

## Nucleation of Carbon Nanotubes without Pentagonal Rings

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We describe a new mechanism for the nucleation of carbon nanotubes which does not require an abrupt transition from pentagonal ring formation to exclusively hexagon formation. This mechanism, the spontaneous opening of double-layered graphitic patches, is quantitatively consistent with the recently discovered temperature dependence of the nanotube diameter.

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The unique one-dimensional structure of single-walled and multiwalled carbon nanotubes [1] depends critically upon a nucleation mechanism which somehow restricts graphitic growth to a single axis. The transient and extreme growth conditions of carbon nanotubes have obscured the mechanism of nucleation. Most hypothetical nucleation mechanisms invoke pentagon formation to produce a hemispherical graphitic cap, with the cap's edges either open [2–4], attached to a substrate via a tubular segment [5–7], or mated with a second cap into a closed fullerene [8–10]. These models all require an abrupt transition from a regime favoring pentagon formation (when the cap is forming) to one that favors exclusively hexagon formation (when the tube is lengthening) once exactly six pentagons have formed [11]. Other models nucleate a nanotube from a  $\sim 40$ -atom polyyne ring [12,13]. Unfortunately, such a large carbon ring is unlikely: carbon clusters change from simple rings to double rings and cages above  $\sim 20$  atoms [14]. Very recently, Bandow *et al.* have discovered that the temperature during synthesis controls the diameter of the nanotubes [15]. Since the diameter of a nanotube is fixed by its size at nucleation, these results provide rare experimental insight into nucleation itself. Here we propose a new nucleation model for carbon nanotubes which (1) contains only hexagonal rings within the tube nucleus and therefore does not require a transition from pentagon to exclusively hexagon formation, (2) can explain the temperature dependence of the nanotube diameter distribution, (3) accounts for the narrow diameter distribution of single-walled nanotubes, and (4) can explain the wider diameter distribution of multiwalled nanotubes.

Carbon nanotube synthesis apparently requires a surface on either an electrode or a metallic particle [16]. Surfaces favor the growth of small flat graphitic patches. (Such graphitic patches can form even in much higher density environments [17].) Although it may be difficult to imagine a means by which a single graphitic patch could curl into the nucleus of a nanotube without the incorporation of pentagons to produce the needed curvature [18], we herein describe a natural kinetic pathway by which a *two-layered* graphitic patch can transform into the nucleus of a nanotube.

Figure 1 illustrates schematically such a nucleation model. A double-layered graphitic patch forms on a surface, with edges on adjacent layers interconnected via bridge atoms [19]. When edges are bridged on opposite sides of the patch, such a two-layered patch looks similar to a very short flattened nanotube [20]. A small-diameter flattened nanotube is unstable towards popping open, since the attraction between the inner surfaces cannot counteract the excess curvature energy on the edges. If a double-layered patch pops open, then growth in the bridged direction is arrested and further carbon addition lengthens the nucleus axially to form a nanotube [21]. Since no pentagons are involved, the mechanism need not appeal to a fortuitous transition from pentagon formation to exclusive hexagon formation during growth. The curvature necessary to form a tube nucleus arises not from pentagons, but from the extreme curvature induced by bridging across the interface between two adjacent parallel graphitic patches.

Although this model is qualitatively attractive, detailed numerical modeling is necessary to determine if the energetic balance actually favors this route to nucleation under realistic conditions. We use a tight binding total energy model [22] to simulate the edge-mediated opening of a double-layered graphitic patch into a single-walled nanotube nucleus. The tight binding parametrization accounts for the covalent electronic energetics and the nearest-neighbor repulsion of atomic cores. The weak

