Molecular dynamics study of radial pressure transmission in multiwalled carbon nanotubes

X. Ye,[1] D. Y. Sun,[2] and X. G. Gong[1]

[1]*Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai 200433, China*

[2]*Key Laboratory of Optical and Magnetic Resonance Spectroscopy and Department of Physics, East China Normal University, Shanghai 200062, China*

The pressure response of multiwalled carbon nanotubes (MWCNTs) to the radial hydrostatic pressure is studied by using constant pressure molecular dynamics simulations for finite systems. The inner tube is effectively protected by the outer tube against the external pressure. The pressure transmission efficiency of MWCNTs depends upon both the size and morphology combination of the tubes. The larger the tube is, the higher the pressure transmission efficiency will be. The pressure transmission in commensurate MWCNTs is more efficient than that in incommensurate ones. Based on the present simulations, an experimental method is suggested for measuring the pressure transmission efficiency of MWCNTs.

PACS number(s): 61.48.+c, 78.67.Ch, 71.15.Pd

I. INTRODUCTION

The high-pressure property of materials is one of the most important subjects in condensed matter physics. The high pressure experiments are considered as a standard tool for probing the structural transformation and stability, as well as the new structures. Recently, carbon nanotubes, one of the most exotic materials discovered in the past decades,[1–3] have been the objects of high-pressure experiments. The high-pressure studies provide most straightforward information on mechanical properties and structural changes of these unique quasi-one-dimensional materials. For single-walled carbon nanotubes (SWCNTs), the high-pressure experiments have demonstrated a pressure induced structural transformation.[4–9] The theoretical researches[10–13] are also carried out on either isolated SWCNTs or SWCNT bundles. These studies have shown a pressure induced hard-to-soft transition of SWCNTs, together with shape of the cross section changed from circular to elliptical.

Recently, high-pressure experiments on multiwalled carbon nanotubes (MWCNTs) have also been performed. Contrast to the simple structure of SWCNTs, MWCNTs consist of a set of concentric layers, which represent curved graphite sheets interacting with van der Waals (vdW) forces. Such a configuration of MWCNTs is also an excellent example for the core-shell structures commonly found in nature. The remarkable feature of this kind of shelly structure is its encapsulation effects, especially when the system is undergoing pressure, the outer shell acts as protector of the inner shell. Recently, high-pressure Raman spectroscopy has been successfully used in the study of MWCNTs.[14–17] It was found that the pressure transmission from outer tube to inner one is very small.[14] In one of the high-pressure experiments, Arvanitidis *et al.* found that the outer tubes do act as a protection shield for the inner tubes whereas the latter increase the structural stability of the outer tubes upon pressure application.[15] In addition, double-walled carbon nanotubes (DWCNTs), the simplest type of MWCNTs, have been studied theoretically.[18,19] A structural transformation similar to that of SWCNTs is found; however, the transition pressure is quite different from that of the SWCNTs due to the existence of the inner tube. All these studies show that MWCNTs have quite different response behavior to pressure from SWCNTs.

Although experimental efforts have been made to probe the pressure response of MWCNTs, we are still lacking a systematic understanding on how the pressure transmission happens between the individual tubes. For example, usually the outer tube is much softer than the inner tube, by what the outer tube protects the inner one; what is the key factor that affects the protection behavior; more important, can this protection effect be measured in a quantitative way? To the best of our knowledge, there is no any theoretical study carried out on the above questions.

In the present paper, we address the above-mentioned questions using the constant-pressure molecular dynamics method for finite systems.[20] Our results confirm that the pressure acting on the inner tube is much smaller than the external pressure before the MWCNTs structural transition occurs. The pressure transmission efficiency depends upon both the size and morphology combination of the MWCNTs. The paper is organized as follows. Following the computational details described in Sec. II, the calculated results are presented in Sec. III, and summary remarks are given in Sec. IV.

