

## Mechanically induced defects and strength of BN nanotubes

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We identify, by dislocation theory and molecular dynamics simulations, possible dislocation dipoles (5|7|7|5 and 4|8|8|4) as defect nuclei under tension in boron nitride nanotubes. The formation energies of the dipoles are then evaluated by *ab initio* gradient-corrected density functional theory. The 5|7|7|5 dipole appears to be more favorable in spite of its homoelemental B-B and N-N bonds. Compared to carbon nanotubes, the formation energy of the primary defect is higher and remains positive at larger strain in boron nitride nanotubes, thus suggesting greater yield resistance.

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The quest for mechanically strong and failure-resistant materials is driven by various engineering needs and fundamental interest in the physics underlying structural relaxation.<sup>1</sup> This has created a long history of experimental and, more recently, theoretical and computational investigations. The newly discovered nanometer thin filaments of carbon nanotubes (CNTs) appear to be promising units for materials and structures.<sup>2</sup> The mechanical strength of the CNTs is well established,<sup>2,3</sup> and so is its ability to reversibly accommodate extreme deformations without fracturing.<sup>3,4</sup> The mechanisms for mechanical failure were studied comprehensively and are well understood today.<sup>5-7</sup> The nanotubes exceptional resistance to failure is ultimately due to the inherent strength of the constituent chemical bonds and their nearly perfect organization over the microns of length of the rolled graphite sheet. The similarly rolled sheet of “white graphite” gives rise to band-gap insulating boron nitride nanotubes (BNNTs).<sup>8,9</sup> BNNTs are possibly the stiffest insulating nanofibers<sup>10</sup> since their Young’s modulus according to both experiment ( $Y = 1.1-1.3$  TPa) (Ref. 11) and theory<sup>12</sup> is approaching that of CNTs ( $Y = 1.3-1.8$  TPa),<sup>13</sup> while their resistance to failure can possibly surpass that of CNTs, as this report suggests.

Below we first identify, from the viewpoint of yield nucleation, the simplest defect structures as dislocation dipoles that can emerge in response to great tension. We distinguish and then compare two possible dislocation types: one with the smaller Burgers vector and lower lattice strain, but disrupting the alternating atomic order preferred in the binary BN lattice, and another one that preserves the BN alternation but corresponds to greater Burgers vector and therefore requires more lattice distortion. Such choice is corroborated by high temperature molecular-dynamics (MD) simulation, which indeed yields, under tension, one of these dislocation dipoles prior to any other atomic rearrangements. For a more accurate evaluation, we then perform *ab initio* quantum mechanical computations (for both plane and tubular cluster geometries) to assess the energies of these defects as the failure nuclei. We further analyze the dependence of these energies on the external mechanical load and draw conclusions on the relative strength of BNNTs by comparing with results for the analogous pure CNTs.

The *ab initio* computations reported here were performed with a development version of the Gaussian program.<sup>14</sup> Geometries of stationary points on the potential energy surfaces (PES) were optimized using *ab initio* Kohn-Sham density-functional theory with the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) (Ref. 15) and the STO-3G and 3-21G basis sets.<sup>16</sup> We studied hydrogen terminated armchair (5,5) and zigzag (10,0) BNNTs ( $B_{90}N_{90}H_{20}$  and  $B_{80}N_{80}H_{20}$ ) as well as planar BN sheets where the dislocation dipole is surrounded by a closed array of six-membered rings ( $B_{21}N_{21}H_{16}$  for 5|7|7|5 and  $B_{26}N_{26}H_{18}$  for 4|8|8|4). In finite temperature MD simulations we utilized the tight-binding (TB) approximation following Hernandez and co-workers<sup>12,17</sup> with the parameters for BN derived by Widany *et al.*<sup>18</sup>

As BNNTs and CNTs are isoelectronic, a similar failure mechanism in response to a large tension might be expected. The resemblance of the hexagonal lattices of graphite and  $\alpha$ -BN allows one to follow similar logic in determining the approximate structure (topology) of primary defects. Yield to great tensile strain must generate a dislocation dipole of a certain type, while the simplest individual dislocation can formally be constructed by removing a (or adding an extra) half crystal plane [Fig. 1(a), top]. Such a dislocation has a Burgers vector  $\mathbf{b} = \pm(0,1)$ ,  $|\mathbf{b}| = 0.25$  nm, and its core corresponds to an adjacent pentagon and heptagon. Therefore, the dipole made of two cores will be a 5|7|7|5, which can be formed by a Stone-Wales 90° rotation of a bond in the hexagonal lattice of C or BN. Such a dislocation dipole was established to be responsible for primary yield in CNTs under large tension.<sup>5,6</sup> However, the important difference in the BN case is the incurred formation of the two less favorable homoelemental B-B and N-N bonds.

