## **Collapse of Single-Wall Carbon Nanotubes is Diameter Dependent**

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(Received 3 December 2002; published 2 March 2004)

We present classical molecular dynamics simulations demonstrating that single-wall carbon nanotube (SWNT) bundles collapse under hydrostatic pressure. The collapse pressures obtained as a function of nanotube diameter are in excellent quantitative agreement with new data presented here for small diameter ( $d \approx 0.8$  nm) SWNTs, and the majority of previously published results, although there remain some unreconciled contradictions in the literature. The collapse pressure is found to be independent of the nanotube chirality, and a lower limit on the largest SWNT that remains inflated at atmospheric pressure is established (d > 4.16 nm).

DOI: 10.1103/PhysRevLett.92.095501

PACS numbers: 61.46.+w, 02.70.Ns, 62.50.+p, 78.30.Na

Introduction.-Since their identification in 1991, interest in carbon nanotubes has continued to grow, focusing on both their intrinsic properties and potential applications. The behavior of individual tubes has been explored via experiment [1-3] and computer simulation, e.g., [4-7], in both axial and bending geometries. Elastic properties have generally been found to be broadly consistent with the in-plane properties of graphite, but strengths have proved harder to assess, with simulation results consistently predicting higher values than have been observed experimentally, probably as a result of defects in the real materials. Carbon nanotubes have also been explored under hydrostatic pressure, using Raman spectroscopy [8–13], x-ray diffraction [14,15], and neutron diffraction techniques [16]. Raman spectroscopy, in particular, has proved to be a very useful tool in the characterization of single-wall carbon nanotubes (SWNTs), revealing information about crystallinity, diameter, and even chirality. Under increasing hydrostatic pressure, the Raman peaks shift to higher frequencies, corresponding to a stiffening of the carbon framework. Some authors have noticed that the peak position of the tangential mode, corresponding to in-plane vibrations of adjacent carbon atoms in the graphene sheet, shifts linearly over two regimes with a change in gradient at a critical pressure of approximately 2 GPa, depending on the type of nanotube material used. A number of studies also reported the disappearance of the radial breathing mode (RBM) from the spectrum above that critical pressure. Similarly, x-ray results demonstrate the disappearance of scattering associated with the hexagonally close-packed lattice into which the SWNT bundles are organized [14]. Clearly, a structural phase transition occurs at this critical pressure, but the exact nature of this change has proved controversial. Most authors seem to favor a transition to a close-packed structure of hexagonally deformed nanotubes ("polygonization"), while others propose a complete flattening or "collapse" [17]. A previous TEM study of multiwall nanotubes (MWNT) found evidence for collapse to form ribbons, although the cause was unclear [18].

In a recent study [19], we used Raman spectroscopy to compare the behavior of bundles of single and a range of MWNTs to that of graphite, under hydrostatic pressure. The initial gradient of the peak shift could be explained entirely in geometric terms, using a continuum mechanics model and the relevant internal and external diameters. Above the critical pressure, the gradient was equal to that of the graphite, which exhibited no transition over the pressure range up to 10 GPa. We interpreted these results as evidence supporting the complete collapse of the hollow core of the nanostructures to produce materials resembling graphite in terms of density and hybridization. The peak shifts appeared to be completely reversible within experimental accuracy, as long as the maximum pressure was kept below 10 GPa. The SWNTs in this experiment were supplied by Tubes@Rice, and are generally considered to be predominantly either (10,10) nanotubes or other chiralities with similar diameters. The critical pressure for these nanotubes to collapse was found to be  $2.1 \pm 0.2$  GPa.

This Letter describes a series of molecular dynamics simulations intended to examine the proposed mechanism of collapse, and explore the response of other diameters and chiralities of nanotubes. In the light of these predictions, we then performed further Raman pressure experiments that proved to be in excellent agreement with our simulations, as described below.

Simulation methodology.—A common approach to modeling the mechanical behavior of carbon nanotubes has been the use of *ab initio* quantum methods, e.g., [5–7,20,21]. However, such techniques are computationally expensive for large molecular systems. Although second-generation reactive empirical bond order (REBO) potentials [22] offer an improvement in this respect, for simulations in which there is no change in intramolecular bonding, and where intermolecular forces play a dominant role, conventional many-body expansions of the potential energy can be used effectively.

In this study, since we are concerned with studying reversible geometric changes in structure driven by a combination of hydrostatic pressure and van der Waals forces, a standard generic macromolecular force field, DREIDING [23], was parametrized for carbon nanotubes by fitting to high pressure x-ray crystallographic measurements of graphite between 0 and 14 GPa [24]. N $\sigma$ T ensemble (constant particle number, stress, and temperature) molecular dynamics (MD) simulations were carried out on hexagonally close-packed bundles of ideal SWNTs with pseudoperiodic boundary conditions, using the DL\_POLY code developed at Daresbury Laboratory, U.K. The system temperature (T = 298 K) and stresses were regulated using the Berendsen algorithm, and the simulation time step was 1 fs.