II. COMPUTATIONAL DETAILS

The present calculations are performed on six commensurate armchair/armchair DWCNTs $(n,n)@(n+5,n+5)$ (with $n=5,6,7,8,9,10$), two commensurate zigzag/zigzag DWCNTs $(10,0)@(19,0)$ and $(17,0)@(26,0)$, two incommensurate DWCNTs $(6,6)@(19,0)$ and $(10,10)@(26,0)$, and a triple-walled carbon nanotube (TWCNT) $(5,5)@(10,10)@(15,15)$. MWCNTs consisting of tubes which have the same chirality are typically commensurate; otherwise they are incommensurate. The radius difference between adjacent layers of all the tubes studied here is ~ 3.4 Å, which is very close to the ideal layer spacing of graphite.

The present studies use constant-pressure molecular dynamics (MD) method developed for finite systems.[20] The key point of this method is to write the volume of system as a function of atomic positions. This method is successfully

used for the SWCNT and MWCNT systems. For details of this method, the readers are referred to the original papers.[13,20] In all simulations, the periodic boundary condition in axial direction is adopted to mimic infinitely long tubes without any caps. For MWCNTs, pressure is applied on radial direction of the outer tube directly, the pressure transfers to the inner (middle) tube through the vdW forces between the tubes. Most simulations are carried out at 300 K, while the system temperature is controlled by using a Nosé-Hoover thermostat,[21] and all the atoms are allowed to move and kept to touch with the *heat bath*. The Nosé-Hoover thermostat is widely used in studying this kind of system.[13,22,23] The equations of motion are solved by using standard MD based on the Verlet type algorithm. A time step of 1.0 fs is used. The pressure is increased from 0 GPa, 100 ps equilibration is set for each increment of pressure. The equilibrated structure at 0 K is obtained by the simulated annealing method. The system is first heated up to around 1000 K, then the system is slowly cooled down with cooling rate ~0.01 K/fs. This process is repeated several times, the most stable configuration is thus obtained. With the stable structure for different pressure, the dynamic matrix is numerically calculated using the standard way.[24] By diagonalizing the dynamic matrix, one can easily obtain the phonon dispersive relation for each pressure.

To characterize the pressure transmission, we define a response pressure for the tubes. The response pressure is calculated in terms of Virial[25] and it is the actual pressure the tube "really" experiences. All the interactions contribute to the response pressure of MWCNTS as a whole, and the volume is defined as the volume encircled by the outer-most tube. The response pressure of an individual tube is calculated by taking only its own intratube interaction into account, and the volume is the volume encircled by the tube itself.

The Tersoff-type many-body potential[26] with the parameters given by Brenner (in this work we adopt the parameters from potential I),[27] is used for the covalent interactions between carbon atoms. This potential has been widely used to simulate diamond, graphite, carbon nanotubes, and many hydrocarbon complexes[28–33] and also used in our previous simulations.[12,13,18] The intertube and intratube vdW interactions are modeled by the Lennard-Jones (LJ) potential, $V_{vdW} = C_{12}/r^{12} - C_6/r^6$, where $C_6 = 20$ eV Å^6 and $C_{12} = 2.48 \times 10^4$ eV Å^{12}.[34,35] This approach has been successfully used to describe the mechanical properties and the phase transition of isolated DWCNT.[18] The cutoff of LJ potential is set as 15 Å in present work. The equilibrium pair separation of LJ potential is shifted to intratube equilibrium distance.

