wall nanotubes of different chiralities, as well as armchair tubes, showed exactly the same behavior as the $(n, 0)$ tubes reported here.

To compare the stability of single- and double-walled tubes, we carried out annealing studies for tubes in the ≤ 2 nm range. These results are summarized in Table I. Essentially, at any given temperature, the time required to close the double-wall tube is longer than, but still comparable to, the time needed to close the single-wall tube having the same diameter as the inner double-wall tube. The longer closure time for the double-wall tubes is due to the time it takes for atoms to transfer from the outer to the inner tube. Note also that the 7 ps closure time of the $(10, 0)$ single-wall tube is in excellent agreement with *ab initio* simulation results [25]. In all of our simulations, the outer, larger diameter, single-walled tubes take substantially longer to close than those of the inner diameters, so that the stability is set by the inner tube diameter. Extensive annealing simulations of even larger, single-walled tubes show that their closing is initiated by the nucleation of stable pentagon pairs, as previously surmised from total energy calculations [17].

While these simulations show that the lip-lip interaction alone cannot stabilize open-ended nanotubes, it may still be possible that these interactions exert a stabilizing influence if they act in conjunction with other effects [13]. We have therefore carried out an extensive simulation of growth on a large diameter double-walled tube, which should be quite stable. Two saw-toothed $(38, 0)@(47, 0)$ tubes having diameters of 3.0 and 3.7 nm and heights of 12 atomic layers were constructed. To form the lip-lip interaction, 38 atoms were added between the nanotube tips, and the system was annealed for a short period of time. As with the relatively narrow tubes, the network was observed to reform itself rapidly in such a way as to minimize the number of twofold coordinated carbon atoms. The resulting structure is shown in Fig. 3(a). During the MD run, the temperature of the tips was kept at 3000 K, but a constant temperature gradient was imposed along the length of the tube, so that the bottom layers were kept at 1700 K. Carbon atoms were deposited at random around the circumference of the tube, with kinetic energies in the 1–8 eV range. The primary effect of the electric field was assumed to simply focus the incoming atoms onto the nanotube tips.

In the simulation, carbon atoms were deposited at a rate of one atom per 290 ps. While this rate is considerably higher than the estimated experimental rate of one atom per 10^2–10^4 ns, it is mandated by the substantial computational requirements of the simulation. However, previous investigations of possible defect structures show that these anneal out on a 10–100 ps time scale [17]. This is fast enough for our simulation to capture the essential annealing processes, even at the high deposition rate. Moreover, although the atoms were deposited largely at random, the successive places for deposition were constrained to be relatively far apart on the tips so that the actual, local deposition rate was considerably lower, estimated at one atom every 2 ns. We also note that all of the conditions of this MD simulation are precisely the same as in previous deposition simulations on single-walled carbon nanotubes, where straight, defect-free growth was obtained [17].

Figure 3 shows the resulting structures. As with the narrow tubes, atoms are readily incorporated into the tips

TABLE I. Mean time for closure τ for a series of annealing runs for single- and double-walled tubes.

Tubes	Diameter (nm)	Temperature (K)	τ (ps)
$(10, 0)$	0.78	3500	7
$(10, 0)$	0.78	3000	45
$(18, 0)$	1.41	3000	650
$(10, 0)@(18, 0)$		3000	154
$(13, 0)$	1.02	3400	48
$(21, 0)$	1.64	3400	250
$(13, 0)@(21, 0)$		3400	64
$(18, 0)$	1.41	3500	140
$(26, 0)$	2.03	3500	212
$(18, 0)@(26, 0)$		3500	180

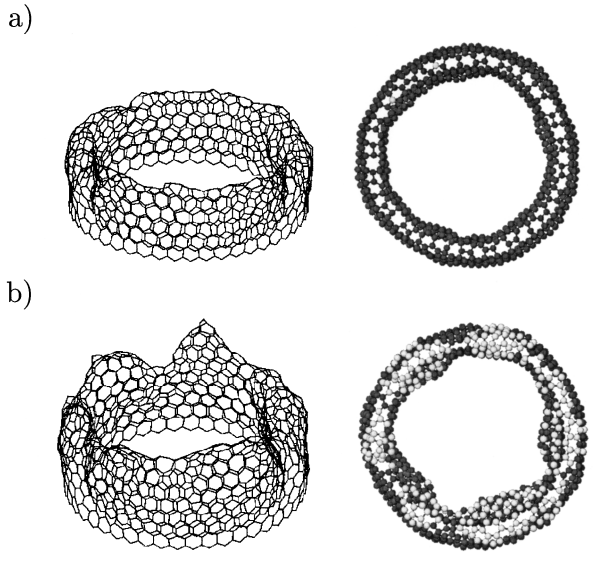

FIG. 3. Snapshots of growth simulation of a large double-wall nanotube: (a) the initial structure is formed after addition of 38 atoms and subsequent annealing; and (b) the final configuration after deposition of ~200 atoms, colored light gray on the top views.

of tubes. However, most of the incorporation takes place either on top of the lips, or at the "bends," where the curvature is the highest. This, however, does not lead to open-ended and straight growth. Instead, disordered, cap-like "ballooning" structures are formed with considerable deviations from the perfect structure. The question of whether this disordered growth would simply continue, or mark the beginning of the tube closure, cannot be answered with current computational resources.

How then can growth proceed without a catalyst? One possible scenario is that initially a single nanotube with a fairly large diameter forms. Shells can then readily nucleate and grow using the initial nanotube surface as a template, as observed in transmission electron microscopy [3]. Provided that there is sufficient feedstock and the carbon flux is sufficiently high, the outer shell is likely to catch up with the inner tube, since atoms arriving both at its stem and at the protruding stem of the inner tube can diffuse to the edge of the outer shell and incorporate there, thereby increasing its growth rate compared to the inner tube. The growth of the resulting multiwalled tube will then continue for some period of time, which is dependent on both the temperature and the tube diameter. These notions are supported by the apparent independence of the lengths of the different shells, the varying number of shells per nanotube, and the often observed multiwalled closure of nanotubes, sometimes with nested inner caps.

In summary, we have carried out extensive MD simulations of the growth of double-walled carbon nanotubes. Contrary to initial expectations, we find that the lip-lip interactions are unable to prevent closure of nanotubes. This closure time increases with the nanotube diameter, and typically takes place on a hundreds of picoseconds time scale for tubes of ~ 2 nm diameter at temperatures of 3000 K or higher. Annealing studies show that the larger-diameter, single-wall nanotubes are actually more stable than the double-walled tubes, and that the lip-lip interactions aid nanotube closure by mediating the transfer of atoms from the outer to the inner shell. Furthermore, simulations of deposition on a large diameter, double-wall tube lead to significantly distorted structures, while deposition on single-wall tubes under identical conditions leads to defect-free, straight-tube growth.

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Note added.—A recent Letter [Young-Kyun Kwon *et al.*, Phys. Rev. Lett. **79**, 2065 (1997)], which appeared after this paper was submitted, presents *static* calculations showing that the formation of a lip-lip interaction is favored energetically. These results are reproduced by the present calculations. However, our *dynamical* simulations show that the lip-lip interaction does not prevent tube closure at the experimental growth temperatures.

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