STRUCTURAL STABILITY OF CARBON NANOTUBES

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We examine mechanical deformations of carbon nanotubes. Tubes within certain geometrical parameter ranges (# of walls and tube diameter) are shown to be susceptible to complete collapse. Tubes subjected to sharp bending show both periodic and aperiodic deformations. By selectively weakening carbon bonds in the fabric of a tube with a high energy electron beam, a cylindrical tube can be induced to collapse along its length.

1 Introduction

Graphite in the in-plane direction has the highest elastic modulus of any known material. This suggests that defect-free carbon nanotubes constitute the most structurally ideal lightweight fibers possible, with outstanding tensile strength in the axial direction. It has been estimated[1] that the axial Young's modulus of nanotubes is of order 7000 GPa, in contrast to 200 GPa for steel and 520 GPa for iridium. On the other hand, nanotubes are less robust in the radial direction, and substantial mechanical deformations are expected if non-symmetric radial forces are applied.

2 Nanotube Deformations

2.1 Cylinders versus Flat Ribbons

Nanotubes are generally thought of as high aspect ratio cylindrical structures. However, a tube with a circular cross-section is not the only stable (or metastable) configuration. Imagine pressing a nanotube between two parallel plates, with the tube axis parallel to the plate surfaces. As the plate separation decreases and the tube is deformed, its cross-section assumes a stadium-like shape. The elastic energy of the "stadium" tube is higher than that of the "circular" tube (the increase in curvature energy at the stadium ends is not sufficiently offset by the lowering of curvature energy at the straight stadium walls). The deformed tube is not stable. However, if the plates compress the tube to such an extent that the flat sections of the tube walls become very close and are van der waals attracted, the total tube energy, elastic + van der waals, may actually be as low as or lower than the corresponding energy for the circular tube. In such a case the plates can be removed and the deformed tube configuration will be stable-- resulting in a fully collapsed nanotube.

Fig. 1 shows a computer graphic view down the center of a fully collapsed nanotube. The cross-section seen at the far end of the tube is "dog-bone" like; this predicted cross-section reflects a trade-off between minimizing curvature energy and maximizing van der waals attraction.

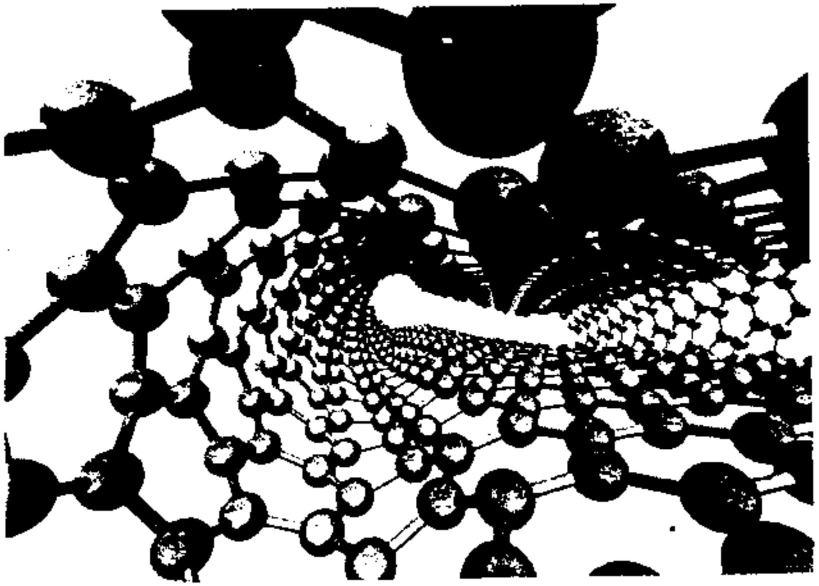

Figure 1: Computer-generated central-axis view of collapsed nanotube. Image courtesy of V. H. Crespi.

Clearly tubes with large diameters and few walls are more susceptibl to collapse (a large diameter increases the area of the "flat" sections an enhances the van der waals force; adding additional walls to a tube onl increases the elastic energy with no additional van der waals benefit Benedict and coworkers[2,3] have investigated the energetics of collapse nanotubes using continuum elasticity theory. The stability criterion fo the collapsed tube is that it has the same total energy as the "inflate tube with circular cross-section. For a single-wall tube, the predicte critical tube radius is R_{crit} (1) = 8d, while for an 8-wall tube, the critic tube radius is $R_{crit}(8)$ = 19d. d is the interplanar spacing in graphite ar R is the radius of the outermost shell. Of course, tubes with smaller rac may still exist in the collapsed state; the activation barrier between t collapsed and inflated configurations can lead to metastable collapse configurations (similarly, of course, many circular cross-section inflated tubes may be in a metastable inflated state).