III. RESULTS AND DISCUSSIONS

The zero temperature structures of MWCNTs are obtained by a simulated annealing method, it is found that the circular cross sections of the tubes remain almost unchanged. Without external pressure, the response pressure of the inner tube of DWCNTs is negative, while the outer tube has positive response pressure. This implies an attractive interaction existing between the two tubes, which coincides with our previous work.[18]
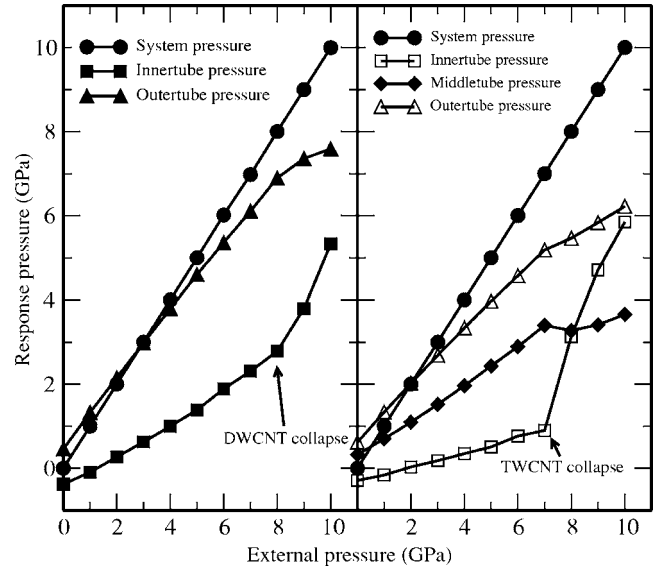

FIG. 1. Response pressure as a function of the external pressure for (5,5)@(10,10) DWCNT (left) and (5,5)@(10,10)@(15,15) TWCNT (right). The system response pressure is exactly the same as the external pressure. The response pressure of the inner tube is much smaller than that of the outer one before structural transition occurs.

vious work.[18] The similar behavior for TWCNT is also found. For all the cases, the residual pressure (response pressure without external pressure) is quite small, showing that the geometry configurations of the studied tubes match well.

The response pressure of the inner tube of all the studied MWCNTs is much smaller than the external pressure. Compared with the inner tube, the response pressure of the outer tube is much closer to the external pressure. The left panel of Fig. 1 shows the response pressure as functions of external pressure in (5,5)@(10,10) DWCNT. From this figure, it can be seen that the response pressure of both the inner and outer tube increases linearly with the external pressure below 8 GPa, while the value for the inner tube is about two times smaller than the outer one. As expected, the response pressure of (5,5)@(10,10) DWCNT as a whole is exactly the same as the external pressure. The present results clearly show that the outer tube does act as a shield for the inner tube. To further study response behavior of MWCNTs, TWCNT (5,5)@(10,10)@(15,15) under external pressure is also investigated. The result is shown on the right panel of Fig. 1. The protection is obvious for both the middle and the inner tube, as the response pressure of both the inner and the middle tubes is much smaller than the external pressure. Interestingly, for all the studied tubes, when the external pressure is higher than a certain value (~8 GPa for (5,5)@(10,10) and ~7 GPa for (5,5)@(10,10)@(15,15), see Fig. 1) the response pressure of the inner tube increases sharply, while increasing the response pressure of the outer tube slows down. According to our previous results,[18] the structural phase transition of carbon nanotube happens at this pressure, i.e., the cross section of carbon nanotube collapses from circle to ellipse. As soon as the tube collapses, the shield effect of the outer tube disappears. This behavior is
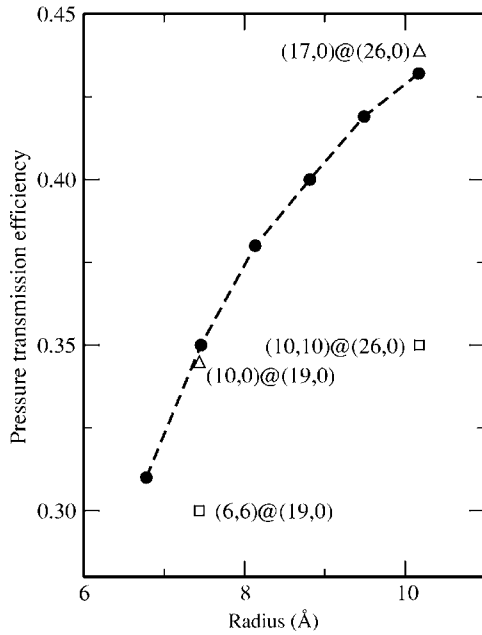
FIG. 2. Pressure transmission efficiency of commensurate armchair/armchair $(n,n)@(n+5,n+5)$ DWCNTs (with n $=5,6,7,8,9,10$) vs the outer tube radius (solid cycles). The commensurate zigzag/zigzag $(10,0)@(19,0)$, $(17,0)@(26,0)$ (open triangles), and incommensurate $(6,6)@(19,0)$, $(10,10)@(26,0)$ (open squares) DWCNTs are also shown for comparison. The transmission efficiency increases with the tube radius. The transmission efficiency of incommensurate DWCNTs is smaller than that of commensurate ones with the same size.

