Atomistic theory of mechanical relaxation in fullerene nanotubes

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Abstract

A discussion of recently developed theoretical basis of the inelastic behavior of fullerene nanotubes is presented. Defect formation by a Stone–Wales bond rotation, its topology, and energy is calculated as a function of nanotube type, and an analytical equation is derived. Inter-defect interaction is analyzed due to its importance in the relaxation process. Strength of the nanotube-bundle is estimated for a broad range of parameters. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Carbon, especially in its sp\textsuperscript{2}-hybridized form, is able to form two-dimensional networks of strongly bonded nodes–atoms. Various geometrical and topological structures of graphite and fullerenes are discussed in the literature, mostly with the emphasis on chemistry and topology. The relation of the curvature with the presence of pentagon- or heptagon-disclinations has been well known in fullerene science [1,2]. More recently, the appreciation of mechanical ‘charge’ associated with these topological entities has led us to the dynamic topology theory [3,4], that allowed in principle to predict with atomic precision the details of mechanical relaxation in fullerenes under external forces. This is especially important in the case of carbon nanotubes due to their potential for strong materials applications. Unlike other fullerene molecules, the elongated carbon nanotubes (CNT) call for study of their mechanical properties, in a way similar to graphite fibers. Their record-high stiffness and expected record-high strength make the understanding of theoretical limits and the mechanisms of failure important.

Below we review briefly the logic of fullerene dynamic topology, which is essentially a dislocation theory applied to a molecular-size structure. We then refer to the computer simulations presenting compelling evidence of the validity of theoretical analysis [5,6]. Then we proceed with an outline of more recent results: we derive equations for a single-defect formation energy, and then analyze the inter-particle correlation effects, critical for the nanotube relaxation mechanisms. The limiting factors of the strength of nanotube bundles are identified and quantitative model estimates are presented.

2. Why the Stone–Wales transformations under strain?

Locally, the wall of a nanotube (or another large fullerene cage) differs little from a single graphite sheet, a two-dimensional crystal of carbon. When a uniaxial tension \( \sigma \) (N/m – for the two-dimensional wall it is convenient to use force per unit length of its circumference) is applied it can be represented as a sum of expansion (locally isotropic within the wall) and a shear of a magnitude \( \sigma/2 \), directed at \( \pm 45^\circ \). Generally, in a macroscopic crystal the shear stress relaxes by a movement of dislocations, the edges of the atomic extra-planes. Burgers vector \( \mathbf{b} \) quantifies the mismatch in the lattice due to a dislocation. Its glide requires only local atomic rearrangements and presents the easiest way for strain release, provided sufficient thermal agitation. In an initially perfect lattice such as the wall of a nanotube, a yield to a great axial tension begins with a homogeneous nucleation of a slip, when a dipole of dislocations (a tiny loop in the three-dimensional case) first has to form. The formation and further glide are driven by
the reduction of the applied-stress energy, as characterized by the elastic force on a dislocation.

The graphene wall of the nanotube is not isotropic. Its hexagonal symmetry governs the three glide ‘planes’ – the lines of closest zigzag atomic packing, oriented at 120° to each other (corresponding to the \{101 1\} set of planes in three-dimensional graphite). At non-zero shear these directions are prone to slip. The corresponding c-axis edge dislocations involved in such a slip are indeed known in graphite [7]. The six possible Burgers vectors \(1/3a(2111)\) have a magnitude \(b = a = 0.246\ \text{nm}\) (lattice constant), and the dislocation core is identified as a 5/7 pentagon–heptagon pair in the honeycomb lattice of hexagons. Therefore, the primary nucleated dipole must have a 5/7/7/5 configuration (a 5/7 attached to an inverted 7/5 core). This configuration is obtained in the perfect lattice (or a nanotube wall) by a 90° rotation of a single C–C bond, well known in fullerene science as a Stone–Wales (SW) diatomic interchange. One is led to conclude that the SW transformation is equivalent to the smallest slip in a hexagonal lattice and must play a key role in the nanotube relaxation under tension. Indeed, detailed computer simulations, either with classical potentials or quantum ab initio, demonstrate exactly this mechanism of initial strain release in CNT [5]. The SW formation energy and the activation barrier are high – several eV – consistent with the sessile type of the 5/7 dislocation core.