Do fully collapsed, ribbon-like nanotubes exist? TEM studies[2] have convincingly demonstrated the existence of such tubes. Fig. 2 shows an example of a collapsed nanotube. This particular tube has 9 walls and R = 8.0 nm for the outermost shell. R_{crit} (9) is predicted[3] to be of order 7.5nm, which implies that the total energy of the collapsed tube in Fig. 2 is at a global (tube) minimum, not just local metastable minimum.

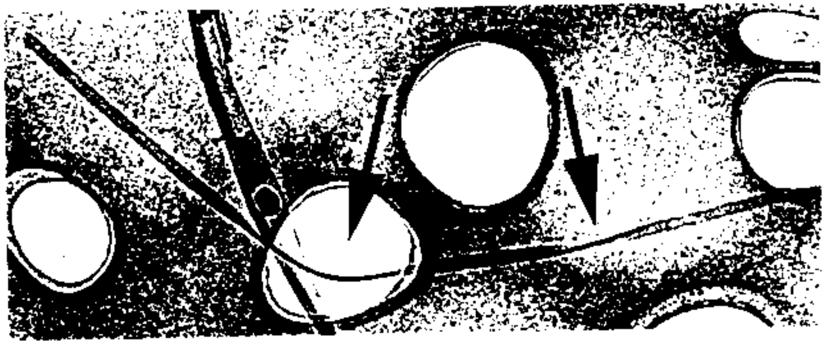

Figure 2: TEM image of a collapsed nanotube. The arrows identify 180° twists in the tube.

2.2 *Nanotube Instabilities Induced by Bending*

How did the tube shown in Fig. 2 come to be collapsed? It is possible that it was locally mechanically deformed (perhaps by twisting and/or bending) and "kinked". The "kink" could then propagate along the length of the tube, effectively "zipping" the tube shut into a fully collapsed state.

We have examined the local deformations of carbon nanotubes subjected to severe bending. We observe that if the nanotube parameters are well outside the parameter range for energetically favorable "collapse", the bending does not result in tube collapse, but rather induces unusual instabilities along the inner curve of the bent tube.

The inset of Fig. 3 shows a TEM image of a 16-wall, 20 nm outer diameter tube bent through a 90-degree angle (a larger structure forms the left support for the bent tube). Fig. 3 is a line drawing reproduction of a high resolution TEM image of the bent region of the tube. The inner curve of the tube shows a well-defined periodic ripple, with wavelength 16 nm.

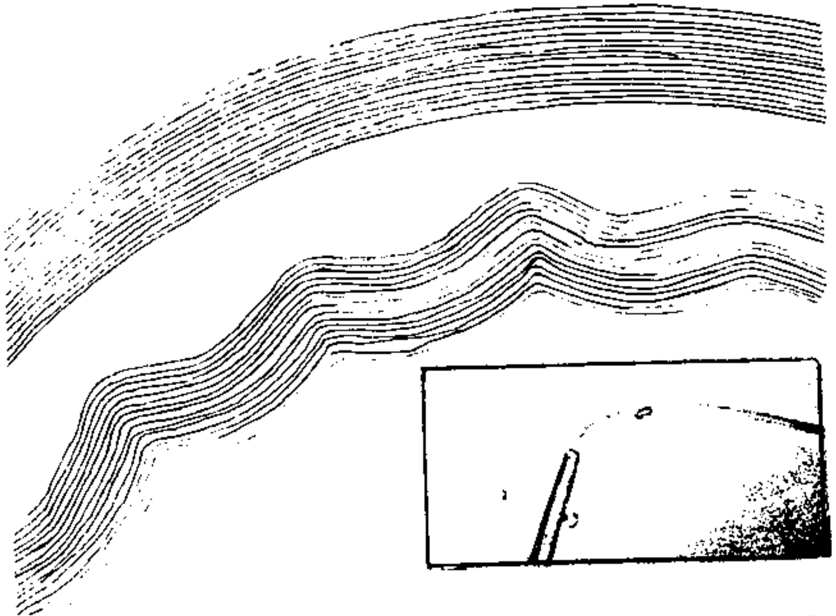

Figure 3: Line drawing reproduction of RHTEM image of bent region of a nanotube; note the periodic modulation. The inset shows a lower magnification TEM image of the bent tube.

Fig. 4 shows an 8-wall (collapsed) nanotube bent through a severe 90-degree bend. Here no periodic instability is observed; rather the inside curve shows a tortuous folding of the nanotube wall fabric. The high resolution TEM image shows no evidence for tube fabric breakage, despite the small overall radius of curvature of the bend (approximately 20 nm) and the extremely small local radius of curvature at the folds (as small as 0.3 nm). Collapsed nanotubes are extremely flexible and strong.

