Plastic Deformations of Carbon Nanotubes

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Although the elastic properties of a carbon nanotube are nearly independent of wrapping indices, we show that the onset of plastic deformation depends very strongly on the wrapping index. An $(n, 0)$ nanotube has an elastic limit nearly twice that of an (n, n) tube with the same radius. Such great variation has important consequences for structural applications of carbon nanotubes. In addition, the remnant bond rotations remaining after strain release strongly affect the electronic structure of the distorted nanotube. [S0031-9007(98)07887-9]

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Structural applications proposed [1] for carbon nanotubes [2] rely upon the extreme elastic strength of the sp^2 bonding network [3]. However, elastic response alone provides a limited picture of mechanical properties. Beyond a certain stress, the elastic limit, a material deforms plastically via changes in chemical bonding topology. A carbon nanotube is defined by its radius and wrapping angle [see Fig. 1(a)]. Since the high symmetry of a graphite sheet implies isotropic elastic properties, the nanotube's radius dominates its elastic response. In contrast, we show that symmetry-breaking plastic distortions are very sensitive to wrapping indices.

A $\pi/2$ bond rotation in a graphitic network transforms four hexagons into two pentagons and two heptagons. The structure elongates along the axis connecting the pentagons and shrinks along the perpendicular direction. Thus, in a nanotube, rotation of a bond from a predominately circumferential to a predominately axial orientation lengthens the tube, as shown in Fig. 1(b). If the tube is under tension, such defects relieve strain and constitute a fundamental mode of plastic deformation. The efficiency of this strain release depends sensitively on the alignment between the defect and the tube axis. For example, essentially no strain is relieved by rotation of a bond initially oriented $\pi/4$ from the circumference. One-third of the bonds in an (n, n) tube are aligned precisely with the circumference, the optimal orientation from which to rotate for the release of strain. In contrast, the most favorable bonds in an $(n, 0)$ nanotube are misaligned by $\pi/6$ from the circumference.

We use tight binding molecular dynamics [4] calculations to investigate the plastic deformation of carbon nanotubes under strain. This technique accounts for quantum effects while allowing efficient simulation of large systems. To separate the effects of tube radius from those of wrapping indices, we study two families of tubes, a series of $(n, 0)$ tubes of different radius and a series of (n, m) tubes of nearly equal radius. We first consider transitions at constant tension, later addressing the transitions at constant length.

Figure 2 shows the energy versus length for the pristine and plastically deformed $(8, 0)$ tube. Since a single defect would produce an inconvenient kinked unit cell, the deformed tubes contain a pair of well-separated rotated bonds on opposite sides (with all quoted results normalized to a single defect). The common tangent of the energy-versus-length curves gives the critical force (F_c) at which the Gibbs free energies $G = E - FL$ of the two configurations are equal; $F_c = \delta E/\delta L$, where δE and δL are the energy difference and elongation across the transition [5]. This structural phase transition to a defective phase is eventually arrested

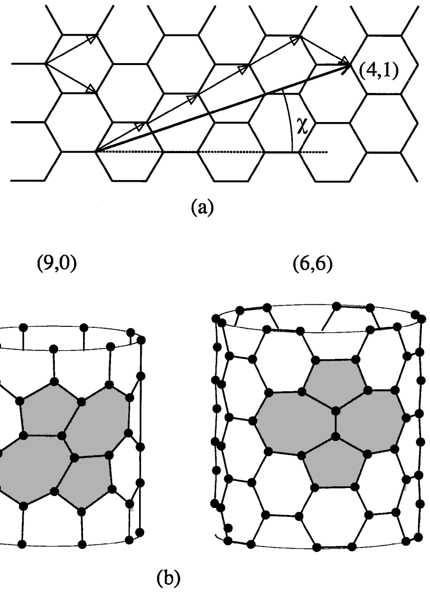

FIG. 1. (a) Wrapping index and wrapping angle notation. A tube is specified by a vector in the plane which maps the graphite sheet into itself and thereby defines the tube circumference. We describe this vector (and the resulting nanotube) by its graphitic lattice components, e.g., the $(4, 1)$ nanotube. χ is the angle between the circumference vector and the $(1, 1)$ direction, within the range $0 \leq \chi \leq \pi/6$. (b) Bond rotation defects oriented as shown can lengthen a nanotube, with the greatest lengthening for the (n, n) tube (on the right).

