Comment on "Collapse of Single-Wall Carbon Nanotubes is Diameter Dependent"

Recently, Elliott *et al.* [1] reported classical molecular dynamics (MD) simulations on single-wall carbon nanotube bundles (SWCNTBs) using $N\sigma T$ ensemble (constant particle number, stress, and temperature) with the Berendsen algorithm [2] and demonstrated that SWCNTBs collapse under hydrostatic pressure. While accepting the validity of these calculations, here we show that the stress induced herringbone structure, which was also reported before by first principles calculations [3], is not energetically the most favorable.

We have performed MD simulations using both the Parrinello-Rahman constant-pressure method [4] and the Berendsen algorithm, with a supercell containing a 4×4 (10, 10) SWCNTB of length 2.95 nm. The covalent interaction between carbon atoms are modeled by the Tersoff-Brenner many-body potential [5,6] with the parameters given by Brenner [6], and the intratube and intertube van der Waals interactions by the Lennard-Jones potential [7]. The system temperature ($T =$ 200 K) is set by a Nosé-Hoover thermostate [8].

The carbon nanotubes in the 4×4 bundle collapse at a pressure of $\sim$1.2 GPa, in agreement with the results in Ref. [1]. However, these tubes are aligned in parallel and are distinct from the herringbone structure obtained by Elliott *et al.* [1], as shown in Fig. 1. Although both structures are stable during molecular dynamics simulations at 1.5 GPa and 200 K, the parallel structure is energetically more favorable than the herringbone structure in the total energy, the PV term, and the enthalpy, as determined by annealing to zero temperature at constant pressure, as shown in Table I. Furthermore, the parallel phase is even more favorable when the pressure increases.

To understand the enthalpy difference between the parallel structure and the herringbone structure, we have calculated the interstitial volume V_{inter} between carbon nanotubes and the intravolume V_{intra} inside carbon nanotubes. While the intravolume is similar for both structures, the parallel structure has less interstitial volume, as indicated by a V_{inter} to V_{intra} ratio of 1.082 for the parallel phase and of 1.134 for the herringbone phase, at zero temperature and 1.5 GPa. It can be attributed to the larger interstitial region around the ends of the "dumbbell" sections in the herringbone structure. Thus the herringbone structure has a large PV term and the parallel structure should be more stable in actual experiments.

TABLE I. Energies and enthalpies of the parallel and herringbone structures for the pressure of 1.5 GPa at zero temperature (values in parentheses for 1.8 GPa). The differences (Δ) between two structures show that the parallel structure has a lower energy and a lower enthalpy than the herringbone one.

Structure	E/atom (eV)	PV/atom (eV)	H/atom (eV)
Parallel	−6.7515	0.0981	−6.6534
	(−6.7503)	(0.1164)	(−6.6339)
Herringbone	−6.7485	0.1044	−6.6441
	(−6.7472)	(0.1235)	(−6.6237)
Δ	−0.0030	−0.0063	−0.0093
	(−0.0031)	(−0.0071)	(−0.0102)

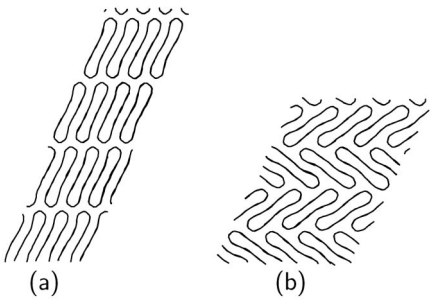

FIG. 1. Snapshots of the cross section of a 4×4 (10, 10) SWCNTB at 1.5 GPa ($T = 200$ K): (a) parallel structure and (b) herringbone structure.

This work is supported by the National Science Foundation of China, the special funds for major state basic research, and CAS projects.

X. H. Zhang,[1] Z. F. Liu,[2] and X. G. Gong[1,3]
[1]Surface Physics Laboratory (National Key Laboratory)
Fudan University
Shanghai 200433, China
[2]Department of Chemistry
The Chinese University of Hong Kong
Shatin, Hong Kong, China
[3]Institute of Solid State Physics
Chinese Academy of Sciences
Hefei 230031, China

Received 2 April 2004; published 27 September 2004
DOI: 10.1103/PhysRevLett.93.149601
PACS numbers: 61.46.+w, 61.50.Ks, 71.15.Pd, 73.63.Fg

[1] J. A. Elliott *et al.*, Phys. Rev. Lett. **92**, 095501 (2004).
[2] H. J. C. Berendsen *et al.*, J. Chem. Phys. **81**, 3684 (1984).
[3] S.-P. Chan *et al.*, Phys. Rev. B **68**, 075404 (2003).
[4] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980); J. Appl. Phys. **52**, 7182 (1981).
[5] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).
[6] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[7] L. A. Girifalco and R. A. Lad, J. Chem. Phys. **25**, 693 (1956); L. Henrard *et al.*, Phys. Rev. B **60**, 8521 (1999).
[8] S. Nosé, Mol. Phys. **52**, 255 (1984); W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