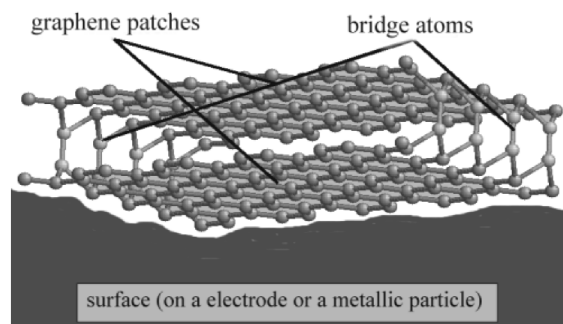


FIG. 1. A schematic diagram of the nucleation model in which a nanotube forms via edge-mediated opening of a double-layered graphitic patch.

interlayer attraction is incorporated through an empirical Lennard-Jones potential which yields the correct equilibrium interlayer distance and interlayer binding energy ( $0.035 \pm 0.015$  eV/atom [20]) for graphite. We model two parallel layers of graphite 3.4 Å apart with periodic boundary conditions along one direction and bridge atoms connecting the exposed transverse edges in the perpendicular direction. For simplicity we set  $T = 0$  in the molecular dynamics simulation; the primary effects of finite temperature are easily incorporated as will be explained later. Within a few femtoseconds, bulbs form at the bridged edges as the bridge atoms incorporate themselves into an energetically favorable continuous  $sp^2$  bonding network. If the energetic cost of curvature in the bulbs overcomes the interlayer attraction between the two layers, then the incipient tube pops open to a circular cross section, which then defines a preferential axis for one-dimensional growth. Figure 2a shows this opening process during nucleation of a (10, 10) tube [23]. In contrast, the nucleus of a (20, 20) tube (Fig. 2b) does not pop open, as the interlayer attraction dominates the energetics.

Figure 3 shows the total energy during the opening process for incipient nuclei of  $(n, n)$  nanotubes with radii 20, 27, and 33 Å [similar results are expected for other wrapping indices  $(n, m)$ ]. Nuclei smaller than the cross section of a  $D = 23$  Å diameter tube have no energetic barrier towards popping open. The size of the barrier scales with the length of the tube segment; we choose a length of 1 nm, which produces a roughly square patch with a plausible aspect ratio (we return to this point later). In larger tube nuclei, the energetic barrier against assuming the circular cross section increases roughly linearly with size as  $E_B = \epsilon(D - 23 \text{ Å})$  eV with  $\epsilon \approx 0.2$  eV/Å. The linearity follows from the

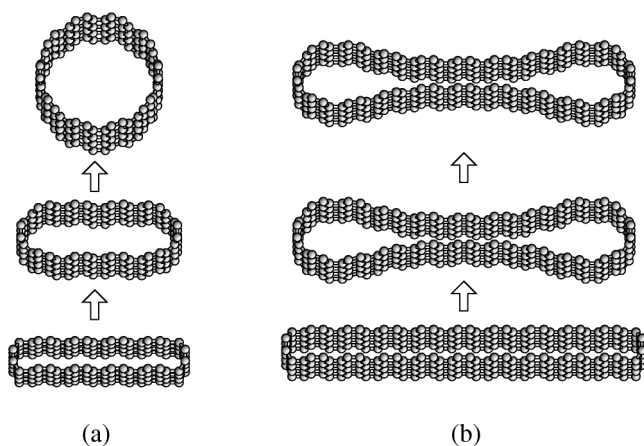


FIG. 2. The relaxed structures from  $T = 0$  molecular dynamics for two-layered graphitic patches of sizes necessary to form nanotube nuclei of diameters (a) 13.7 Å and (b) 27.4 Å. The smaller nucleus spontaneously opens into a circular cross section which defines a strong preferential growth axis, whereas the larger nucleus remains flattened.

linear dependence of the interlayer “glue” area on the diameter  $D$ . Above  $D = 34$  Å the circular cross section is energetically disfavored. Since the curvature energy is more important in multilayered structures while the interlayer binding energy of the inner surfaces is constant [20], multiwalled tubes could nucleate at larger diameters; double-walled nanotubes with inner diameters of  $\sim 45$  Å have been observed [1].