3. Energetics of a 5/7 glide, rigorous results

The orientation of the glide and the slip-dipole depends on how the graphene strip is rolled-up into a cylinder. This is usually specified by the vector which becomes the circumference, \(e = c_1a_1 + c_2a_2\) in the basis standard for nanotubes. [The same basis allows one to present the nanotube names, ‘zigzag’ \((\chi = 0^\circ)\) and ‘armchair’ \((\chi = 30^\circ)\) below as a leading term in the Fourier series, describes the essential effect: SW rotation gains more energy in the armchair \((\chi = 30^\circ)\) nanotube, making it the weakest, most inclined to SW nucleation of the dislocations, in contrast to the zigzag \((\chi = 0^\circ)\) where the nucleation is least favorable [3,4,9,10].

\[
E_s = -\left|f_{SD}\right| = -Ca^2/2 \cdot \sin(2\chi + 60^\circ) \cdot \varepsilon \tag{1}
\]

per one displacement, \(a\). Here \(\varepsilon\) is the applied strain, so that \(\sigma = Ce\). The graphite sheet in-plane stiffness \(C = Yc = 342\ \text{N/m}\) [8] is derived from the Young modulus of \(Y = 1020\ \text{GPa}\) and the interlayer spacing \(c = 0.335\ \text{nm}\) in graphite; one then obtains \(C_a^2/2 = 64.5\ \text{eV}\). Eq. (1) allows one to compare different nanotubes (assuming similar amount of pre-existing dislocations): the more energetically favorable is the glide in a tube, the earlier it yields to applied strain.

4. Energetics of a 5/7/7/5 nucleation

In a pristine nanotube-molecule, the 5/7 dislocations have first to emerge as a dipole, by a prime SW transformation. Topologically, the SW defect is equivalent to either one of the two possible dipoles (Fig. 1), each formed by an \(\sim a/2\) slip. Geometrically, its higher \(D_{2h}\) symmetry requires that the best representation of the SW-induced lattice relaxation be a half-sum of that produced by the representing dipoles. Further, a direct comparison of different bonds shows the largest energy release for the SW rotation of \((1,1)\)-directed bond, the closest to the equator, when the two representing slips are at \(60^\circ - \chi\) and \(-\chi\) to the circumference. Applying Eq. (1) to each of the two constituent slips one obtains,

\[
E_{sw} = E_{sw0} - A \cdot \varepsilon - B \cdot \sin(2\chi + 30^\circ) \cdot \varepsilon \tag{2}
\]

The first two terms, the zero-strain formation energy and isotropic dilatation, do not depend on nanotube symmetry. The symmetry-dependent third term, which is re-derived below as a leading term in the Fourier series, describes the essential effect: SW rotation gains more energy in the armchair \((\chi = 30^\circ)\) nanotube, making it the weakest, most inclined to SW nucleation of the dislocations, in contrast to the zigzag \((\chi = 0^\circ)\) where the nucleation is least favorable [3,4,9,10].

![Fig. 1. Stone–Wales defect 5/7/7/5 in a strained carbon nanotube. The arrows indicate two elastic fields that affect the energy of defect formation: \(\varepsilon\) is the external strain applied to the tube, and \(1/d\) marks the internal field due to the wall curvature (\(d\) is nanotube diameter).](image)
5. ‘Single-particle’ theory of defect formation

A result similar to Eq. (2) but more general, can now be derived in a more formal fashion. A SW defect is essentially a dilatation center (symmetry $D_2h$) in the body of the cylindrical nanotube under tension, and it is exposed to the two fields (Fig. 1). One is externally induced by the strain $\varepsilon$ along to the axis. Another one is built-in due to the curvature and is inversely proportional to the diameter, $1/d$. With the SW formation energy in a plane unloaded graphite sheet as a zero-order term, one can write a perturbation series with respect to the two small (and additive, within the linear response theory) fields,

$$E_{\text{SW}} = E_{\text{SW,0}} + \sum_{k,m,n} C_{kmn} (1/d)^n \varepsilon^n \cos[2n(\chi + 60^\circ)],$$

$$k, m, n \geq 0.$$  \hspace{1cm} (3)