coincident to the softening of the tube after structural transition.[13]

Assuming a linear relationship between the response pressure and the external pressure before the structural transition happens, we define pressure transmission efficiency β by

$$P_r = \alpha + \beta P_e,$$

where P_r and P_e are the response pressure of the inner tube and the external pressure, respectively, α is the response pressure of the inner tube without external pressure. Figure 2 presents the pressure transmission efficiency of as a function of the radius of the outer tube. The pressure transmission efficiency is found to increase with the tube radius. This is understandable. The pressure acting on the inner tube is mainly attributed to the pressure-induced reduction of the interlayer spacing, the larger the radius is, the softer the tube will be. With the same external pressure, the outer tube with larger radius would be easier to compress and deform, then the intralayer vdW interaction becomes stronger. Therefore the pressure acting on the inner tube shielded by the larger outer one would be higher at the same external pressure. We note that the pressure transmission efficiency of all the commensurate tubes, regardless of zigzag/zigzag or armchair/amchair ones, follows the same trend.

In comparison to commensurate DWCNTs, the incommensurate DWCNTs have lower transmission efficiency. The pressure transmission efficiency are 0.30 and 0.35 for $(6,6)@(19,0)$ and $(10,10)@(26,0)$, respectively, while the
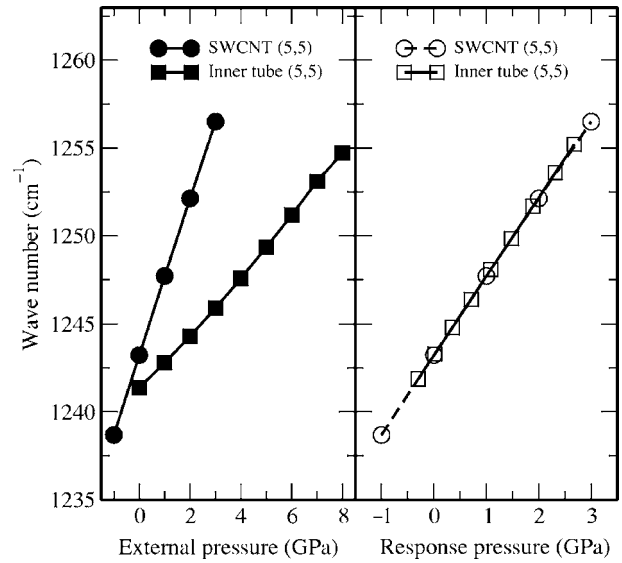

FIG. 3. Energy of the highest E_{2g} mode vs external pressure (left) and response pressure (right) for $(5,5)$ SWCNT and the same tube as inner one in a $(5,5)@(10,10)$ DWCNT.

pressure transmission efficiency of their commensurate counterpart $(6,6)@(11,11)$ and $(10,10)@(15,15)$ are 0.35 and 0.43, respectively. The present calculations show that the pressure transmission of the commensurate DWCNTs is more efficient. The morphology combination does affect the vdW interaction between inner and outer tubes. For the tubes with the same chirality, their periodic length in the axial direction is the same, which results in each atom having the optimal interaction with atoms in other tubes. This well-matched cases were also found to show large friction.[33,36] While for incommensurate ones, all the atoms cannot simultaneously reach the optimal interaction with neighbor tubes, thus the interaction between the inner and outer tubes is weaker. We can probably attribute the different pressure transmission efficiency to different interaction strengths in commensurate and incommensurate DWCNTs.

