

## Anisotropic nanomechanics of boron nitride nanotubes: Nanostructured “skin” effect

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The stiffness and plasticity of boron nitride nanotubes are investigated using generalized tight-binding molecular dynamics and *ab initio* total energy methods. Due to boron nitride (BN) bond rotation effect, compressed zigzag BN nanotubes are found to undergo anisotropic strain release followed by anisotropic plastic buckling. The strain is preferentially released toward N atoms in the rotated BN bonds. The tubes buckle anisotropically toward only one end when uniaxially compressed from both. A “skin-effect” model of smart nanocomposite materials is proposed, which localizes the structural damage toward the skin or surface side of the material.

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The discovery of carbon (C) nanotubes by Iijima,<sup>1</sup> has set off an explosion of general interest in these quasi-one-dimensional structures. The single-wall nanotubes consist of rolled-up graphene sheets of different diameters and chiralities. Depending on the chiralities, the nanotubes can be either metallic or semiconducting.<sup>2–6</sup> Various applications as components in molecular electronics or nanostructured quantum wire have been proposed. Investigations of mechanical and material properties reveal these materials to be of the highest stiffness and strength characteristics. The possibility of the existence of nanotubes made of noncarbon elements such as BN has also received significant attention.<sup>7–16</sup> Successful synthesis of pure boron nitride nanotubes by the arc discharge method was reported initially.<sup>11</sup> Alternative methods yield large quantities and a reduced number of layers.<sup>12</sup> Recently, bundles of single-wall C nanotubes have been converted to BN nanotubes via substitutional reactions.<sup>13</sup>

Theoretical investigations of BN nanotubes have been restricted mainly to comparing and contrasting the behavior of BN nanotubes with that of similar C nanotubes. The initial studies were primarily focused on the electronic behavior.<sup>7,8</sup> Recent studies using both *ab initio* density functional<sup>14</sup> and static<sup>15</sup> and dynamic<sup>16</sup> nonorthogonal tight-binding methods have addressed the structural and nanomechanics issues as well.<sup>14–16</sup> Two prominent structural features have been noted in all three studies. (i) *Bond frustration effect*: The presence of B-B and N-N bonds in nanotubes makes them structurally unstable.<sup>17</sup> (ii) *Bond rotation effect*: Structural relaxation causes each BN bond to be slightly rotated so that each N is rotated out and B is rotated into the surface of a BN nanotube.<sup>16</sup> An important consequence of the bond frustration effect is that the odd numbered topological ring defects such as pentagons and heptagons are structurally unstable.<sup>14,16</sup> This has led to predictions that the zigzag BN nanotubes are more stable and easily made in experiments.<sup>16</sup> Recent experiments have indeed confirmed our prediction that, regardless of the growing methods used, zigzag arrangement dominates BN nanotubes,<sup>18</sup> and this indicates that there are significant structural and nanomechanics differences between C and BN nanotubes.<sup>19</sup> The *ab initio* molecular dy-

namics methods, on the other hand predicted the armchair BN nanotubes to be most stable.<sup>14</sup>

In this paper, we investigate the implications of the BN bond rotation, and the serrated nature of the BN nanotube surface, on the nanomechanics of the nanotubes. The rotated BN bonds are aligned parallel to the tube axis in zigzag nanotubes and perpendicular to the tube axis for armchair nanotubes. Consequently, the strained BN bond is expected to affect the compression and tension behavior in zigzag nanotubes and the bending and torsion behavior in armchair nanotubes. In isotropically compressed zigzag BN nanotubes, our quantum molecular dynamics simulations reveal anisotropic strain release and plastic buckling, which are attributed directly to the BN bond rotation. This leads us to propose the concept of a nanostructured “skin effect” in axially aligned zigzag BN nanotube reinforced composites that will tend to transfer the axial strain induced damage toward the outer (skin) side of the material, while keeping the inner core side of the material intact.

