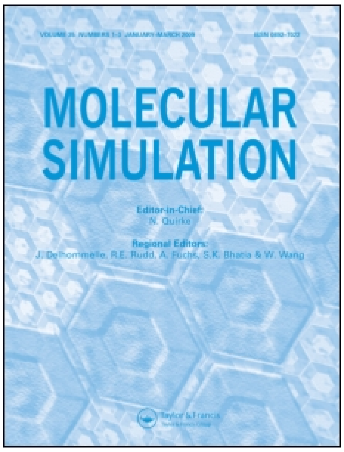

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THEORETICAL INVESTIGATIONS OF CARBON NANOTUBE GROWTH

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The growth of carbon nanotubes was investigated using a variety of complementary simulation techniques. Currently, a number of experimental methods are used to synthesize carbon nanotubes suggesting that different mechanisms play a role in their formation. However, it has been shown that growth of nanotubes takes place primarily at the open-ended tips of nanotubes. *Ab initio* simulations show that the high electric fields present at the nanotube tips in carbon arc discharges cannot be responsible for keeping the tubes open. Rather, the opening and closing of tubes is controlled by the formation of curvature-inducing defects such as adjacent pentagon pairs. On narrow tubes, the formation of such defects is favored leading to the rapid closure of the tubes. By contrast, the formation of hexagons, which lead to straight open-ended growth is favored on large-diameter tubes, with an estimated crossover radius of about 3 nm. Large-scale molecular dynamics and kinetic Monte Carlo simulations have been used to verify these ideas. We have also explored the role of the so-called lip–lip interactions during growth. Such an interaction is important in producing multiwalled nanotubes, where the interaction between two open nanotube tips leads to the formation of a network of bonds. Simulations show that such an interaction is indeed significant, but does not provide the additional stabilization required for straight, open-ended, multiwalled nanotube growth. Finally, we consider the formation of nanotubes in the presence of large and small catalytic particles. In the former case, growth is believed to take place *via* a root-growth mechanism, while the direct adsorption and extrusion of carbon from the vapor dominates the latter. Both mechanisms lead to the formation of small-diameter, single-wall nanotubes.

Keywords: Carbon nanotubes; large-scale molecular dynamics; kinetic Monte Carlo

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I. INTRODUCTION

Carbon is unique among the elements in its ability to create a wide variety of network-like structures termed fullerenes. Based primarily on sp2 type bonding, these range from the highly publicized C60, to other large carbon cages [1], to buckyonions [2]. However, it is the most recently discovered carbon nanotubes [3] that currently elicits most of the excitement within the scientific community. In particular, carbon nanotubes possess unique mechanical and electrical properties. Experiments and theoretical calculations [4–9] show that they are superstrong, light-weight fibers with a remarkable resilience towards deformations, which should allow for future applications as structural components in composits. Turning to their electronic properties, single-wall carbon nanotubes may either be metallic or semiconducting depending upon their helicity (*i.e.*, the way the graphene sheet is rolled when the nanotube is formed), which is generally denoted by a pair of integers (n, m) [10–14]. It has been shown [15] that nanotubes of different helicities may be joined together with the aid of one or more pentagon-heptagon (5–7) defects, thereby forming different electronic heterojunction. It is therefore possible, in principle, to form nanotube-based all-carbon microelectronic devices [16, 17]. Some of these remarkable predictions have recently been confirmed *via* scanning tunneling microscopy (STM) studies [18]. Carbon nanotubes also hold considerable promise as catalysts, field emitters, photonic material, molecular straws and switches [19–24].

Since their initial discovery in 1991 by Iijima [3], carbon nanotubes have been synthesized in carbon arc discharges, *via* laser vaporization methods, through ion bombardment, catalytic combustion and *via* chemical vapor deposition [24–30]. Given all of these different methods of production, it is likely that a variety of mechanisms play a role in their formation [29–34]. However, two common trends have emerged. First, the type of nanotube that is formed depends crucially upon the presence of metal catalysts. If small amounts of transition metals such as Fe, Co, Ni or Y are introduced in the target graphite, then single-wall carbon nanotubes are the dominant product. In the absence of such catalysts, the formation of multiwall carbon nanotubes is favored. Second, it is clear from the experiments, that during noncatalytic growth, the nanotubes actually remain open [35]. This is surprising, because from an energetic point of view, the large numbers of dangling bonds present at the tips of the open nanotubes definately favors a closed-tube geometry.