We have also compared the energy of the Raman active highest E_{2g} mode[37] as a function of pressure for both SWCNT and the same tube as inner one in a DWCNT. The left panel of Fig. 3 shows the energy versus pressure for the highest E_{2g} mode of $(5,5)$ SWCNT and the same tube as inner tube in a $(5,5)@(10,10)$ DWCNT. It can be seen that the energy shift is fairly linear for both cases. More importantly, we find that the energy of the highest E_{2g} mode is the same for one tube as SWCNT or shielded by an outer tube if actual pressure is taken into account. These results suggest that the pressure experienced by each individual tube itself determines the energy of the highest E_{2g} mode, no matter if it is SWCNT or a tube in MWCNT. Based on this fact, one can use Raman spectroscopy experiment to measure the energy of the highest E_{2g} mode and determine the actual pressure experienced by the inner tube. Then the pressure transmission efficiency can be determined experimentally. Fortunately, the high energy Raman active mode of individual tube in MWCNTs can already be measured through high pressure Raman spectroscopy,[15] which makes the suggested experimental method more realizable.

IV. SUMMARY

By using the constant-pressure molecular dynamics method specially developed for finite systems, the radial pressure transmission behavior of MWCNTs is studied. It is found that the response pressure of inner tube is much lower than the external pressure before structural transition happens. After structural transition, the response pressure of inner tube would increase sharply because the protection effect of the outer tube disappears. The pressure transmission efficiency increases with tube radius. Meanwhile the pressure transmission efficiency also depends upon morphology combination of MWCNTs. With the same size, the pressure transmission efficiency of commensurate MWCNTs is higher than that of incommensurate ones. We have found that the energy of the highest E_{2g} mode is only determined by the actual pressure the individual tube experiences, no matter if it is SWCNT or a tube in MWCNT. Based on the simulation results, we propose an experimental method to determine the pressure transmission efficiency of MWCNTs.

[1] S. Iijima, Nature (London) **354**, 56 (1991).

[2] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).

[3] B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, P. Bernier, and P. Poulin, Science **290**, 1331 (2000); R. H. Baughman, *ibid.* **290**, 1310 (2000).

[4] M. J. Peters, L. E. McNeil, J. P. Lu, and D. Kahn, Phys. Rev. B **61**, 5939 (2000).

[5] U. D. Venkateswaran, A. M. Rao, E. Richter, M. Menon, A. Rinzler, R. E. Smalley, and P. C. Eklund, Phys. Rev. B **59**, 10928 (1999).

[6] A. K. Sood, Pallavi V. Teresdesai, D. V. S. Muthu, Rahul. Sen, A. Govindaraj, and C. N. R. Rao, Phys. Status Solidi B **215**, 393 (1999).

[7] Pallavi V. Teredesai, A. K. Sood, D. V. S. Muthu, Rahul. Sen, A. Govindaraj, and C. N. R. Rao, Chem. Phys. Lett. **319**, 296 (2000).

[8] J. Tang, L. C. Qin. T. Sasaki, M. Yudasaka, A. Matsushita, and S. Iijima, Phys. Rev. Lett. **85**, 1887 (2000).

[9] S. Rols, I. N. Goncharenko, R. Almairac, J. L. Sauvajol, and I. Mirebeau, Phys. Rev. B **64**, 153401 (2001).

[10] S. P. Chan, W. L. Yim, X. G. Gong, and Z. F. Liu, Phys. Rev. B **68**, 075404 (2003).