The theoretical methods used in the present work are the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy,<sup>6</sup> which allows for dynamic relaxation of the system with no symmetry constraints, and *ab initio* density functional theory using the pseudopotential method<sup>20,21</sup> for energetics comparisons. Successful applications of the GTBMD method to C,<sup>6</sup> Si,<sup>22</sup> and BN systems<sup>16,23</sup> have been reported elsewhere. In the present work we use the GTBMD method to obtain a structural and nanomechanics characterization of BN nanotubes.

In our study of the effects of BN bond rotation, we consider the axial compression of a relaxed (8,0) BN nanotube. The axial compression is achieved by keeping the edge atoms transparent to the forces generated in the GTBMD method. The positions of the edge atoms are moved axially inward at a fixed rate to compress the nanotube. Each 1% compression in the linear response regime, and 0.25% compression near the elastic limit, are accompanied by a GTBMD relaxation of 900 steps. Corrections for edge atom relaxation are similar to that described recently for compression of a C nanotube,<sup>24</sup> and are incorporated in the stress

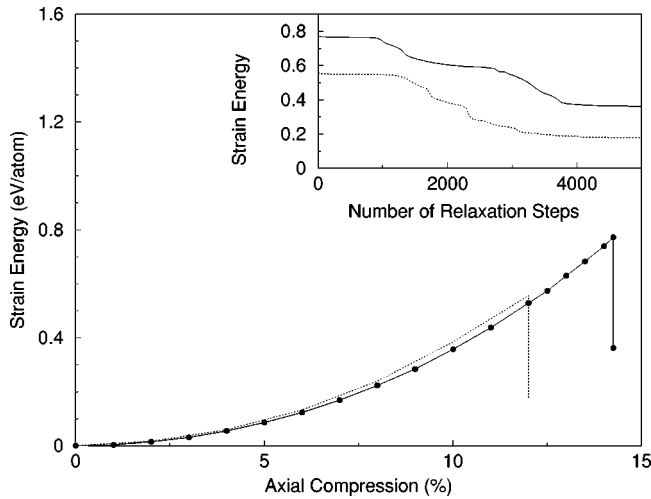


FIG. 1. Strain energy as a function of axial compression in (8,0) BN (solid) and C (dotted) nanotubes. Both the curves are computed with the quantum GTBMD method. Inset shows the strain energy minimization for BN (solid) and C (dotted) nanotubes at 14.25% and 12% strain, respectively.

energy versus strain plot shown in Fig. 1. At the elastic limit [14.25% compression of the (8,0) BN nanotube], the compressed tube was allowed to equilibrate for 5000 GTBMD steps, during which a spontaneous “anisotropic” strain release and resulting local plastic deformation were observed. In the following we discuss the Young’s modulus and the anisotropic plastic deformation of zigzag BN nanotubes.<sup>25</sup>

The starting configurations of the BN nanotubes had the “perfect” smooth geometry that is typical of carbon nanotubes. The symmetry unconstrained relaxation results in a sawtooth or “rippled” surface in which the B atoms rotate inward to an approximately planar configuration, whereas the N atoms move outward into a corresponding pyramidal configuration.<sup>16</sup> A quantitative description of the BN bond rotation is discussed later. The accumulation of strain energy as the tube is compressed at both ends as a function of percentage strain is shown in Fig. 1. For comparison we also show the recently reported results, using the same method,<sup>24</sup> for a zigzag (8,0) C nanotube in the same figure. For low applied strain (1–5%), the Young’s modulus in the two cases was computed and compared by both GTBMD and *ab initio* methods. The computed Young’s modulus of 1.2 TPa for an (8,0) BN nanotube by the GTBMD method is about 92% of that for a similar C nanotube (1.3 TPa) using the same method. The Young’s modulus as computed by the *ab initio* method is found to be 1.3 TPa, which is about 93% of the value reported<sup>24</sup> for a similar C nanotube (1.4 TPa) using the same *ab initio* method.<sup>20,21</sup> This is also in agreement with static nonorthogonal tight-binding results of Hernandez *et al.*,<sup>15</sup> where it was noted that the Young’s moduli of a wide variety of BN nanotubes are within 80–90% of those of similar C nanotubes. The elastic limit of an (8,0) BN nanotube, however, is larger than that of an (8,0) C nanotube. This might be expected, since for a similar structure the lower value of Young’s modulus in a BN nanotube is compensated by a higher value of the strain to generate forces of

similar strength at the elastic limit in the two cases.<sup>26</sup> Additionally, the increase in the elastic limit can also be attributed to the rotated BN bonds as will be explained later.

