# Frustration Effects and Microscopic Growth Mechanisms for BN Nanotubes

X. Blase,* A. De Vita, J.-C. Charlier,† and R. Car
*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), INR-Ecublens, CH-1015 Lausanne, Switzerland*

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Using *ab initio* molecular dynamics simulations, we have studied the growth mechanisms of boron-nitride (BN) nanotubes. In the experimental conditions of temperature, the behavior of single-wall BN nanotubes strongly depends on their helicity. Open-ended "zigzag" tubes close into an amorphouslike tip, preventing further growth. In the "armchair" case, the formation of squares traps the tip into a flat cap able to revert to a growing hexagonal network by incorporating incoming atoms. These findings are related to the greater stability of B-N bonds as compared to B-B or N-N bonds. [S0031-9007(98)05301-0]

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While carbon nanotubes [1] have attracted a lot of attention in the last few years, boron-nitride (BN) nanotubes [2–4] have been studied much less extensively. BN nanotubes are insulating with a ~5.5 eV band gap [5]. More generally, it has been shown that controlling the $(x, y, z)$ stoichiometry of composite $B_xC_yN_z$ nanotubes can be used as a means to tailor their electronic properties [6]. In addition, the lack of chemical reactivity displayed by BN nanotubes leads to the idea that BN nanotubes could be used as "protecting cages" or "molds" for any material encapsulated within [7]. These potential applications provide a strong motivation for pursuing the experimental and theoretical effort of better understanding BN tubular systems.

Recent experimental studies [3,4] have shown that the morphology of BN nanotubes differs significantly from the one of their carbon analogs. BN nanotubes tend to have amorphouslike tips or closed-flat caps, which are very rarely observed in carbon systems. In order to understand the origin of these differences, we have studied the growth mechanisms of BN nanotubes by means of first-principles molecular dynamics simulations [8,9]. We find that the high energy cost of "frustrated" B-B and N-N bonds strongly affects the modalities of growth. In particular, odd-member rings are not stable at the growing tube edge at experimental temperatures. In the case of single-wall armchair [10] (SW) nanotubes, a metastable "open" tip structure with even-member rings only and no frustrated bonds is created. Furthermore, the calculations suggest that these SW tubes may grow uncatalyzed by chemisorption from the vapor phase. On the contrary, if the network helicity imposes the presence of frustrated or dangling bonds (e.g., zigzag [10] nanotubes), these bonds are unstable, breaking and forming during the simulation. This leads to an amorphous tip structure, which is likely to prevent growth.

Our simulations are carried out within the local density approximation [11] to density functional theory [12]. We adopt periodic boundary conditions and a plane wave expansion for the wave functions with a 36 Ry energy cutoff. We keep a minimum distance of 6–10 Å between neighboring tubes. Standard nonlocal pseudopotentials [13] are generated for B, N, and H atoms [14]. The system sizes are ranging from 70–120 atoms per unit cell with a typical simulation time of ~10 ps per system. The diameter of the studied BN nanotubes (~0.8 nm) is consistent with a dominant peak observed in the diameter frequency histogram of pure SW carbon nanotubes [15] and comparable, even though smaller, with the diameter of the BN nanotubes observed so far (~1.2–4 nm) [4].

First, we evaluate the energy cost associated with a frustrated N-N or B-B bond as compared to a B-N bond. Starting from an isolated BN hexagonal sheet, we exchange two neighboring B and N atoms, creating two B-B bonds and two N-N bonds. The computed energy cost of this antisite defect is 7.1 eV, after atomic relaxation. Second, we study various isomers of small $C_{24}$ and $B_{12}N_{12}$ clusters. In particular, we compare the energies of two fullerenelike closed structures, one with pentagons and hexagons only (labeled [5,6]), the other with squares and hexagons (labeled [4,6]). In the case of carbon, we find that $C_{24}$[5,6] is more stable than $C_{24}$[4,6] by 1.5 eV, while in the case of BN compounds, the $B_{12}N_{12}$[5,6] isomer is less stable than $B_{12}N_{12}$[4,6] by 7.8 eV [16]. Assuming that elastic energies are equivalent for both C and BN compounds, we can estimate the cost of the six frustrated bonds present in the $B_{12}N_{12}$[5,6] isomer to be 9.3 eV, that is ~1.6 eV per frustrated bond. This is consistent with the energy found above for a planar geometry.

