

ABSTRACT

Keywords:

1. INTRODUCTION

Previous investigators have attempted to predict when and how nanotubes collapse into nanoribbons. As the nanotube's wrapping angle (pitch) and length do not affect collapse greatly, the critical parameter is the radius. There are typically two critical radii investigated. The smaller one, r_{c1} , is the minimum radius at which the tube is bistable, i.e. the minimum radius at which a meta-stable collapsed state exists. The larger one, r_{c2} , is the minimum radius at which the energy in the collapsed state is less than that in the inflated state, i.e. the collapsed state is stable and the inflated state is meta-stable. Since, from the previous section, the inflated state is always an energy minimum, all tubes with a radius larger than r_{c1} have (at least) two energy minimum. Unfortunately, the literature is not consistent. Values from 6.34Å to 10.28Å for r_{c1} and 9.511Å to 29.62Å for r_{c2} have been reported for methods ranging from quantum to molecular to continuum mechanics. Unfortunately, very little experimental data on this phenomenon have been obtained; the authors are aware only of high resolution transmission electron microscopy for multi-walled nanotubes that had collapsed at an indeterminate point prior to imaging.[?] Here we investigate the energetics of the transition between the collapsed and inflated states, attempt to reconcile the discrepancies reported in the literature, and suggest why experimental verification may be difficult to obtain and nanoribbons infrequently observed.[?] The level of physical approximation used to determine the critical radii is not the sole factor determining discrepancies; different investigators using the same reported degree of physical approximation have obtained results that span the range mentioned above. For example, Gao *et al.*[?] used "an accurate force field, derived through QM calculations, to represent the interactions between the carbon atoms" and found $r_{c1} \sim 10.28\text{Å}$ and $r_{c2} \sim 29.62\text{Å}$. Tang *et al.*[?] used the polymer consistent force field (pcff) to find $r_{c1} = 6.34\text{Å}$ and $r_{c2} = 9.511\text{Å}$. This suggests that the results are strongly dependent on the specific potentials used in the simulation. Verification of the molecular dynamics results is often difficult since the exact potentials (for both bonded and non-bonded interactions) and simulation parameters are not given. Umeno *et al.*[?] used a "four-orbital TB (tight binding) calculation with the potential proposed by Papaconstantopoulos and Mehl"[?] to investigate the deflection caused by forces on opposing pairs of atoms acting to compress (8,0), (12,0), and (14,0) tubes. In this study the tubes were compressed until they were fully collapsed and non-bonded repulsive forces acted to resist the applied load. For the tubes studied in,[?] the force never became negative and the authors state that the deformation was elastic and reversible. Thus, while not actually investigating collapse in nanotubes, Umeno's study suggests that r_{c1} is greater than 5.48Å. Liu *et al.*[?] used a bonding potential recently developed by Brenner[?] and, apparently, the same isotropic Lennard-Jones potential used here to find that tubes smaller than (15,15) (with a radius of $\sim 10\text{Å}$) were not bistable and that tubes larger than (30,30) (with a radius of $\sim 20\text{Å}$) had a lower energy in the collapsed state. They also suggest that larger tubes are not stable in the inflated state, which is inaccurate, at least at 0 K, since the inflated state possesses a finite barrier against collapse (albeit vanishing in the limit of infinite radius). Liu *et al.* also investigated the effects of lattice registry on collapsed tubes and it is not clear if they used a more accurate registry-dependent non-bonded potential to do this as in Kolmogorov, *et al.*[?] Also, the Brenner potentials significantly underestimate the stiffness of a graphene sheet when compared to more accurate quantum mechanical methods. Results using continuum approaches also vary widely, although enough information is typically provided to reproduce the results and determine the source of the discrepancy. In one of the first reports of collapsed nanotubes, Chopra *et al.*[?] used a simple continuum energy analysis considering just flat and circular regions to show that

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the collapsed state of various multiwalled nanotubes was energetically favorable to the inflated state. Benedict *et al.*² used a bending resistance per unit length of 1.4 eV and a slightly more sophisticated model that assumed the flat and semi-circular bulb regions were connected by a transition region described by “ $(\chi + \gamma) + \delta$.” They used high resolution transmission electron microscopy images of collapsed multiwalled tubes to approximate the intersheet attractive energy as 0.035 eV/atom. Extrapolating, they estimated the r_{c1} and r_{c2} to be roughly 13.5Å and 30Å, respectively. Tang *et al.*² used the Lennard-Jones and carbon-carbon bond potentials in pcff to find estimates of the adhesion energy between graphite layers ($0.4 \text{ J/m}^2 = 2.50 \text{ eV/nm}^2 = 0.131 \text{ eV/atom}$) and the bending resistance per unit length ($9.11 \times 10^{-20} \text{ N-m} = 0.569 \text{ eV}$). A deformation with two variable parameters predicted results close to that of their molecular dynamics results mentioned earlier. They modeled the central portion of the collapsed tube as a flat bilayer with opposing sides separated by 3.5Å over a region of unknown length. The bulb regions were assumed to be semi-circular with an unknown radius, while the transition region was approximated as a polynomial that matched the geometric constraints of displacement and zero slope at the ends. They approximated the length of material in the transition regions as simply the length projected onto an axis parallel to the flat regions. By using a polynomial that only matched the geometric constraints at the ends of the transition regions, the authors implicitly assume that a point moment exists at these points. While this might be justifiable at the points of connection between the flat and transition regions (were there is a sign change in the Van der Waals force), it is difficult to justify a point moment at the points of connection between the transition and bulb regions, where one does not expect rapid spatial variations in the Van der Waals force. While their results matched closely the MD results presented in the same paper, the energies stored in the bending and the Van der Waals interactions for their continuum model were obtained from simple MD simulations using the same potentials as the full MD simulation.²

2. ELASTICA MODEL

We study the uniform collapse of a carbon nanotube by modeling the cross-section using the equations governing the inextensible, geometrically large deformations of an elastic rod (Euler’s elastica)

$$p' + f = 0 \tag{1}$$

$$m' + \mu + x' \times p = 0 \tag{2}$$

where m and p are the internal moment and load vectors in the rod. The distributed load and moment are given by f and μ , respectively, and primes denote differentiation with respect to an arc-length, material coordinate along the curve such that x' is the unit tangent to the curve. The distributed moment is only necessary when considering the anisotropic polarizability of graphene.² For planar deformations of initially straight, stress-free rods, these equations are written most compactly in terms of the angle between the tangent vectors to the deformed (x') and undeformed () curve at each material point on the rod. Thus, let $x' = \cos \psi + \sin \psi$. Then (1) and (2) become

$$D\psi'' + \mu_z + p_y \cos \psi - p_x \sin \psi = 0 \tag{3}$$

$$x' = \cos \psi, \quad y' = \sin \psi \tag{4}$$

$$p'_x + f_x = 0, \quad p'_y + f_y = 0 \tag{5}$$

where x and y are rectangular coordinates giving the deformed position of each point on the curve; see Figure ?? . The internal load vector has components in the x and y directions p_x and p_y , respectively. The distributed load has x - y components f_x and f_y , respectively, and the distributed moment would have a single component, μ_z perpendicular to x - y . The internal moment is assumed proportional to the (change in) curvature of the curve; the proportionality constant is D , the bending stiffness. It is most natural to consider quantities per unit tube length. Thus, let D be the bending stiffness per unit length with unit of energy, p be the internal load per unit length, and f and μ be the force and moment per unit area applied to the tube.

REFERENCES