To address these and other issues, we have carried out extensive investigations of the kinetics of carbon nanotube growth using a number of complementary numerical techniques [31–33]. The methodolgy used range from *ab initio* studies, classical molecular dynamics (MD) and kinetic Monte Carlo (MC) simulations. We are therefore able to address issues related to the growth over a large range of length and time scales. A brief outline of the paper is as follows. In Section II we review our work on the growth of single-wall carbon nanotubes based on the incorporation of species from the vapor; in Section III, we review the role of the so-called "lip–lip" interaction and the growth of multiwalled carbon nanotubes. Section IV is where ideas related to catalytic growth are discussed, while Section V is reserved for a short summary.

II. OPEN-ENDED GROWTH OF NANOTUBES

It was initially believed that carbon nanotubes grow through the addition of atoms to the caps of closed nanotubes. However, experiments have subsequently shown that the tubes are in fact open during growth [35]. This is surprising, because energetically the large number of dangling bonds present on open tubes definately favors a closed tube geometry. A number of theories have been put forward to explain the open-ended growth of the nanotubes. Amongst these, the idea that it is the large electric fields present (estimated initially to be about one volt per angstrom) at nanotube tips is quite appealing [36], especially as carbon nanotubes were initially only observed in arc discharges. To test this hypothesis, we carried out *ab initio* total energy calculations of carbon nanotubes in the presence of electric fields of different strengths which were characteristic of different nanotube lengths [31]. The results for the narrowest nanotube, which makes the strongest possible case for the electric field argument, is shown in Figure 1. The data shows that a nanotube must have a minimum length of about 49 nm before the electric field alone can stabilize an open-ended carbon nanotube. Since this length is very long, it is therefore quite likely that the nanotube would have closed long before the electric field effect becomes dominant. Clearly, the electric field by itself cannot play a significant role in keeping the nanotubes open for growth [37]. Indeed, in recent years other techniques of nanotube synthesis such laser ablation methods, in which there are no significant electric fields, have been discovered [38].

If the electric field effect is not dominant, some other mechanism must be responsible for the open-ended growth. Other mechanisms based on the temporary saturation of the dangling bonds with hydrogen, thermal and concentration gradients at tips can similarly be eliminated. It is therefore

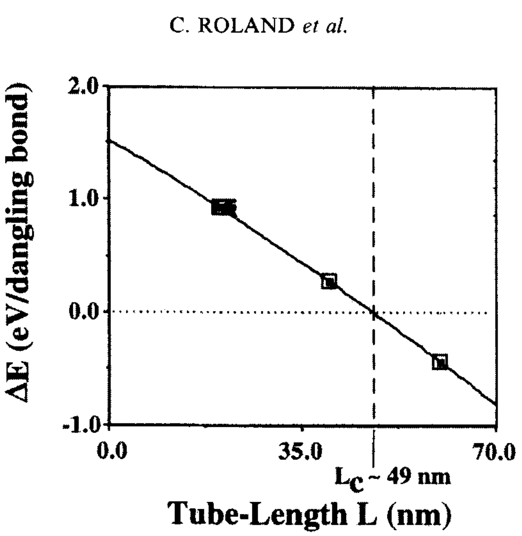


FIGURE 1 The total energy of an open metallic top of diameter 0.7 nm in the presence of an electric field as a function of tube length. The energy is normalized per dangling bond and measured relative to a closed tube of the same length and diameter in zero field. The crossover in the tube stability occurs at about 0.49 nm.