[11] J. A. Elliott, J. K. W. Sandler, A. H. Windle, R. J. Young, and M. S. P. Shaffer, Phys. Rev. Lett. **92**, 095501 (2004).

[12] X. H. Zhang, D. Y. Sun, and X. G. Gong, Phys. Rev. B **70**, 035422 (2004); X. H. Zhang, Z. F. Liu, and X. G. Gong, Phys. Rev. Lett. **93**, 149601 (2004).

[13] D. Y. Sun, D. J. Shu, M. Ji, Feng Liu, M. Wang, and X. G. Gong, Phys. Rev. B **70**, 165417 (2004).

[14] P. Puech, H. Hubel, D. J. Dunstan, R. R. Bacsa, C. Laurent, and W. S. Bacsa, Phys. Rev. Lett. **93**, 095506 (2004).

[15] J. Arvanitidis, D. Christofilos, K. Papagelis, K. S. Andrikopoulos, T. Takenobu, Y. Iwasa, H. Kataura, S. Ves, and G. A. Kourouklis, Phys. Rev. B **71**, 125404 (2005).

[16] R. Pfeiffer, F. Simon, H. Kuzmany, and V. N. Popov, Phys. Rev. B **72**, 161404(R) (2005).

[17] P. Puech, 1, A. Bassil, J. Gonzalez, Ch. Power, E. Flahaut, S. Barrau, Ph. Demont, C. Lacabanne, E. Perez, and W. S. Bacsa, Phys. Rev. B **72**, 155436 (2005).

[18] X. Ye, D. Y. Sun, and X. G. Gong, Phys. Rev. B **72**, 035454 (2005).

[19] Vikram Gadagkar, Prabal K. Maiti, Yves Lansac, A. Jagota, and A. K. Sood, Phys. Rev. B **73**, 085402 (2006).

[20] D. Y. Sun and X. G. Gong, J. Phys.: Condens. Matter **14**, L487 (2002).

[21] S. Nosé, Mol. Phys. **52**, 255 (1984); W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).

[22] Zhenhua Yao, Jian-Sheng Wang, Baowen Li, and Gui-Rong Liu, Phys. Rev. B **71**, 085417 (2005).

[23] Ping-Chi Tsai, Yeau-Ren Jeng, and Te-Hua Fang, Phys. Rev. B **74**, 045406 (2006).

[24] Lei Liu, C. S. Jayanthi, and Shi-Yu Wu, Phys. Rev. B **68**, 012303 (2003).

[25] R. J. Swenson, Am. J. Phys. **51**, 940 (1982).

[26] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).

[27] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).

[28] D. H. Robertson, D. W. Brenner, and J. W. Mintmire, Phys. Rev. B **45**, 12592 (1992).

[29] B. I. Yakobson, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett. **76**, 2511 (1996).

[30] M. B. Nardelli, B. I. Yakobson, and J. Bernholc, Phys. Rev. Lett. **81**, 4656 (1998).

[31] Y. Xia, Y. Ma, Y. Xing, Y. Mu, C. Tan, and L. Mei, Phys. Rev. B **61**, 11088 (2000).

[32] Y. Ma, Y. Xia, M. Zhao, R. Wang, and L. Mei, Phys. Rev. B **63**, 115422 (2001).

[33] A. N. Kolmogorov and V. H. Crespi, Phys. Rev. Lett. **85**, 4727 (2000).

[34] L. A. Girifalco and R. A. Lad, J. Chem. Phys. **25**, 693 (1956).

[35] L. Henrard, E. Hernndez, P. Bernier, and A. Rubio, Phys. Rev. B **60**, R8521 (1999).

[36] Wanlin Guo, Yufeng Guo, Huajian Gao, Quanshui Zheng, and Wenyu Zhong1, Phys. Rev. Lett. **91**, 125501 (2003).

[37] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College, 2003), p. 200.