At finite temperature the system can thermally activate over a barrier towards popping open. Experimentally, the yield of the smallest-diameter nanotubes ( $D \leq 1$  nm) is only weakly dependent on temperature [15], in accord with our model, as small nanotube nuclei have no energetic barrier to opening. In contrast, the yield of larger-diameter nanotubes is very sensitive to synthesis temperature with higher temperatures yielding larger-diameter tubes [15]. Given the energetic barrier towards opening as a function of the incipient tube diameter, simple kinetic arguments can then estimate the theoretically expected temperature and size dependence of the nucleation rate for experimentally relevant time scales.

These kinetics are dominated by the size dependence of the activation barrier, as discussed below. The thermally activated opening rate for incipient nanotube nuclei is approximately  $f(R, T)\omega_{\text{vib}}e^{-E_B/k_B T}$ , where  $f(R, T)$  gives the temperature-dependent size distribution of appropriately shaped graphitic patches,  $E_B$  is the calculated energetic barrier, and  $\omega_{\text{vib}}$  is the attempt rate (comparable to the characteristic phonon frequency for transverse vibrations of a graphitic sheet at a wave vector comparable to the inverse tube radius, i.e.,  $\omega_{\text{vib}} \sim 10^{12}$  Hz) [24]. For small-radius tubes with no energetic barrier the exponential factor

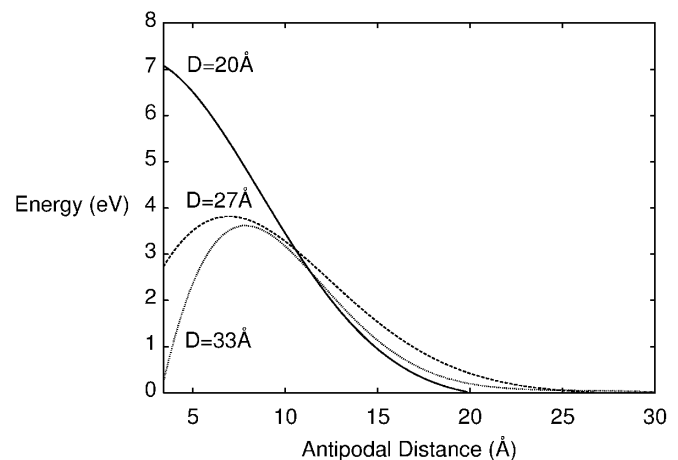


FIG. 3. The energy as a function of a reaction coordinate (i.e., the distance between opposite inner surfaces as the tube nucleus opens) for nucleation patches of varying diameter when opened and of length 1 nm. The smallest patches have no barrier to opening. For sufficiently large patches the opened state is energetically disfavored. For intermediate sizes, thermal excitation can activate over the barrier to opening on experimental time scales.

is absent, hence the number of small-radius tubes produced reflects directly  $f(R < R^*, T)$  where  $R^*$  is the largest diameter without an activation barrier to opening. In fact, the number of smallest-radius tubes ( $R < 1$  nm) produced is nearly independent of temperature from 780 to 1000 K [15]. Therefore  $f(R < 1 \text{ nm}, 780 \text{ K} < T < 1000 \text{ K})$  is a weak function of  $T$ . Since the emergence of an energetic barrier at larger radii has no direct influence on  $f(R, T)$ , the prefactor  $f(R, T)$  should have a relatively weak temperature dependence at slightly larger  $R$  as well, a regime in which the temperature dependence of the nucleation rate is therefore dominated by the rapidly varying exponential term [25]. Experimentally, the number of large-radius tubes falls off rapidly as a function of diameter [15], consistent with the rapid falloff of the exponential term. Therefore we focus on the exponential term in analyzing changes in the nanotube diameter distribution at larger diameters for  $780 \text{ K} < T < 1000 \text{ K}$ .