natural to examine models based on the different structures and kinetic pathways that are possible during the growth from the vapor phase. To explore the relative stability of the various adatom structures, we performed total energy calculations using the classical Tersoff [39] potential with a parameterization due to Brenner [40]. The main result of these studies is as follows. If one thinks of adding, say a dimer, to an open nanotube this can be done in two significant ways in terms of the opening and closing of the tubes. One can form a hexagon or a pair of adjacent pentagons at a "step edge", *i.e.*, where a row of hexagons terminates at the tube tip. The adjacent pentagon pairs saturate three dangling bonds, while the hexagons saturates two dangling bonds. However, at the same time, the adjacent pentagons curve the nanotube structure inwards. Thus, one has a classic competition between dangling bond *versus* induced strain energy in the structure. As can be expected, the formation of adjacent pentagon pairs is favored on small diameter, high curvature nanotubes while hexagons, which lead to straight, open-ended growth, are favored on large diameter tubes. With classical MD methods, the crossover radius is estimated to be about 3 nm.

These considerations, which are based on static, total energy calculations, are in fact borne out in realistic MD simulations. Figure 2 shows an example of the closing of a narrow, 1.5 nm diameter nanotube. Even without the addition of additional atoms, the narrow nanotube spontaneously form

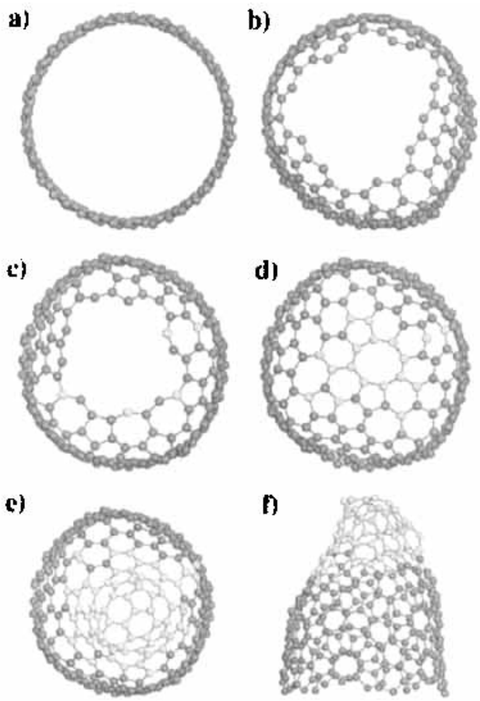


FIGURE 2 Snapshots from a growth simulation of a 1.5 nm tube: (a) initial all-hexagon tube; (b) five pentagons forming sponateously after annealing for 1.9 ns; (c) tube after 5 deposits (3.7 ns); (d) tube closed after 18 atoms deposited (6.6 ns); (e,f) top and side views of disordered cap structure after deposition of 68 atoms (16.4 ns) on the closed tube.

curvature-inducing defects such as adjacent pentagon pairs. The addition of more adatoms rapidly leads to the closure of the tube. Furthermore, adding even more atoms leads to the formation of a disordered cap structure illustrating that open-ended tubes are required for the growth of straight nanotubes. By contrast, numerical simulations of depositon on large-diameter nanotubes lead to the formation of defect-free nanotubes, provided that the deposition time is long enough to allow for the proper annealing of defects. Because of the inherent mismatch between MD simulation timescales (nanoseconds) and the experimental timescales (seconds), kinetic MC simulations were required to properly simulate the growth of carbon nanotubes. To construct such a model, we carefully measured the energetics of all of the relevant bond transformations as well as their rates. A sample simulation illustrating straight-opened growth for a large diameter nanotube is shown in Figure 3. With the MC simulations,

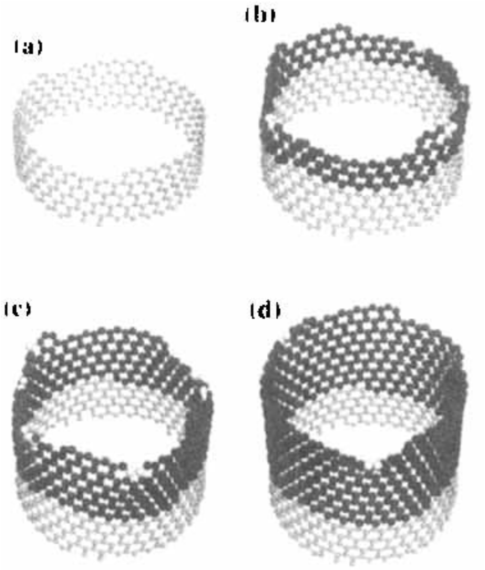


FIGURE 3 A typical growth sequence of a 3-nm-wide tube of helicity (35,5): (a) the initial all-hexagon tube; (b) after addition of 200 atoms; (c) after 400 atoms and (d) after 600 atoms. Note that the tube contains a small number of isolated pentagon defects.