It was speculated that it is not possible to generate defects with odd membered rings in BNNTs due to the inevitable formation of the homoelemental bonds.<sup>10</sup> Indeed, very recent experimental evidence indicates that odd membered rings are avoided in BN systems.<sup>9</sup> The caps of BNNTs are known from high resolution tunneling electron microscopy and transmission electron microscopy experiments to differ from those of CNTs: the flat caps of BNNTs indicate the incorporation of four-membered rings,<sup>9,19</sup> whereas the curved CNT’s

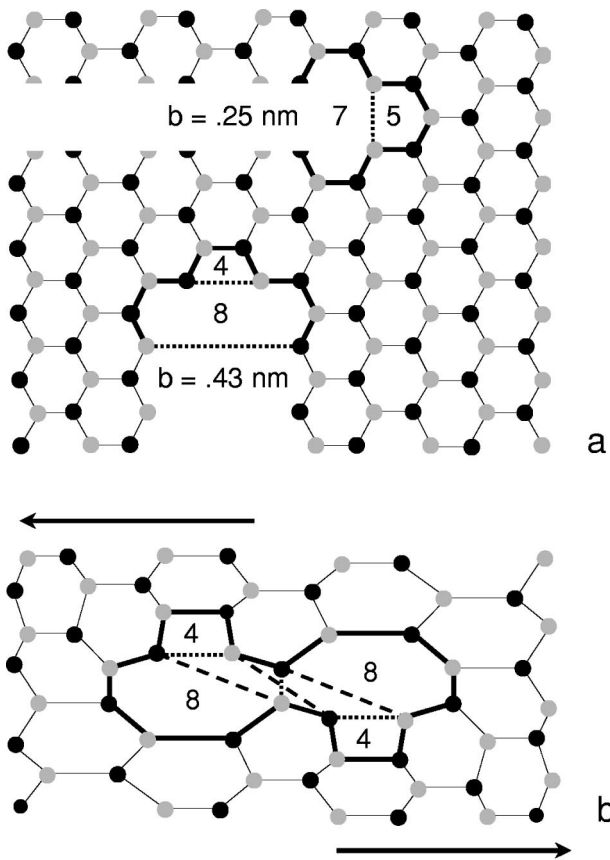


FIG. 1. (a) The construction of a  $5|7$  dislocation (top) by removing or adding an extra half crystal plane of the hexagonal BN lattice, and of a  $4|8$  dislocation (bottom) by removing or adding a perpendicular half crystal plane, and (b) schematic representation of the generation of the  $4|8|8|4$  dislocation dipole and the corresponding change of lattice topology. Dotted lines identify newly formed bonds, while the dashed lines indicate broken bonds in hexagonal lattice.

caps involve pentagons. Note that Fowler *et al.*<sup>20</sup> suggested recently that three isolated pentagon pairs could also explain the flat BNNT's caps (although a slight nitrogen excess is necessary,  $B_xN_{x+4}$ ,  $n \gg 1$ ), and that Saito and Maida discovered BNNTs with “triangular flag” like caps possibly due to odd membered rings.<sup>21</sup>

Therefore, an important alternative of a somewhat larger dislocation [Fig. 1(a), bottom] must be considered, for which the lattice rearrangement does not create homoelemental bonds. Its Burgers vector  $\mathbf{b} = \pm(1,1)$ ,  $|\mathbf{b}| = 0.43$  nm, and the core contains a tetragon-octagon configuration. The corresponding dislocation dipole  $4|8|8|4$  can be formed in a perfect lattice as a result of the transformation depicted in Fig. 1(b). Formation of this dislocation dipole does not necessarily occur in a concerted manner, but Fig. 1(b) simply indicates the correspondence between initial and final lattice topology.