We now turn to the study of the dynamics and growth mechanisms of BN nanotubes. In particular, we consider here the issue of further growth, once an initial tubular structure has already been formed [17]. We consider first the case of a (5,5) armchair nanotube. Starting from an "ideal" cleaved geometry [Fig. 1(a)], we gradually raise the temperature up to 3000 K which is typical of the experimental synthesis conditions. At relatively low temperature (~1500 K), the topmost BN hexagons bend inside connecting each other. This creates five squares and a decagon [Fig. 1(b)]. In this configuration, all atoms are threefold coordinated and no frustrated bonds are present

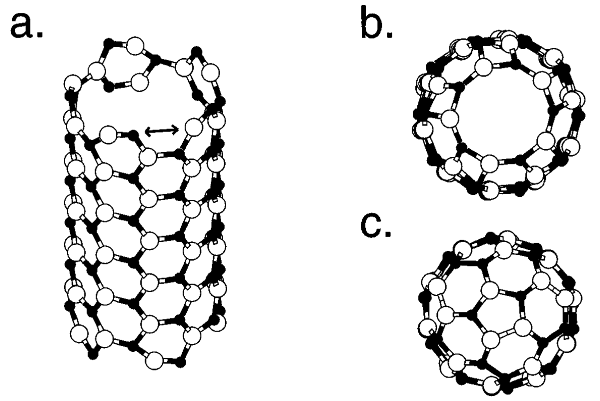

FIG. 1. Symbolic ball-and-stick representation of the (5,5) BN nanotube. Large white and small black circles are, respectively, B and N atoms. (Only the atoms in the "front" of the structure are displayed.) In (a), the initial configuration of the molecular dynamics simulation is shown (0 K). In (b), the final configuration at 3000 K exhibits the [4,6,10]-rings geometry discussed in the text. In (c), the hypothetical $C_{60}$-like capping is shown. The arrows indicate the motion of the atoms.

[18]. Brought to 3000 K for more than 5 ps, the squares and the decagon never open and no further reorganization is observed. This suggests that tip structures containing several squares and a "large" even-member ring are quite stable in the case of BN based systems. An analogous molecular dynamics study has been performed for a BN(4,4) nanotube leading to the creation of a [4,6,8] tip containing four squares and an octagon.

Further, we test the stability of the obtained caps against arrival of incoming B and N atoms from the plasma. We send a B atom at 3000 K thermal velocity along the axis of the BN(4,4) nanotube onto the [4,6,8] tip structure. We find that the impinging atom is rapidly incorporated by reopening a square [Fig. 2(a)] to create a pentagon. We repeat the same "experiment" with a BN dimer and, again, the dimer is rapidly incorporated by a square in order to form a perfect hexagon [Fig. 2(b)]. The picture which emerges therefore is that armchair BN nanotubes can be stabilized into an intermediate "semiopened" metastable cap, consisting of squares and a large even-member ring, which is able to incorporate incoming B or N atoms (or BN dimers) from the plasma phase. This contrasts significantly with the case of armchair carbon nanotubes where the formation of pentagons leads to closure into a hemi-$C_{60}$ cap which does not incorporate any incoming atoms, preventing further growth [9].

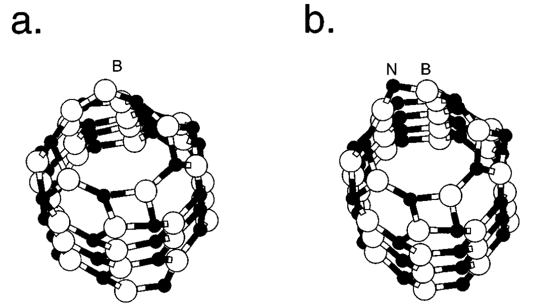

FIG. 2. Symbolic ball-and-stick representation of a (4,4) BN nanotube after incorporation of (a) a B atom and (b) a BN dimer. The incorporated atoms have been labeled by their chemical element symbol.

We consider now the case of a (9,0) zigzag nanotube. In the chosen starting configuration, the final ring of atoms is made of B atoms only and important frustration effects can be expected in an attempt to close this configuration. For temperatures lower than 3000 K, the only observed process is a dimerization of some B atoms at the top [Fig. 3(a)]. However, around 3000 K, a remarkable "diffusion" process at the tip of the nanotube brings N atoms above the terminal B ring [Fig. 3(b)] in order to create a BN square [Fig. 3(c)]. The formation of two more squares by the same mechanism is subsequently observed in the simulation. This first reorganization is followed by the formation of a "bridging" bond across the open end of the nanotube. However, contrarily to the armchair case, the system does not evolve towards a stable minimum energy configuration but samples several tip structures. We plot in Fig. 3(d) the configuration reached by the system after 3 ps of simulation at 3000 K.