we have also estimated a minimum temperature of about 1000 K required for defect-free growth, which is in good agreement with experimental observations.

In summary, our simulations show that the electric field does not appear to play a significant role in keeping the nanotubes open for growth. Rather, it is the formation of curvature-inducing defects such as adjacent pentagonal pairs that leads to the closing of nanotubes. Open-ended growth is associated with the addition of hexagons to large-curvature tubes. The estimated crossover diameter is about 3 nm.

III. ROLE OF LIP–LIP INTERACTIONS AND MULTIWALL TUBE GROWTH

While the open-ended growth of single-wall carbon nanotubes appears to be dominated by the nucleation of curvature-inducing defects, multiwall tubes have another kinetic alternative open to then in the form of the so-called "lip–lip" interaction [27]. Such an interaction arises when small atoms or clusters from the vapor deposit themselves near the tips of two open, adjacent nanotubes. These then form bridges or "spot-welds" between the tubes, which may thereby be kept open for continued growth. Such a lip–lip interaction is also conjectured to be an important factor in stopping the unraveling of carbon nanotubes under conditions of field emission [23].

To investigate the importance of the lip–lip interaction during growth, we carried out extensive MD simulations of double-wall tubes [33]. These simulations show, that while the lip–lip interaction does indeed play an important role in the growth of multiwalled tubes, it cannot keep the nanotubes open. As an example, consider a (10,0) @ (18,0) double-wall tube, which was uniformly heated up from 0 to 3000 K over a 40 ps period of time, as shown in Figure 4. While there are no initial interactions between the adjacent tube tips, bridging bonds were observed to form at about 1000 K, when the radial distortions of the tips where large enough to bring the tubes into interaction range. The network of bonds that forms has a fluctuating nature in so far as the network of bonds breaks and reforms into similar configurations on a time scale of several picoseconds. These observations are completely consistent with recent *ab initio* simulations [41].

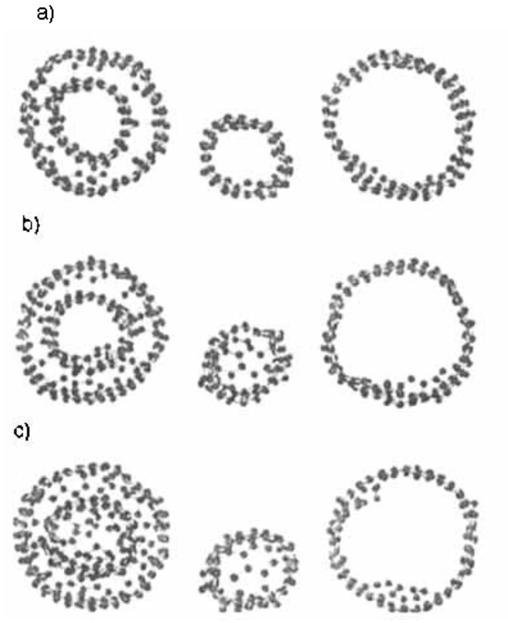


FIGURE 4 Top view of a (10,0) @ (18,0) double-wall and the corresponding single-wall tubes at different times: (a) 0 ps; (b) 45 ps, and (c) 154 ps. Note that the double-wall tube is closed at (c), while the outer, single-wall shell is still open.