To support the dislocation theory analysis, we proceed to rule out the possibility of “unexpected” relaxation defects. Finite temperature MD is an established tool to search for such atomic rearrangements. As classical potentials are not available for B and N and as first-principles MD remains

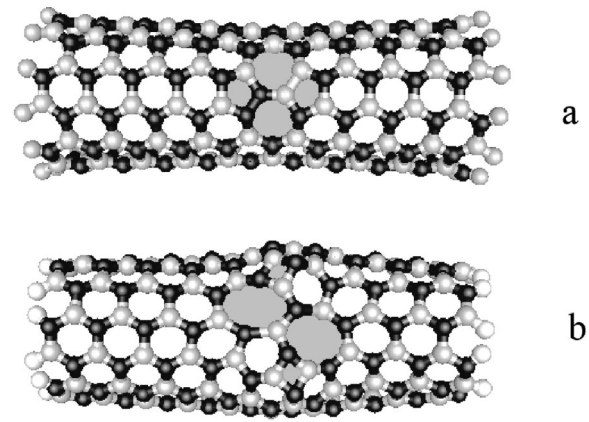


FIG. 2. The geometries of (5,5) BN nanotubes with (a)  $5|7|7|5$  defect emerging spontaneously at high temperature and tension, and (b)  $4|8|8|4$  dislocation dipole. The structures displayed were completely optimized at the PBE/3-21G level of theory.

beyond current computational possibilities, a density-functional based TB MD approach is the alternative method feasible for our problem. Utilizing a nonorthogonal TB scheme, we performed simulated annealing computations for a strained (5,5) BNNT supercell. The temperature was carefully increased by 20 K each 4 ps, while the system was evolved in conjunction with a Nose-Hoover thermostat.<sup>22</sup> At 0.09 tensile strain and  $T = 2750$  K, a  $5|7|7|5$  structure emerged via spontaneous B-N bond rotation as the primary relaxation defect [Fig. 2(a)]. However, the absence of  $4|8|8|4$  defect generation in TB MD test cannot be entirely conclusive due to limited quantitative accuracy of TB for the highly distorted nonequilibrium configurations. A quantitative comparison of the formation energies for these defect types, as well as comparison with CNTs, can be better achieved with *ab initio* methods as presented below.

In order to separate the contribution of local chemical and extended elastic lattice distortions, we first compute the energies for a very small cluster “free” from the surrounding lattice, then for a larger plane lattice sheet, and finally for a nanotube with cylindrical curvature. We find that the “free”  $5|7|7|5$  structure is more favorable, in spite of its weaker B-B and N-N bond pair, than the free  $4|8|8|4$  defect by 0.9 eV. Both structures are local minima on their respective PES. Note that the “free”  $5|7|7|5$  structure is planar, whereas the “free”  $4|8|8|4$  is strongly twisted. The energy difference increases significantly for an extended BN sheet which can accommodate the  $5|7|7|5$  defect (formation energy 5.5 eV) much more easily than the  $4|8|8|4$  dislocation dipole (11.0 eV), as the former is associated with less geometrical strain (Table I). It is instructive to compare the range of computed values with the elastic strain energy of a dislocation in a BN lattice  $E_{elast} \approx Cb^2/[8\pi(1-\nu^2)] \approx 5$  eV ( $\nu = 0.23$  Poisson ratio, in-plane stiffness  $C = 280$  J/m<sup>2</sup>,<sup>12</sup>  $b = 0.25$  nm).

The curvature of the (5,5) or (10,0) BNNT hardly affects the energies of the dislocation dipoles (Table I and Fig. 2). The formation of a  $5|7|7|5$  defect in a (5,5) BNNT is endothermic by 5.6 eV, whereas the formation of the  $4|8|8|4$  dislocation dipole is endothermic by 10.6 eV. Clearly the formation of a B-B and N-N bond pair involving odd membered

TABLE I. Formation energies (eV) of the 5|7|7|5 and 4|8|8|4 dislocation dipoles in planar and tubular BN and carbon systems at various levels of theory.