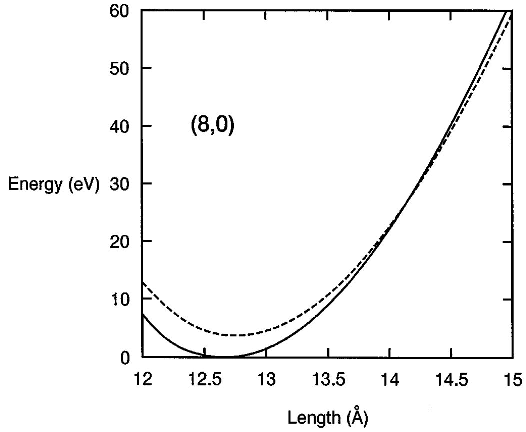

FIG. 2. Energy versus length for pure (solid line) and defective (dashed line) (8, 0) nanotubes. The cell contains 96 atoms per bond rotation defect with $E = 0$ for the pure undistorted tube.

by a repulsive defect-defect interaction at high defect density. In our study the defect density is low enough that this interaction does not significantly disturb the onset of plastic deformation (doubling the defect separation changes the transition tension by less than 1%). Since one expects F_c to be roughly proportional to the radius R of a tube, we define the *reduced* transition tension $f_c \equiv F_c/R$ which should vary weakly among nanotubes of an identical wrapping angle.

The wrapping angle χ, illustrated in Fig. 1(a), gives the angle between the circumference and the best bonds to rotate. χ ranges from zero for an (n,n) tube to $\pi/6$ for an $(n,0)$ tube. The C_{2v} symmetry of a bond rotation defect implies that physical quantities are even functions of χ with period π. Hence, to lowest order in angular dependence, they are well approximated by $a(R) + b(R)\cos 2\chi$, with radius-dependent coefficients $a(R)$ and $b(R)$. Figure 3 reveals a nearly linear dependence of transition tension on $\cos 2\chi$ for the family of nearly equal-radius tubes $\{(12,0),\ (10,2),\ (9,3),\ (8,4),\ (6,6)\}$. The plastic limit varies from about 100 nN/nm for the (6, 6) tube to about 180 nN/nm for the (12, 0) nanotube. The radial dependence of the reduced transition tension is significant only for the smallest tubes.

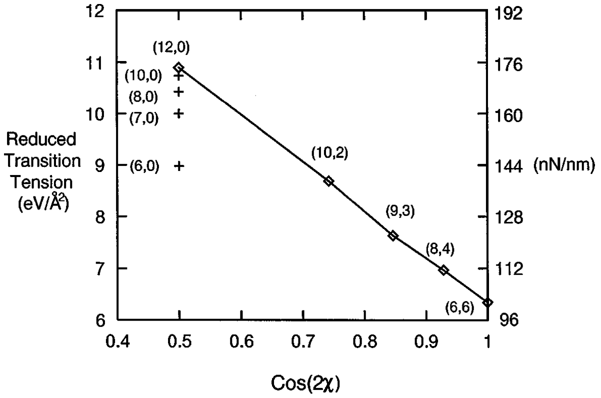

FIG. 3. Transition tensions (divided by tube radius) for the onset of plastic deformation in families of $(n,0)$ and nearly equal-radius (n,m) tubes. The radial dependence is quite weak except for the smallest tubes, whereas the wrapping angle dependence is very strong.