To test the efficacy of the lip–lip interaction in keeping the multiwalled tubes open, we continued annealing the double-wall tube. Surprisingly, we found that the tube closes spontaneously on a hundreds of picoseconds timescale. Because of the fluctuating character of the lip–lip interaction, bonds connecting the tube tips break. This eventually allows a thermal fluctuation to nucleate one of the curvature-inducing defects on the inner tube, which bends the tube inwards. However, because of the two lips are connected by a network of bonds, the outer shell begins to curve inwards as well. Moreover, the connection between the tips allows for the transfer of atoms between the nanotube tips. Once this process begins, the two tubes close relatively rapidly *via* a general collapse of the upper parts of the tips, ultimately leading to the formation of a two-layer cap, which effectively closes off the double-wall tube and prevents further growth.

These observations suggest the following scenerio for the growth of multiwalled tubes. The initial stage involves the nucleation of a single-wall nanotube by an as of yet unknown mechanism. However, once formed, other shells can readily form on top of this tube using the surface as a template. This outer shell is likely to grow through a combination of step flow and/or coalescence of small graphene-like clusters. Ultimately, if there is enough feedstock and if the carbon flux is sufficiently high, the outer shell will catch up with the inner tube until the tips are more or less level. At this point, a lip–lip network of bonds forms. The tubes would then continue to grow for some transient period of time which is dependent on both the nanotube diameter and temperature, and then close. This process can then repeat itself, ultimately leading to the formation of multiwalled tubes with nested inner caps, as observed in the experiments.

This picture suggests that multiwall tubes closure is at least initiated by the lip–lip interaction. It is therefore quite possible, that this mechanism severely limits the length of multiwalled carbon nanotubes that can be formed in the absence of metal catalysts. To address this issue, we carried out extensive annealing studies of the time-to-closure of single-wall carbon nanotubes as a function of tube diameter and radius [33]. We concentrated on single-wall tubes, as the time-to-closure of the largest and smallest diameter shells provide an upper and lower bound for the time-to-closure of a given multiwall tube, respectively. An upper bound estimate for the length of nanotube shells *l* that can be formed may then be obtained from *l* , where is the fastest rate of defect-free growth. Estimates for each of these quantities have previously been obtained with MD simulations [31]. The resulting predictions are summarized in Figure 5, which presents a plot of the estimated upper-bound lengths for noncatalytically grown nanotube

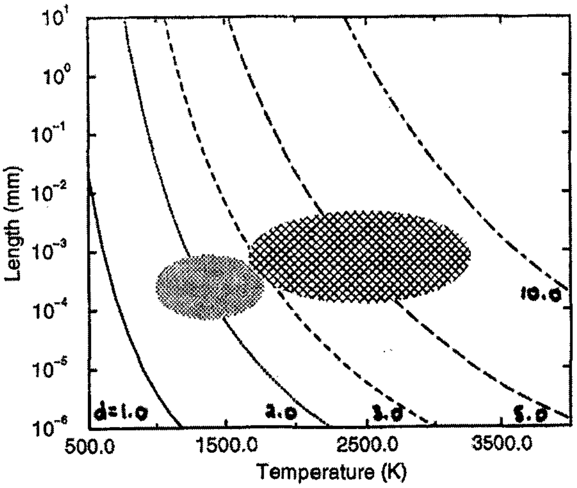
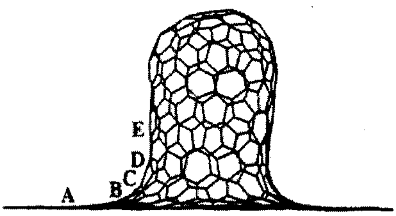


FIGURE 5 Estimated maximum lengths of non-catalytically grown nanotubes as a function of temperature, as extroplated from MD annealing studies. The different lines mark different nanotube diameters. Upwards from the solid line: solid line, 1.0 nm; dotted, 2 nm; dashed, 3 nm; long-dashed, 5 nm; long-dashed dotted, 10 nm. The approximate experimental regions are marked with grey ellipses. Data from laser vaporization is centered about $T = 1500$ K (light grey), while carbon arc data is centered about 3000 K (cross hatched).

shells of various diameters as a function of temperature. As expected, the higher the temperature, the shorter the length of the nanotube that can be formed due to a more rapid rate of defect nucleation. The plot also suggests that lower temperatures optimize the length of nanotubes, which is consistent with experimental observations of tubes grown both by laser vaporization and carbon arc methods. For example, laser ablation leads to defect-free tubes with diameters in the 2–20 nm range and lengths of 200–300 nm at about 1473 K, consistent with our theoretical results [23]. In carbon arcs, growth temperatures are much higher – estimated to be 2500–3000 K. Large 10 nm diameter tubes are typically observed to grow out to several *m*, which is again consistent with the theoretical prediction [42].