System	TB	5 7 7 5			4 8 8 4
		PBE/3-21G	PBE/6-31G* <sup>a</sup>	MP2/6-31G* <sup>a</sup>	PBE/3-21G
“free” defects <sup>b</sup>	1.8	4.3	4.4	4.7	5.2
sheets <sup>c</sup>	2.9	5.5	5.6	5.9	11.0
(10,0)-BNNT <sup>d</sup>	2.8	5.3	-	-	-
(5,5)-BNNT <sup>e</sup>	2.6	5.6	-	-	10.6
(5,5)-CNT <sup>e</sup>	-	2.9	-	-	-

<sup>a</sup>Using the PBE/3-21G geometries.

<sup>b</sup>The “free” defects are compared to the  $B_8N_8H_{10}$  and  $B_9N_9H_{12}$  tetracyclic systems for 5|7|7|5 and 4|8|8|4 dislocation dipoles, respectively.

<sup>c</sup> $B_{21}N_{21}H_{16}$  for 5|7|7|5 and  $B_{26}N_{26}H_{18}$  for 4|8|8|4.

<sup>d</sup> $B_{80}N_{80}H_{20}$ .

<sup>e</sup> $B_{90}N_{90}H_{20}$  and  $C_{180}H_{20}$ .

rings is energetically much more favorable than that of a dislocation dipole with only even membered rings. Therefore, we focus on the 5|7|7|5 dislocation dipole in comparing its formation energy and strain resistance in BNNTs and CNTs at a uniform level of theory. (Note that the observed preference, e.g., the very recent study by Bengu and Marks,<sup>9</sup> for even membered rings in BNNT’s endcaps, kinks, and bends does not contradict the present computational results, as in those experimental structures the four- and eight-membered rings are not confined to close proximity.)

We find that the Stone-Wales transformation in a (5,5) CNT is endothermic by 2.9 eV at PBE/3-21G, in agreement with the *ab initio* data of Nardelli et al.<sup>6</sup> Thus, the formation of a strain releasing dislocation dipole is thermodynamically more favorable in the (5,5) CNT than in the corresponding BN analogue (5.6 eV). We simulate axial strains  $\epsilon$  of 0.03, 0.06, and 0.12 in order to evaluate the energies of the 5|7|7|5 dislocation dipoles under external mechanical load. The geometries of the nanotubes are optimized (PBE/STO-3G) under the constraint of fixed distances between pairs of atoms located at opposite ends of our nanotube models. In agreement with earlier investigation of CNTs by Nardelli et al.,<sup>6</sup> our computations for CNTs indicate that the defect energy decreases linearly with strain, as  $E = 3.0 - 45\epsilon$  (all in eV), and at  $\epsilon = 0.07$  the formation of a 5|7|7|5 defect becomes thermodynamically favorable. For the (5,5) BNNT we find  $E = 5.8 - 49\epsilon$  and a critical strain about  $\epsilon = 0.12$  (Table II and Fig. 3). The (10,0) BNNT appears to be even more stable, with  $E = 5.6 - 36\epsilon$ . This agrees with predicted

TABLE II. Formation energies (eV) of 5|7|7|5 dislocation dipole under uniaxial strain ( $\epsilon$ ) for (10,0) and (5,5) BNNTs, and (5,5) CNT as obtained at the PBE/STO-3G level of theory.

$\epsilon$	(10,0)-BNNT	(5,5)-BNNT	(5,5)-CNT
0	5.4	5.6	3.3
3	4.7	4.6	2.1
6	3.6	2.9	0.3
12	1.2	-0.1	-

chirality-dependent yield strength, which is greatest in tension for zigzag and lowest for armchair tubes.<sup>5,7</sup> Much larger tensile strain is thus necessary in BNNT to yield a defect in the hexagonal BN network, and the onset of failure according to our density-functional theory (DFT) computations is expected to occur at significantly larger mechanical load than for CNT.<sup>23</sup> In a complementary constant stress approach, the critical yield tension<sup>24</sup>  $F \sim E/l$  can be estimated. Defect energy  $E/eV$  values are 5.5 and 3.2 and the elongations  $l/\text{\AA}$  are 0.66 (0.36) and 0.64 (0.28) for armchair (zigzag) orientations of free 58-atom cluster-sheets, for BN and C respectively. The obtained critical force is higher for BN.