The radial and angular dependences of the critical tension can be understood by treating the defect as an extended strain in an elastic continuum with parameters extracted from the atomistic calculations. For the tension F_c at the edge of the transition the defect density is vanishingly small, and the energy (δE) and length (δL) changes upon introduction of one defect are close to their values at zero tension. Therefore the reduced transition tension is well approximated by

$$\frac{F_c}{R} = \frac{1}{R}\,\frac{\delta E}{\delta L}\bigg|_{F=0}. \tag{1}$$

Since the length change δL depends only upon R and the integrated strain of the defect (with units of length squared), δL scales as R^{-1} with angular dependence in the form $a + b\cos 2\chi$. Fitting to the atomistic data gives

$$\delta L \approx \frac{3.4\ \text{Å}^2}{2\pi R}\,(0.05 + \cos 2\chi), \tag{2}$$

which differs by only 15% from a very simple geometrical analysis assuming regular polygons. The $1/R$ dependence of the elongation cancels the normalization prefactor of Eq. (1) and therefore implies that the radial dependence of the critical tension f_c arises through only the defect energy δE. The nanotube at zero tension can freely relax the defect strain both axially and circumferentially, so this defect energy in tubes of moderate radius is a weak function of the wrapping angle [4.0 ± 0.1 eV for the family $\{(12,0),\ (10,2),\ (9,3),\ (8,4),\ (6,6)\}$]. Therefore the angular dependence of the plastic limit arises mainly from the angular dependence of the defect-induced elongation, and the radial dependence of the plastic limit arises mainly from the radial dependence of the defect energy.

The detailed radial dependence of the defect energy is a complex combination of bare defect energy, the elastic energy induced in the surrounding medium, and the curvature-induced rehybridization of the defect. The bare energy is of the order of 5 eV. The elastic term is small, of the order of $\mu(2\pi R)^{-2}(\int \epsilon\, d^2x) \approx 0.03\ \text{eV}\,\text{nm}^2/R^2$, where $\mu \approx 0.08\ \text{eV/nm}^2$ is an elastic modulus, and ϵ is the strain. The rehybridization energy dominates the radial dependence; narrower nanotubes of the same χ typically have lower defect formation energies since (i) the additional distortions due to bond rotation are more easily accommodated into the curved surface of a narrower tube, and (ii) the defective region has a slightly lower mean curvature modulus than a corresponding pristine region. This reduction in defect formation energy with decreasing radius explains the lower plastic threshold in the smallest

$(n, 0)$ tubes. Note that the radial dependence of the plastic threshold asymptotes at a relatively small radius, whereas the pronounced χ dependence remains at all sizes.

Beyond the threshold for plastic deformation, the defect density is more easily controlled by fixing the length rather than the tension. At a constant length, the linear defect density ℓ is proportional to the fractional extension beyond the critical length: $\ell = (L - L_c)/L\delta L \approx (\epsilon - \epsilon_c)/(1 + \epsilon_c)\delta L$, where $\epsilon = (L - L_0)/L_0$ is the axial strain with ϵ_c its critical value. Just as the critical force is very sensitive to the wrapping angle, so the critical strain varies from about 6% extension for a $(6, 6)$ tube to 12% extension for a $(12, 0)$ tube [6]. Above this critical extension the defect density increases rapidly with length, varying as $24(\epsilon - 0.06)\ \mathrm{nm}^{-1}$ for the $(6, 6)$ tube and as $43(\epsilon - 0.12)\ \mathrm{nm}^{-1}$ for the $(12, 0)$ tube. The defect concentration increases most rapidly in the $(n, 0)$ tubes since in these tubes each individual defect is least efficient in relieving strain. Since δL varies as $1/R$, larger tubes will contain more defects than smaller tubes of the same wrapping angle at a fixed relative strain, although the *areal* density of defects remains constant (except for the smallest tubes, where the defect formation energy is a strong function of the radius).

Under an external force above the plastic threshold, proliferation of bond rotation defects is eventually halted by a repulsive defect-defect interaction. The elastic interaction of two defects a distance D apart varies roughly as μ/D^2 times the product of their integrated strains. The strength of this interaction is on the order of $0.08\ \mathrm{nm}^2/D^2$ eV. This simple estimate is consistent with tight binding total energy calculations on the $(6, 0)$ tube, which yield a 0.13 eV increase in the repulsive defect-defect interaction for a reduction in D from 7 to 13 Å. A uniform density of defects then has an interaction per defect quadratic in the linear density λ (neglecting alteration of the tube's spring constant by the defects), so that $\lambda \propto \sqrt{(F - F_c)}$ at a constant force.