To identify the coefficients, and therefore to derive an analytical expression of the defect formation energy in a tube of arbitrary type and as a function of applied stress is important and generally a difficult task [11]. However, since the magnitudes of both fields are small ($\varepsilon \ll 1, a/d \ll 1$), we only need to retain $k, m \leq 1$. Similarly, based on the ‘smoothness’ of these fields, one can neglect the high-order Fourier harmonics, $n \leq 2$. We have performed a massive molecular-mechanics relaxation on approximately a thousand nanotubes of all chiral symmetries, and the diameters ranging from 1 to 2 nm, at the strain levels of $\varepsilon = 0, 0.01$, and 0.06. The Tersoff–Brenner potential was used in these calculations, following the same version as in our earlier work [8,12,13]. The obtained large array of computed formation-energies is sufficient for a reliable fit of the coefficients in Eq. (3). We performed fast Fourier transform with respect to the chiral angle $\chi$ at fixed values of the diameter, and thus obtain the numerical values of the Fourier coefficients. Further, these coefficients are matched to polynomials of $1/d$. As a result we obtain (in the units of eV, nm, and degrees for the corresponding values),

$$E_{\text{SW}} = 2.7 - 0.71/d + 0.1/d \sin(2\chi + 30^\circ) + 0.1/d^2 \sin(4\chi - 30^\circ) - 3.2 \varepsilon \sin(2\chi + 30^\circ) - 4\varepsilon + [1 + 3.1 \sin(2\chi + 30^\circ)]\varepsilon/d + o(\varepsilon, 1/d)$$

$$\hspace{1cm} (4)$$

Since the formation energy controls the nucleation of defects and the yield of material, a measure of material permittivity to external load can be introduced as $|dE_{\text{SW}}/d\varepsilon|$,

$$|dE_{\text{SW}}/d\varepsilon| = 32 \sin(2\chi + 30^\circ) + 4 - [1 + 3.1 \sin(2\chi + 30^\circ)]/d$$

$$\hspace{1cm} (5)$$

Eq. (5) essentially solves the single-particle problem associated with the yield strength. This compact equation reproduces very accurately (1–2%) the result of explicit molecular-dynamics computation of the energies, as Fig. 2 illustrates. While the numerical values can somewhat change if another or more refined interatomic forces are used (other empirical potentials, tight-binding, or ab initio approximations), the general form and the approach remain valid. Generally, the low-order in $(1/d)$ terms, and the lower Fourier harmonics are not sensitive to the short-
range details in the interatomic potential, while the higher term contributions are not too large, as our analysis demonstrates.

6. Correlation effects

Eqs. (4) and (5) answer the question of when the defects begin to emerge and in what quantities, at least thermodynamically. This ideal-gas approximation does not reflect any possible inter-particle (inter-defect) correlation, caused by the attraction or repulsion between them. The next level of the theory must include these effects, since they are of crucial importance for the mechanical relaxation (failure) pattern: the defects either emerge at random spots, or tend to aggregate and pile-up (in case of attraction), or can arrange in a regular fashion (in case of repulsion).

In order to avoid a possibly overwhelming number of configurations (Fig. 3) in all varieties of tubules and magnitudes of applied tension, we assume that the interaction between the defects is additive to the effects of the internal curvature force-field, $\approx 1/d$ and the one due to external applied load, $\approx E$. We therefore consider only a plane graphite sheet of large enough size (approximately a square of two to three thousand atoms), and perform multiple molecular relaxation computations of all the relative positions of two Stone–Wales defects. Remarkably, the results (Fig. 4) show that both attraction and repulsion are possible depending on the angular orientation.