The microscopic nature of the anisotropic strain release and the resulting plastic deformation are shown in Fig. 2. At the beginning of the GTBMD relaxation at 14.25% strain, as shown in Fig. 2(a), small deviations from the cylindrical cross section appear near the two ends where strain accumulations are maximum. This is similar to what was reported for a similar compression of C nanotube.<sup>24</sup> The structure starts to undergo a plastic deformation in Figs. 2(b)–(e). This plastic deformation toward the right end is driven by the anisotropic release of the accumulated strain energy in the undeformed region of the tube. The strain release occurs preferentially toward N atoms (shown in blue) as the leading side of the rotated BN bonds, where N atoms have rotated outward and B atoms (shown in red) have rotated inward. This process is facilitated by a correlated “sliding” of N atoms further outward and B atoms further inward. Note that the outward sliding of N atoms is energetically favorable as it tends to reduce the strain due to the curvature of the tube. The inward sliding of B atoms, however, is hindered as it tends to increase the curvature induced strains. Furthermore, there is also a chemical repulsion between neighboring B atoms, preventing the formation of energetically unfavorable B-B bonds. An anisotropy is therefore induced in the structure due to the opposing characteristics of the radial displacements of the B and N atoms, the details of which are analyzed next.

The radial position distribution function illustrating the average radial displacements of B and N atoms as a function of tube compression is shown in Fig. 3(a). At 0% compression, due to intrinsic BN bond rotation, two peaks are seen in this function; an inner peak at 3.03 Å for the average B radius and an outer peak at 3.27 Å for the average N radius. At equilibrium, for 0% compression and for the average BN bond length of 1.42 Å, this corresponds to an average BN bond rotation of about 9.7° away from the direction parallel to the tube axis. As the tube is gradually compressed, as shown in Fig. 3(a), both the separated B and N peaks move outward and also further apart from each other, indicating an increase in the BN bond rotation angle from about 9.6° at 0% compression to about 13.2° at 12% compression. As indicated above, this means that a significant fraction of the axial strain is accommodated by the displacements of B and N atoms perpendicular to the tube axis in a correlated manner. The N atoms are pushed further out while the B atoms are forced further into the tube.

The relative radial displacements of B and N atoms, with respect to their initial radial positions in the uncompressed tube, can be quantified by the relative shifts of B and N peaks in Fig. 3(a) and are shown in Fig. 3(b). The relative displacements of both B and N atoms increase as a function of tube compression. However, for all values of compression, the N atoms are radially displaced more than the B atoms. The excess strain as the tube is compressed is accommodated more by the larger outward displacements of N atoms than by the smaller displacements of B atoms. At the elastic limit, tube failure initially occurs at both ends [Fig.