Collapsed nanotubes are also prone to twisting. The collapsed nanotube shown in Fig. 1 in fact has two distinct 180-degree twists along its length. Nearly all collapsed nanotubes we observe have twists. This feature supports the notion that nanotubes are more flexible in the collapsed state than in the inflated cylindrical state. This dintinction could have important implications for mechanical applications. It is also quite possible that the "kink" that nucleates nanotube collapse originates at a partially twisted region in the originally cylindrical tube.

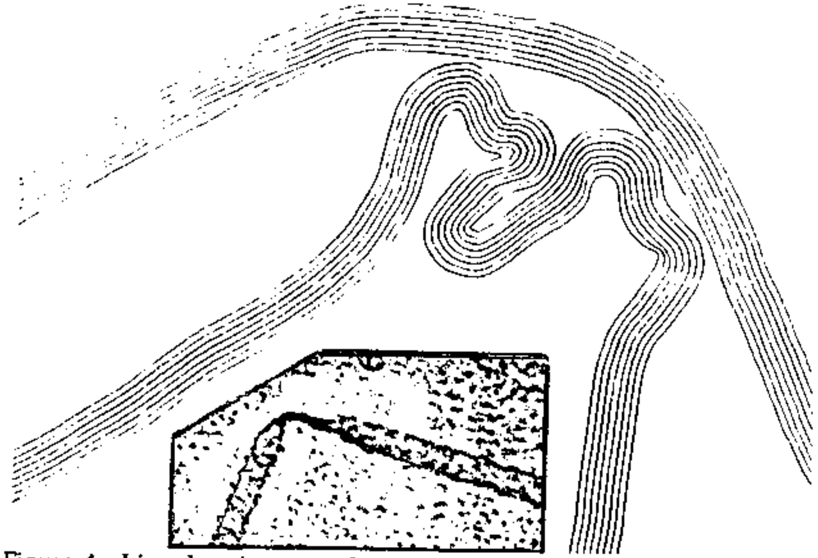

Figure 4: Line drawing reproduction of RHTEM image of sharply bent region of a collapsed nanotube. The inset shows a lower magnification TEM image of the bent tube.

2.3 *Nanotube Collapse Induced by Electron-beam Irradiation*

We have used 800 keV electrons to selectively weaken carbon bonds in a multi-wall carbon nanotube and induce complete collapse[4].

Fig. 5 shows schematically the selective bond damage and tube distortion expected from 800 keV electron irradiation. Molecular dynamics studies by Crespi and coworkers[5] demonstrate that knock-on beam damage to the tube is most severe for the regions of tube surface oriented perpendicular to the beam direction. In this representation, the "top" and "bottom" portions of the tube sustain the most damage; the curvature modulus is significantly reduced in the damaged regions. With sufficient reduction in modulus, the tube will collapse into a ribbon form, with the wide part of the ribbon parallel to the electron beam direction.

Fig. 6 shows an experimental realization[4] of such an induced collapse using 800 keV electrons. The dashed line delineates the tube under study from an adjacent tube. After 60s of exposure time, the tube has begun to collapse. After 165s of exposure time (not shown), the multiwalled nanotube is fully collapsed (complete disappearance of the gap in the center of the tube).

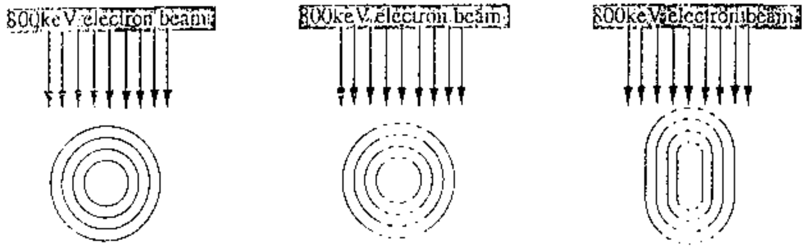

Figure 5: Schematic evolution of nanotube under high energy electron irradiation. The tube collapses as the top and bottom portions of the tube walls lose structural integrity.

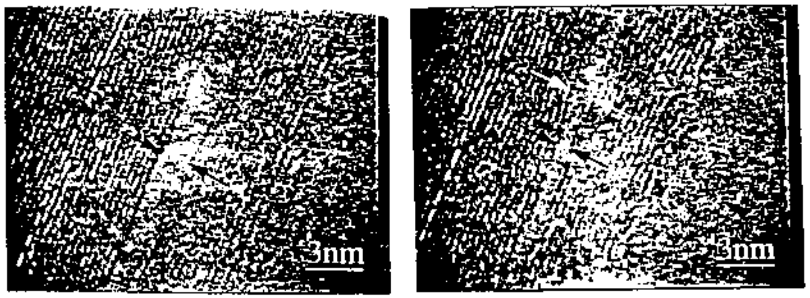

Figure 6: RHTEM images of a nanotube subjected to 800keV electron irradiation. The left image is for t=30s, the right for t=60s. At t=60s the tube has begun to collapse (narrower gap in center of tube).

Acknowledgments

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