The zigzag BN nanotube open edge is therefore very unstable, evolving rapidly towards an amorphouslike tip. The creation of BBN triangles in Fig. 3(a) indicates that the energy cost of two dangling bonds is larger than the cost associated with an homopolar bond. As a result, $\sim 4-5$ homopolar bonds are formed at the tip of our (9,0) system. At given "constant" frustration cost, we may expect that pentagons are preferred over triangles, driving the system towards tip closure. The rearrangements observed in Figs. 3(b) and 3(c) which lead to the replacement of triangles by pentagons and squares are indeed very similar to what was observed in the carbon case [9]. However, rearrangements at the zigzag BN nanotube egde are not as stable as in the case of carbon nanotubes. This is because homopolar bonds are much weaker than B-N bonds. These homopolar bonds are observed to break and form frequently at temperatures $\sim 3000$ K. As a result, the zigzag BN edge does not reach any stable configuration as long as these frustrated bonds are present.

It is likely that a similar amorphous structure would naturally develop at some stage of the growth of any comparable zigzag tip, compromising further growth. This contrasts with the armchair nanotube case, suggesting that the growth of SW armchair nanotubes will be favored as compared to the one of zigzag nanotubes. Even though there is no available experimental data concerning the helicity of SW BN nanotubes, recent experimental results [4,19] indicate that helicity selection mechanisms absent in carbon determine the growth of BN multiwall (MW) tubes. Further, the present simulations lead to the idea that SW BN armchair nanotubes may grow uncatalyzed, in great

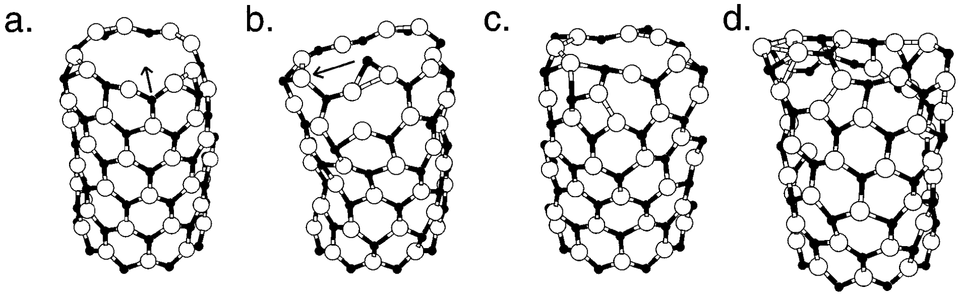

FIG. 3. Symbolic ball-and-stick representation of the (6,0) BN nanotube. In (a), the low-temperature dimerized configuration is shown. In (b) and (c), the flipping over of a N atom followed by the formation of a square is depicted. As a result, a frustrated pentagon has been "buried" inside the hexagonal network. In (d), we represent the final configuration reached by the system at the end of our simulation run. The arrows indicate the motion of the atoms.

contrast with the carbon case. This is consistent with the recent production of SW BN nanotubes [4] which show no trace of catalytic particle incorporated in (or protruding from) their tips. Other clear differences between BN and C tubes are found experimentally. For instance, MW and SW BN nanotubes are found in the same thin deposit collected on the anode [4] differently from what is observed in the case of the arc-discharge catalytic growth of carbon nanotubes [20]. Further, the observed SW BN nanotubes are always terminated by an amorphouslike tip [4]. Our results show that the onset of an amorphization process can be determined by the occurrence of frustrated bonds. This suggests a scenario of tube closure in which a sudden nonstoichiometric fluctuation of plasma phase composition occurs during growth, inducing the formation of a large number of frustrated bonds at the growing edge and thus leading to amorphization.