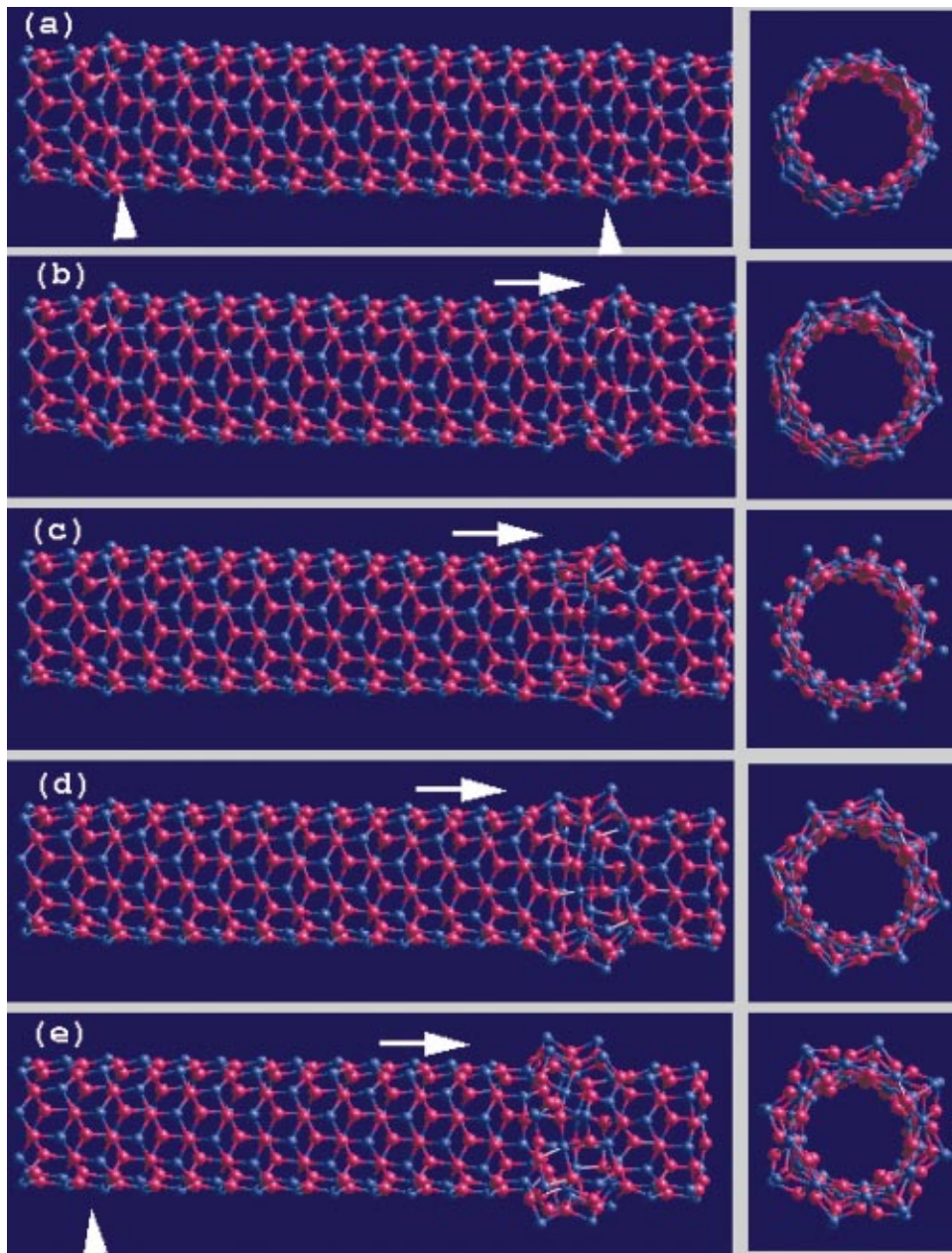


FIG. 2. (Color) Five stages of spontaneous plastic collapse of the 14.25% compressed (8,0) BN nanotube showing (a) nucleation of deformations near the two ends, (b), (c), and (d) anisotropic strain release in the central compressed section and plastic buckling near the right end of the tube, and (e) the final anisotropically buckled structure where all the plastic damage has been transferred toward the right end of the tube; the left end has completely relaxed with no plastic buckling. The cross section of the tube in each of the five cases is also shown.

2(a)]. The resulting strain release in the center region, however, is anisotropically driven toward N atoms because it is still energetically favorable to push or “slide” N atoms further out to accommodate the released strain. The strain release occurs in a concerted outward motion of N atoms, which was observed in the animation of the simulations.