In order to induce a structural phase transition, a stepwise monotonically increasing hydrostatic pressure was applied to a SWNT bundle equilibrated under atmospheric conditions. The change in cell volume was measured as a function of applied hydrostatic pressure, after allowing the cell volume to equilibrate after each pressure increment. The pressure was increased from 0 to 16 GPa in 20 stages, allowing 50 ps between each increment for equilibration, giving a total simulation time of 1 ns. Although the applied compression rate is notionally supersonic, that experienced by the SWNTs is very close to isothermal due to the equilibration procedure used. The number of independent tubes in the bundle and the length of the simulation cell parallel to the tube axis were increased systematically until no further changes could be observed in the equation of state curve. It was found that nine independent tubes  $(3 \times 3 \text{ bundle})$  of length 2.43 nm, corresponding to ten unit cells of a (10,10) SWNT, were sufficient to avoid finite size effects.

*Experimental methodology.*—Full details of the experimental method for the pressure cell experiments and subsequent data analysis may be found elsewhere [19] but a brief description follows. Raman spectra were collected from nanotubes suspended in a 4:1 meth-anol:ethanol mixture, compressed in a gasketed diamond anvil cell. The pressure was calibrated using the Ruby fluorescence method with a HeNe laser, while the carbon nanotube spectra were collected with a 785 nm near-IR laser. HiPco SWNTs with an average diameter of  $0.8 \pm 0.1$  nm were obtained from Carbon Nanotechnologies Inc., while SWNTs with a diameter distribution centered around 1.4 nm were obtained from Tubes@Rice [19].

Simulation results.—At pressures below 2 GPa, (10,10) SWNTs showed only thermal motion of the atoms, with no apparent systematic deviation from the circular cross section. Above a critical pressure, in accordance with our previous interpretation of experimental results [19], the SWNTs spontaneously collapse to form ribbons of oval cross section, where the opposite walls are separated by

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approximately the distance between layers in turbostratic graphite (0.34 nm).

Figure 1 shows two snapshots of a  $4 \times 4$  array of (10,10) SWNTs taken below and above the transition pressure. A plot of the cell volume for a  $3 \times 3$  bundle, normalized to the equilibrium volume at zero pressure, is shown in Fig. 2, and clearly demonstrates the discontinuous nature of the transition. The loading curve (solid line) gives a critical transition pressure of  $2.1 \pm 0.1$  GPa, with an apparent unloading transition (dashed line) at  $1.5 \pm$ 0.1 GPa. The former result is in very good agreement with the value of  $2.1 \pm 0.2$  GPa that we previously identified experimentally for SWNTs from Tubes@Rice. Unfortunately, the hysteresis could not be observed in the experimental unloading data points, which were too widely spaced. The degree of order in the herringbone structure visible in Fig. 1(b) is related to the number of independent tubes in the bundle, and may be very different for a finite bundle, but the collapse pressure remains unchanged for those bundles containing more than nine independent tubes. The hysteresis is due to the van der Waals attraction between opposing walls of the collapsed tubes.

In order to explore the possible effect of chirality on the collapse pressure, a set of four bundles containing SWNTs with very similar diameters but varying chirality was selected. The pressure-volume relationships for (19,0), (16,5), (13,9), and (11,11) SWNT bundles showed no significant variation within the accuracy of the simulation.

In order to investigate the effect of diameter on collapse pressure, simulations of a range of SWNTs were carried out, and the resulting loading curves are plotted in Fig. 3. There is a clear decrease in collapse pressure with increasing nanotube diameter, as shown in Fig. 4. The inset to Fig. 4 shows that there appears to be an inverse proportionality between collapse pressure and tube diameter for smaller tubes, however no power law relationship fits the behavior satisfactorily over the entire range of pressure. Note that the collapse behavior is distinct from the polygonization of the SWNTs within their bundles that has been previously suggested, and which gradually becomes more pronounced in these simulations, even at ambient pressures, for tubes with diameters above about 3 nm.



FIG. 1. A  $4 \times 4$  (10,10) SWNT bundle at 298 K and (a) p = 0.1 GPa, and (b) p = 3 GPa, viewed parallel to the tube axis.



FIG. 2. Loading and unloading curves for a  $3 \times 3$  (10,10) SWNT bundle as a function of hydrostatic pressure.