Concerning the growth of large $(n, n)$ shells, we note that the bending inside of the dangling dimers cannot lead to the formation of exactly $n$ squares as in the cases considered above [21]. However, local fluctuations of curvature at 3000 K can allow for the creation of one or several squares through the same mechanism. Since these squares do not survive the arrival of impinging atoms, the final closure of the BN tube shell (apart from the amorphization mechanism discussed above) can occur only under the unlikely event that such squares are incorporated in the hexagonal network. This is consistent with the topological models proposed in Refs. [3,4] for BN tubes. The presence of squares in the hexagonal network induces flat tips of the kind observed experimentally. Our dynamical simulations suggest that the number of squares in the final tip may be larger than three, implying that large even-member rings may be present at BN nanotube tips [22]. This possibility was pointed out in Ref. [3] on the basis of Euler's theorem for even-member ring systems.

The present results together with those of previous calculations on carbon nanotubes lead to a few more speculative considerations on the growth mechanism of MW BN nanotubes. In the case of MW carbon nanotubes, lip-lip interactions stabilize the open edge of each nanotube by forming bridging bonds between concentric shells. We expect that this mechanism would apply also to BN concentric nanotubes, with the additional constraints introduced by frustration effects. Contrarily to the carbon case, SW BN nanotubes [4] are always imaged by wavy lines [23] and have amorphous tips, while MW nanotubes (even bilayers) are imaged with perfectly straight lines and present generally well ordered caps. This suggests that the lip-lip interactions contribute to reduce the number of frustrated bonds and hence the number of residual defects in the grown structure. In particular, zigzag edges should benefit strongly from this effect since such a geometry, by alternating B and N edges, would ensure that all lip-lip bonds are heteropolar (this would not be the case in general for helical tubes). Further, as we saw above, the open edge of individual armchair tube shells can be already metastable and frustration free, and in this case lip-lip interactions are simply expected to further favor the growth. The stability of the isolated armchair edge and the efficiency of the lip-lip interaction may explain why recent experiments [4,19] always show, for a given MW BN nanotube, a narrow dispersion of the helicities centered around the armchair or zigzag geometry.

In conclusion, we have shown that very different growth mechanisms can be expected for BN nanotubes with different chiralities. In particular, it appears that SW armchair BN nanotubes can develop an ordered metastable edge, and thus may grow uncatalyzed. SW zigzag BN nanotubes, on the contrary, rapidly evolve into an amorphouslike structure. This difference originates in the ~1.6 eV average frustration energy associated with N-N or B-B bonds as compared to B-N bonds. The role played by frustration effects and that of square rings in determining disordered or ordered tube-edge structures are in agreement with the observed morphology of BN nanotube tips and with the helicity selection evidenced experimentally in the case of BN MW nanotubes.

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*Permanent address: Département de Physique de Matériaux, U.M.R. No. 5586, Université Claude Bernard-Lyon I, 43 bd du 11 novembre 1918, 69622 Villeurbanne, France.

†Permanent address: Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium.

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[17] We do not attempt a discussion of the nucleation step which precedes growth. This is a difficult issue, for which a detailed microscopic understanding is missing even in the simpler case of pure carbon nanotubes [see, e.g., E.G. Gamaly and T.W. Ebbesen, Phys. Rev. B **52**, 2083 (1995)]. More work has been devoted to the study of the nucleation steps in the case of the catalytic growth of carbon nanotubes [see, e.g., A. Maiti, C.J. Brabec, and J. Bernholc, Phys. Rev. B **55**, R6097 (1997), and references therein].

[18] The energy of this BN [4,6,10] configuration at $T = 0$ K is 5.7 eV lower than the energy of the cleaved starting configuration and 2.0 eV lower than the energy of a hypothetical BN(5,5) nanotube capped with a perfect hemi-$C_{60}$ structure [see Fig. 1(c)]. This 2.0 eV energy difference is smaller than what would be given by adding $\sim$1.6 eV per frustrated bond of the structure shown in Fig. 1(c). This seems to indicate that the stress energy associated with the decagon ring is quite large.

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[21] Indeed, the length of the BN bonds shared by the squares and the central large even-member ring will increase with increasing tube radius.

[22] To explore the consequences of the presence of such large rings, we have performed static total-energy calculations which show that Li atoms can diffuse without any barrier through the center of octagons and decagons. This suggests that BN nanotubes are potential candidates for a very pure metallic doping, in contrast with the case of carbon nanotubes for which reopening of the cap by oxidation is necessary.

[23] We note that in principle defects in the BN SW nanotubes could also be induced by electron beam damage during scanning tunneling microscopy observations. However, we think that this would not explain why bilayers BN nanotubes (e.g.), which have a comparable size, exhibit a high degree of crystallinity (see Ref. [4]).