The structure in the buckled region was analyzed by a bond length distribution function analysis which showed peaks corresponding to BN bond lengths of about 1.5 Å in the buckled region. This corresponds to about 5% compressed BN bond lengths in cubic BN (the experimentally observed<sup>27</sup> BN bond length in uncompressed cubic BN is

about 1.57 Å). Similarly to the compression and plastic collapse of a C nanotube reported recently,<sup>24</sup> the plastic deformation in BN is also accommodated by an  $sp^2$  (threefold coordination) to  $sp^3$  (fourfold coordination) type of bonding transition at the location of the buckle. The main difference is that N atoms are driven preferentially outward as compared to B atoms. On removing the compression constraints and letting the system relax by the GTBMD method, the tube was found not to relax back to the initial uncompressed structure. This confirmed the plastic nature of the buckle. The simulations of an armchair nanotube of the same radius did not show any anisotropic strain release mechanism when

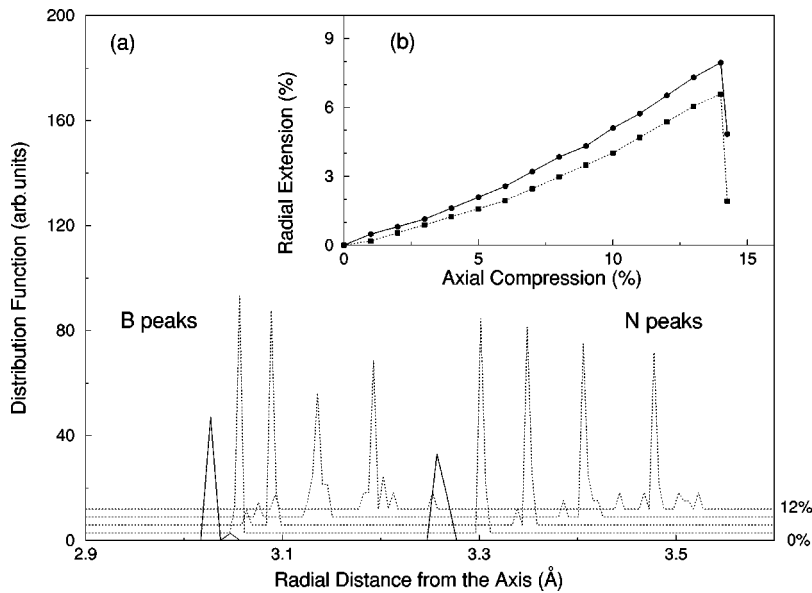


FIG. 3. (a) Radial displacement distribution functions (at different % strain) of B and N atoms as functions of radial distance from the tube axis. (b) Same as (a) except average relative radial displacements (in %) of B and N atoms with respect to their average initial positions at 0% compression.

subjected to similar axial strains. This is because buckled BN bonds in an armchair nanotube are aligned perpendicular to the tube axis and not parallel.

Based on the anisotropic strain release and the resulting plastic deformation mechanism, a hypothetical composite material reinforced by axially aligned zigzag BN nanotubes can be proposed. The proposed material will exhibit a nanostructured skin effect in the sense that the material will have an anisotropic response to external axial strains. When subjected to large external axial strains, the material will react by minimizing the damage to the inner core side, while transferring all the damage to the outer skin or surface side. This skin effect will play an important role under external impulses such as a shock wave, since the composite material will not have enough time to develop a long wavelength geometric instability such as nanotube buckling under uniaxial compression. Such a hypothetical material, if synthesized, will have useful applications in the transportation, aerospace, defense, and armor industries.

In summary, we have investigated the nanomechanics and plastic deformation of axially compressed BN nanotubes. The BN nanotubes are found to be almost as stiff as similar C nanotubes. Furthermore, we have found an anisotropy in the strain release and plastic deformation mechanisms in zigzag BN nanotubes. This phenomenon and the underlying mechanism as explained by the average relative displace-

ments of N and B atoms are general and valid also at smaller values of strain. A hypothetical composite material exhibiting a nanostructured skin effect, or anisotropic shock absorbing properties, is proposed that will have useful applications in a wide variety of industries.

*Note added in proof.* After the submission of our manuscript we became aware of another paper dealing with the plastic deformation of BN nanotubes.<sup>28</sup> This paper also employs tight-binding methods to obtain the nanomechanics results but without the use of molecular dynamics. This work reports that  $(n,0)$  BN nanotubes have a smaller elastic limit than  $(n,0)$  C nanotubes due to plastic deformation upon  $(5,7)$  defects formation, contrary to our findings. Our molecular dynamical simulations show that such defects are unstable in BN systems and, therefore, unlikely to form.

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