Note that the TB approximation consistently gives formation energies of the 5|7|7|5 defect in BN systems which are roughly 3 eV too low compared with DFT and wavefunction-based *ab initio* methods (Table I). Despite their iso-electronic nature, the electronic structures of graphite and BN differ qualitatively. The difference in electronegativity between nitrogen and boron ( $\Delta\chi = 1.0$  according to Pauling<sup>25</sup>) causes a band-gap insulating and partially ionic electronic structure. TB potentials, especially if they are fitted to local density-functional theory,<sup>18</sup> have proven to be extremely valuable for the investigation of C systems, and

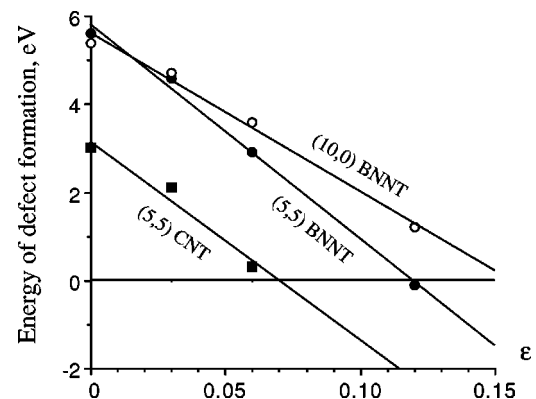


FIG. 3. Dependence of the formation energies of the 5|7|7|5 dislocation dipole in (5,5) CNT, (5,5) BNNT, and (10,0) BNNT. The data were obtained at PBE/STO-3G.

BN structures near equilibrium,<sup>12</sup> but can be expected to be less reliable for the partially ionic situation in the latter, and in distorted configurations where homopolar bonds are formed. As we see above, TB still reproduces satisfactory structure of the defects but apparently fails in quantitative energy evaluation. For example, we found that the energy difference between borazine,  $B_3N_3H_6$ , and its constitutional isomer of  $C_{2v}$  symmetry with one pair of B and N atoms switched (to give one B-B and one N-N bond) is only 0.3 eV using TB. In contrast, correlated *ab initio* methods and gradient corrected DFT give an energy difference of 4 eV for these isomers.<sup>26</sup> This clearly demonstrates that the TB approximation does not properly describe the unfavorable electrostatic interactions arising from the homoelemental B-B and N-N bonds that confine atoms of like charge next to each other. Consequently, the very recent TB study of mechanical properties of BNNTs by Zhang and Crespi has led to the qualitatively opposite conclusion that BNNTs are weaker than the corresponding CNTs.<sup>24</sup>

In summary, we presented the topology and energetics of mechanically significant defects in BNNTs. Besides the 5|7|7|5 defect [Burgers vector  $\mathbf{b} = \pm(0,1)$ ] arising from a Stone-Wales type transformation, we proposed and quantitatively characterized a dislocation dipole comprised from two eight- and two four-membered rings [4|8|8|4 defect, Burgers vector  $\mathbf{b} = \pm(1,1)$ ]. Despite the generation of B-B and N-N homoelemental bonds, the formation of the 5|7|7|5 defect is much more favorable than that of the 4|8|8|4 dipole. Comparing 5|7|7|5 dislocation dipoles in BNNTs and CNTs, we showed here that the primary defect in BNNTs is thermodynamically less favorable than in CNTs, and its formation energy remains positive up to the greater strain. BNNTs might therefore be more resistant towards nucleation of failure and appear to sustain even higher axial strain than CNTs.

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<sup>23</sup>In order to assess the effect of the finite size of our nanotube models, we also studied the formation of two defects lying opposite to each other in the BNNT under periodic boundary conditions at the PBE/3-21G level of theory. We obtain formation energies of 5.6 eV and 5.8 eV per defect in (10,0) and (5,5) BNNT, respectively, in very good agreement with the results for finite hydrogen terminated clusters.

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<sup>26</sup>Second order Möller-Plesset perturbation theory (MP2) and the PBE functional (see Ref. 12) using the 6-311+G(d,p) and 3-21G basis sets give energy differences of 4.1 and 3.9 eV, respectively.