![Fig. 4](image-url) Energy of two defects in carbon nanotube is shown as a function of their positions (slant mutual orientation, first defect in the center while the second is placed around). Lighter gray corresponds to higher energy (repulsion, $6.3 \text{ eV} < E_{\text{SW}} < 10.2 \text{ eV}$), darker gray to lower energy (attraction, $5.4 \text{ eV} < E_{\text{SW}} < 6.3 \text{ eV}$), with the median ($E_{\text{SW}} = 6.3 \text{ eV}$) corresponding to the defects remote from each other, with negligible interaction.
between the defects. This governs the actual spatial pattern of the defect formation, following the formal kinetic scheme,

\[ 0 - \text{SW} \rightarrow 5/7/7/5 - \text{SW} \rightarrow 5/7/7/5 \ldots \]

+ \ldots 5/7/7/5 - \text{SW} \rightarrow ? \quad (6)\]

Here ‘0’ stands for the initially perfect hexagonal lattice, and every reaction step corresponds to one SW bond rotation. One can see (Fig. 4) that the attraction valleys correspond to ‘diagonal’ location of defects with respect to each other, and the most energetically favorable is their position just next to each other (but not overlapping). This important conclusion indicates the most probable scenario of relaxation leading to a slanted stripe (shear band) at a certain level of load. We plan further more detailed analysis of the energetics and kinetics of relaxation, which should lead to a consistent theory of yield and failure mechanisms, and is also important for possible property modification of the nanotube [14].

7. Cooperative strength limits for the ropes/bundles

Although mechanical strength of individual CNT presents significant interest, it may not be the actual limiting factor for overall strength of a bundle of the tubes (a rope). Since the typical length \( L \) of CNT segments in a bundle is much less than the length of the entire rope, a large applied tension \( \sigma \) can cause the slippage between the CNT’s at some level \( \sigma = s \ll s_i \) well below their intrinsic strength, \( s_i \). Some, although not always direct, evidence of such weakness of the ropes due to the lack of inter-tubular adhesion has been reported in several cases [15–17]. We present here the results of the approximate mean-field based model calculation of the overall strength of a rope.

Fig. 5a illustrates that the random discontinuities (terminations of the CNT’s marked \( x \) in the figure) are distributed in the bulk of the bundle with the average distance between them \( L_x = L^{1/3} d^{2/3} \). With this scaling relationship, our calculation is based on the assumption that the tension carried by a terminated segment is reloaded among the neighbors. Since the (weak) inter-tubular friction force (Fig. 5b) must occur along the certain length from the termination point, there is another parameter, \( L_x = \sigma d/f \).

Finally, for short tube segments, the surface tension force \( \gamma d \), due to a fresh surface exposure during the CNT pull-out (corresponding surface energy \( \gamma \), similar to the small \( \gamma \) in graphite), should be taken into account.

There are thus three forces of different nature, together maintaining the rope integrity, that one can list in a per-tubule form: the force \( s d^2 \) due to the intrinsic strength \( s_i \) of the CNT, lateral friction between CNT, \( fLd \), and the ‘capillary’ force \( \gamma d \) (we omit unimportant numerical factors). Correspondingly, three domains can be seen in the plot, Fig. 5c. Strength \( s = \gamma d \) (limit of very short segments, nematic behavior), strength proportional to the segment length and the lateral friction, \( s = fL/d \), and finally the case of very long segments where the observed strength must approach the ideal value, \( s = s_i \). Note, that in the latter case a more conservative estimate can be presented, with the assumption that the reload from a terminated tube is only transferred to the nearest six neighbors, which results to a factor \((1 + 1/6)^{-1} = 0.86\).

The plot shown corresponds to the example set of parameters based on the literature: \( s_i = 100 \text{ GPa} \), \( \gamma = 0.1 \text{ N/m} \), \( f = 0.01 \text{ GPa} \). For example, in order to approach the full strength of CNT, a rope should consist of the segments of the order of 10 \( \mu \text{m} \) long and more. (Currently available SWNT are in submicron range). Although very approximate, this calculation provides useful information about the expected behavior of CNT ropes.

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