IV. CATALYTIC GROWTH OF CARBON NANOTUBES

In the presence of metal catalysts, single-wall nanotubes are the dominant product [29, 30]. A number of different mechanisms have been proposed to explain this, based on the size of the catalytic particle. If the metal catalyst is rather small, it may be entirely encased by the nanotube. In this case, it is believed the nanotube forms by the direct solvation of carbon from the



Handle Site	Energy
A	0.0
B	-0.1
C	-0.5
D	-0.2
E	0.05

FIGURE 6 Geometry illustrating the root-growth mechanism. A 1.0 nm tube can grow out of a flat graphene sheet through the addition of carbon atoms at B, C, D, which mark regions of high-curvature at the base or root of the nanotube.

nanotube cluster [31]. Carbon atoms are absorbed by the metal particle, forming a carbide. Additional carbon atoms then precipitate from such a nanocluster. The lips of the nanotube always remain anchored to the edge of the cluster, which keeps on absorbing and extruding the carbon atoms leading to the growth of the nanotube.

However, there are significant cases where the size of the metal particle exceeds that of the carbon nanotube by several orders of magnitude. In this case, a root growth mechanism is believed to operate [32]. As in the previous case, the carbon atoms are absorbed by the metal forming a carbide. Additional carbon atoms are then extruded ultimately leading to the formation of a graphetic sheath around the nanoparticle. However, as the cluster will be characterized by significant surface roughness on the nanometer length scale, one expects that this surface roughness will be mirrored in the graphetic layer covering the particle. Simulations show that atoms are preferentially added to the base of such height perturbations ultimately giving rise to the nucleation of a carbon nanotubes, as shown in Figure 6. The tube then continues to grow from the "root", which is where carbon atoms are preferentially absorbed and incorporated into the nanotube. Ultimately, single-wall nanotubes form.

V. SUMMARY

In summary, we have investigated the growth of carbon nanotubes with complementary simulation techniques. In agreement with experiments, *ab initio* simulations indicate that electric fields as would be present in a carbon arc discharge do not play a significant role in promoting the open-ended configurations necessary for nanotube growth. Rather, it is the formation of curvature-inducing defects such as adjacent pentagon pairs which controls the opening and closing of carbon nanotubes. Their formation involves a classic competition between dangling bond and strain-induced energy: curvature-inducing defects satisfy a larger number of dangling bonds but strain the tubes inward, while hexagons satisfy a lesser number of dangling bonds but do not strain the tubes. The former is clearly favored on narrow nanotubes and rapidly leads to their closure, while the former leads to straight open-ended growth on relatively large-diameter tubes. The estimated crossover radius is about 3 nm. Multiwalled diameter tubes have, however, other kinetic alternatives available to them in the form of the lip – lip interaction.

Contrary to expectations, the lip – lip interaction does not prevent the closing of tubes. Rather, it provides a natural mechanism for the closing of the nanotubes. Since the timescale for closing of the tube is set by the diameter of the innermost shell, we have been able to estimate the mean time for nanotube closure, as a function of both the temperature and nanotube diameter, through an extensive annealing study. The results are in good agreement with experimental data, and show that the lip – lip interaction provides a natural mechanism for the observed closing of the nanotube shells. Finally, we discuss the catalytic formation of single-wall nanotubes. Two mechanisms appear to play a role depending upon the size of the metal catalysts. Direct solvation and attachment of the carbon nanotube play an important role for small-diameter catalysts, while a root growth mechanism is believed to be dominant in the presence of catalytic particles that are significantly larger than the nanotube diameter.

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