At  $T = 1000 \text{ K}$ , the single-site opening rate for a barrier of  $1.5 \text{ eV}$  is roughly  $10^4 \text{ sec}^{-1}$ . For a barrier of  $2.0 \text{ eV}$  the opening rate is  $\sim 10^1 \text{ sec}^{-1}$ , too slow for significant tube production, while at  $E_B = 1 \text{ eV}$  the opening rate is very fast,  $\sim 10^7 \text{ sec}^{-1}$ . We can take  $E_B \approx 1.5 \pm 0.3 \text{ eV}$  as a characteristic energy barrier above which nucleation is strongly suppressed on the experimental time scale in the laser ablation cloud or the dynamic plasma arc discharge. As tube diameter (and energetic barrier) increases, maintenance of a constant nucleation rate implies a higher temperature,  $E_{B,2}/k_B T_2 = E_{B,1}/k_B T_1$  (in differential form,  $\Delta E_B/\Delta T = E_B/T$ ). In other words, at higher temperatures a fixed nucleation rate occurs at a larger radius. The overall diameter distribution at large diameters should then shift upwards as the temperature is increased. Examining the data of Bandow *et al.* [15], this upward shift is  $(1.0\text{--}1.3) \times 10^{-2} \text{ \AA/K}$  for both the peak and the downslope of the distribution.

Since the characteristic barrier is much larger than  $k_B T$ , a small change in temperature produces a relatively large change in the diameter distribution. As mentioned above, the difference in the opening barrier for two tubes depends linearly on their diameter difference,

$$\Delta E_B = \epsilon \Delta D, \quad (1)$$

where  $\epsilon \approx 0.2 \text{ eV/\AA}$ . Therefore a change in temperature  $\Delta T$  yields a typical diameter change of

$$\frac{\Delta D}{\Delta T} = \frac{E_B}{\epsilon T} \sim 0.8 \times 10^{-2} \text{ \AA/K}, \quad (2)$$

reasonably consistent with the experimental result of  $(1.0\text{--}1.3) \times 10^{-2} \text{ \AA/K}$  for the shift in the upper portion of the nanotube diameter distribution [15]. This pop-open nucleation mechanism sets a temperature-dependent upper limit on the nanotube diameter distribution through suppression of thermally activated nucleation; the relatively temperature-independent lower limit at  $D \approx 0.8 \text{ nm}$  [15,26–28] might then be set by the reduced chemical stability of the highly strained smallest-diameter tubes [26].

Within this simplified model, the predicted diameter distribution is shifted towards larger diameters than those observed (i.e.,  $\sim 29 \pm 9 \text{ \AA}$  versus the  $\sim 15 \text{ \AA}$  observed at  $1000 \text{ K}$ ; the error bar arises primarily from the uncertainty in the strength of the interlayer attraction). This discrepancy is expected, for three reasons. First, an attractive external surface adjacent to one graphitic layer reduces the propensity to popping open. To quantify this effect, we introduced a rigid external surface with the same attractive potential as graphite itself; this additional stabilizing force reduces the characteristic nucleus diameter by  $\sim 3 \text{ \AA}$ . Second, the incipient nuclei of larger-diameter tubes would tend to be longer axially and therefore would have relatively larger barriers to opening than the fixed-length nuclei herein considered. This effect would also increase  $\epsilon$  slightly without affecting the overall consistency with experiment. Third, the calculations simulate an ideal nanotube nucleus wherein periodic boundary conditions suppress interlayer bridging along one direction. In more realistic configurations, the irregular shape and registry of the graphitic patches and the possible competition between bridging on different pairs of edges would reduce the typical size at which popping open occurs. Note that the first edge to bridge induces local bulging, which partially separates the adjacent edges and leaves the opposite edge as the most likely to subsequently bridge. The differing reactivities of the zigzag and armchair graphitic edges might slightly favor wrapping indices around the armchair ( $n, n$ ) configuration [4,15,29,30].

The nucleation mechanism for carbon nanotubes is one of the most important open questions in nanotube synthesis and application [31]. Although definitive determination on this point awaits further experiments, we have described herein a plausible and qualitatively new nucleation mechanism which agrees with experimental results on the temperature dependence of nanotube radii and also produces the required curvature without the necessity for the formation of exactly six pentagonal rings within the incipient tube.

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