The trend at very low SWNT diameters and hence high pressures should be treated with caution, as the force field does not allow for any rehybridization or other changes in bonding. It is known that at sufficiently high pressures an irreversible change in the structure of SWNTs occurs (for 1.4 nm diameters used typically in experiments), although there is some discussion about the value of this critical pressure within the range 10 to 25 GPa.

Turning now to the large diameter SWNTs, which collapse at low pressures, extrapolation of the trend displayed in Fig. 4 would logically suggest that, above some critical diameter, SWNTs spontaneously collapse to form "ribbons" at atmospheric pressure. An inverse relationship between collapse pressure and diameter, as observed for smaller tubes, would suggest a limiting diameter of 2.2 nm, in good agreement with the estimate of 2.4 nm by Chopra [18] who considered a simple balance between van der Waals forces and strain energy due to curvature. However, experimentally, larger SWNTs have been reported [25,26] of up to around 6 nm in the tails of broad distributions that have been determined by AFM or TEM. A closer inspection of our data indicates a deviation from



FIG. 3. Loading curves for SWNT bundles containing tubes of varying diameter and chirality as a function of applied hydrostatic pressure.



FIG. 4. Collapse pressure of SWNT bundles along loading branch as a function of tube diameter, and (inset) as a function of reciprocal diameter, with the six lowest diameters fitted by a linear relationship.

the simple inverse relationship and a higher limiting diameter. This deviation may relate to the increasing polygonization of the SWNT that will lead to a relative increase in stability against collapse. Unfortunately, modeling large diameter SWNTs becomes increasingly difficult as the time taken to reach equilibrium increases dramatically. Nevertheless, a lower limit for the critical diameter can be obtained by considering bundles containing the largest SWNTs that will reinflate at atmospheric pressure, which we find to be at least 4.16 nm. Figure 5 shows (30,30) and (50,50) SWNT bundles under atmospheric pressure, with tube diameters 4.16 and 6.94 nm, respectively, showing that the former are strongly polygonized, whereas the latter are partially collapsed and might be expected to continue their collapse given sufficient simulation time and cell size. Examining the trajectories of the simulations suggests that the collapse mechanism commences with the coordinated flattening of one tube against another, which ultimately leads to the collapse of the whole bundle. Evidence from our unpublished simulation work strongly suggests that the collapse pressure of individual solvated nanotubes is different from those inside a bundle.

*Experimental results.*—In order to test the predictions of the model and our interpretation of the pressure



FIG. 5. SWNT bundles under atmospheric pressure (a) (30,30) diameter 4.16 nm, showing polygonized cross sections, and (b) (50,50) diameter 6.94 nm, showing partially collapsed cross sections.



FIG. 6. Plot of the strongest tangential mode positions for the two types of SWNT materials investigated experimentally, which verifies the dependence of the transition pressure on the diameter of the single-wall carbon nanotubes. The arrows highlight the transition pressures (crossing of linear fits).

behavior of nanotubes, we studied a new sample experimentally (HiPco SWNTs), and compared the result with our earlier work on Tubes@Rice SWNTs [19]. The HiPco SWNTs have a diameter distribution centered around 0.8 nm, and hence would be predicted to have a collapse pressure around 6.1 GPa (from Fig. 4). Loading curves for the two SWNT materials with distinctively different diameter distributions are summarized in Fig. 6. Plotted are the strongest tangential peak positions for the two SWNT samples as a function of increasing hydrostatic pressures up to 10 GPa. The experimentally observed transitions in the Raman peak shift as a function of hydrostatic pressure are marked by the arrows. The pressure-induced behavior matches the predictions from the simulations. The smaller diameter SWNTs collapse at a higher pressure of 6.6  $\pm$  0.8 GPa, compared to the transition pressure of 2.1  $\pm$  0.2 GPa for the larger diameter SWNT material. In addition, the transition is less prominent, consistent with the smaller volume change that was predicted from our simulations.

Conclusions.—We have performed a series of molecular dynamics simulations to test our initial hypothesis, based on experimental results, that carbon nanotubes undergo a discontinuous collapse transition under hydrostatic pressure. The simulations support this interpretation, and demonstrate that nanotube diameter is the key parameter determining the transition pressure since chirality appears to be unimportant. Indeed, the diameter behavior indicates a limited stability for SWNTs once the diameter is sufficiently large; we predict that the critical diameter at atmospheric pressure lies between 4.2 and 6.9 nm. In addition, there was excellent quantitative agreement between the model, simply calibrated with x-ray compression data for graphite, and the experimentally observed transition pressures for laser-grown nanotubes. Experiments stimulated by the modeling work revealed additional quantitative agreement for HiPco nanotubes. This level of agreement raises confidence that this simple and computationally inexpensive force field may be suitable for examining other nanomechanical applications of nanotubes.

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