These defect densities as a function of strain are interesting not only for the mechanical response: The bond rotation defect is also a plausible route towards modulating the electronic properties of carbon nanotubes. An extension of only 1% beyond the critical length induces enough bond rotation defects to significantly alter the electronic structure, increasing or decreasing band gaps and modulating the density of states [7]. The repulsive defect-defect interaction may tend to favor periodic defect arrangements and thereby minimize the random component of the defect-induced potential felt by the electronic states.

The discussion thus far has been in a purely equilibrium context, ignoring the kinetics of defect formation. We have calculated the barrier to defect formation at critical external tension by calculating energy as a function of bond orientation, considering both in-plane and out-of-plane rotations. Of the kinetic pathways examined, the lowest barrier for bond rotation in a $(6, 6)$ tube occurs when the bond is tilted roughly 15° out of plane, which yields an upper bound of approximately 4.0 eV for the barrier at the transition, decreasing with increasing strain. This compares with the 5.4 eV barrier for the related Stone-Wales transformation [8] in C_{60} [9] and the 10.4 eV barrier for bond rotation in flat graphite [10]. External tension lowers the barrier; the same rotational barrier in the nanotube at zero tension is 8.5 eV. The barrier could be further lowered through hyperextension beyond the thermodynamic transition tension or through thermal fluctuations in the local neighborhood (as distinct from thermal excitation of the reaction coordinate itself). The barrier at zero tension for rotation back to the pure hexagonal state is substantial, 5.5 eV, so that the defects should remain metastable at room temperature after the release of the external tension. Bond rotation defects comprise a pair of pentagon-heptagon defects (5-7 and 7-5) which can be separated by means of additional bond rotations. These pairs represent crystal dislocations; the long range strain fields favor the gliding of these pairs in opposite directions under an external stress [11]. However, the local curvature energy of the double pentagon-heptagon structure is minimized when the oppositely directed curvature dipoles are adjacent. In a flat unstrained graphitic sheet, tight binding total energy calculations reveal a strong short range attraction between a 5-7 and 7-5 defect. Separating them by one intervening hexagon costs 4.5 eV, while separation by two hexagons costs an additional 3.5 eV, although in certain situations this barrier may be lower [12]. This tall and wide energetic barrier will help suppress fission of the bond rotation defect.

We propose an experimental geometry in which these defects could be created and measured in a controlled fashion. A nanotube could be securely fixed at each end (e.g., embedded within blobs of solid material) and then pulled taut and pressed transversely in the middle of the free section:

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This geometry would create a very large mechanical advantage of order $\delta H/L$, where L is the suspended length and δH is the transverse deflection. The change in tube length upon bond rotation would yield a similarly amplified transverse deflection. If tube extension decreased the external force, then the defects would appear one at a time, giving a characteristic signature of successive quantized defections of the external probe.

Although the nanotube wrapping angle has strong effects on the electronic properties [13], the nanotube elastic properties are insensitive to these structural details. However, the wrapping angle reasserts its importance under symmetry-breaking *plastic* distortions. This strong sensitivity to the wrapping angle will affect high-load structural applications of carbon nanotubes. In addition, the electronic consequences of these plastic deformations [7] also open a possible new route towards modulating electronic properties of carbon nanotubes.

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Note added in proof.—Recent experiments [14] show embedded multiwalled nanotubes being crushed locally under compressive stresses of approximately 100–150 GPa. Reorienting the bond rotation defects and plausibly assuming similar-magnitude length changes and formation energies under compression as under extension, our results can then be immediately extended to give an estimate for the ideal elastic limit under compressive stress, as long as various forms of buckling are suppressed by the surrounding medium. Our results for elastic limits of 100–170 GPa are very close to the experimental stresses, as would be expected if an initial bond rotation nucleates the crush zone.

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