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Computational investigation of the mechanical properties of nanomaterials

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ABSTRACT

The mechanical responses of carbon nanotubes are examined using classical molecular dynamics simulations. Several different types of nanotubes are considered, including pristine single-walled tubes that are empty, filled with fullerenes to form peapods, filled with other nanotubes to form multi-walled tubes, or chemically functionalized. In addition, the responses of single-walled nanotubes with wall vacancies are considered. The results show how the bending force of filled nanotubes increases relative to the bending force of empty nanotubes and indicates how these increases come about. In addition, the simulations reveal the way in which the magnitude of these increases depend on the type of filling material and, in the case of multi-walled tubes, the number of inner tubes. These simulations further illustrate the way in which the inner nanotubes support higher external loads than the fullerenes in cases when the outer nanotubes are identical. The results also indicate that both the bending and buckling forces depend on temperature and the reasons for this dependence are discussed. Lastly, the simulations demonstrate the way in which the introduction of vacancy defects and covalently bound functional groups to the nanotube walls degrades the nanotubes' mechanical properties.

1. Introduction

Carbon nanotubes (CNTs) have a unique combination of electrical and mechanical properties such as high conductivity, strength and toughness. These properties make them attractive for use as components in nanoelectromechanical systems (NEMS), where they would be subjected to various types of forces such as compression, bending, tension, and torsion. Additionally, CNTs used as tips of atomic force microscopes (AFM) experience both compression and bending during surface contact and scanning. Consequently, there has been intense interest in qualitatively understanding and quantifying the mechanical responses of CNTs.

For example, Ijima et al. [1] found that atomistic simulations of the responses of nanotubes to bending are comparable to images of bent tubes observed in high resolution electron microscope images. Yakobson et al. [2] used similar simulations to examine the mechanical responses of single-walled carbon nanotubes (SWNTs) under axial compression, bending, and torsion. Their results indicated that nanotubes exhibit great flexibility, and may be severely deformed without breaking any chemical bonds. In addition, Garg and Sinnott [3] predicted that heavy chemical functionalization of CNT walls leads to slightly lower SWNT buckling forces because of the disruption of the nanotube wall lattice by the covalent attachment of the functional groups.

The basic mechanical properties of filled SWNTs have been also investigated by Ni et al. [4] who found that filling CNTs with fullerenes, CH_4 or Ne increases the loads at which bucking occurs and decreases the effect of temperature on buckling. Additionally, Danailov et al. [5] predicted that filling SWNTs with Au nanowires increases the maximum bending force and the deflection to buckling. In an analogous study Trotter et al. [6] explored the compressibility of CNTs filled with diamond nanowires, smaller nanotubes, C_{60}, CH_4, Ne, n-C_4H_{10}, or n-C_4H_7 molecules. They observed that nanowire-filled CNTs and multi-walled CNTs (MWNTs) exhibit similar mechanical responses and that filling CNTs increases their stiffness during compression. Jeong et al. [7–9] also investigated the effect of filling CNTs on the tensional, torsional, combined tensional and torsional, and biaxial tensional and torsional properties. They observed that these mechanical properties can be improved by filling CNTs, but the failure criteria are different depending on the deformation modes. Other computational methods besides strictly atomistic simulations have also been applied. For instance, the buckling of single-walled and double-walled nanotubes with molecular mechanics and finite element simulations have been examined by Sears and Batra [10]. In addition, elastic shell model calculations have been used by Wang et al. [11] to investigate the influence of filling nanotubes with other tubes on their response to a combination of bending and axial compression. These studies predict that higher forces are required to deform multi-walled nanotubes relative to single-walled nanotubes.

Here, the mechanical responses of pristine hollow, C_{60}-filled, n-butane-filled, and multi-(dual-, triple- and quadruple-) walled CNTs under bending forces at various temperatures are examined using

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classical molecular dynamics (MD) simulations. The results are compared to the responses of CNTs with covalently bonded functional groups and wall vacancies. They provide insights into the atomic-scale mechanisms responsible for the differing responses under these various conditions.

2. Computational details

In the simulations of bending CNTs, the forces and the deflections are calculated using the second generation reactive empirical bond order (REBO) potential [12] for the short-range covalent interactions between carbon atoms, and the Lennard–Jones (LJ) potential for the long-range van der Waals interactions between the CNT wall and the filling materials, including C_{60}, organic molecules, or another CNT wall. These van der Waals interactions may play a critical role in influencing the mechanical behavior of the filled CNTs as they do in phase transitions of solid C_{60} [13], and the Raman spectra [14] and vibrational modes of CNT bundles [15] where non-bonded interactions between separate carbon structures are important.

The second generation REBO potential is descended from the Tersoff [16] potential, which has been widely used to model covalently bound materials. In 1990 Brenner extended the capabilities of the Tersoff potential to model solid state carbon materials and hydrocarbon molecules [17]. This potential, originally known as the Brenner and now referred to as REBO, was subsequently used to provide insights into a number of processes, including, for example, the compression of CNTs [2,18], nanoindentation [19], and tribochemistry [20]. The second generation version improved on the properties of the first by both making the analytic functions more physical and extending the fitting database, while maintaining the potential's ability to describe a diverse set of carbon-based materials. In addition, unlike standard molecular models, it allows covalent bond breaking and forming.

There have been several comparisons of the predictions of the REBO potential to experimental data and *ab-initio* results [21–24]. These comparisons indicate that it provides reasonable predictions, but, as is the case with most empirical potentials, there are instances where it performs less well. For instance, the energies of adjacent pentagons in fullerenes are not well described [25,26], and the short cutoff distance for covalent bonds (0.2 nm for C–C bonds) affects phase transitions [27–29], sticking coefficients in low-energy deposition [29,30], and bond-stretching in tensile stressing of CNTs [31–33]. Nonetheless, the REBO potential has previously been shown to do well at predicting the bending of CNTs as compared to experiment [1] and the torsional deformation of CNTs as compared to classical mechanics [7–9,33], which gives confidence in the results reported here.

The CNTs considered in this paper are hollow (10,10) SWNTs, (10,10) SWNTs filled with n-butane, (10,10) SWNTs filled with C_{60} (peapods), (10,10) SWNTs filled with (5,5) SWCNTs (called a (10,10)@(5,5) double-walled CNT or DWNT), (15,15)@(10,10)@(5,5) triple-walled carbon nanotubes (TWNTs), (20,20)@(15,15)@(10,10)@(5,5) quadruple-walled carbon nanotubes (QWNTs). All these CNTs are about 10 nm long and capped at both ends except for the outermost (20,20) CNTs in the QWNTs.

Three different types of vacancies are introduced on the surface walls of the hollow (10,10) SWNTs: a single vacancy, two vacancies that are next to each other along the nanotube circumference, and two vacancies that are facing each other along the nanotube circumference. As determined theoretically in previous studies [34–36], each of the three carbon atoms near a vacancy has one dangling bond. In addition, hollow (10,10) SWNTs that have $H_2C{=}C$ groups covalently bound and randomly distributed along the walls are considered to address their influence on mechanical responses. The density of functional groups considered is 0.05 g/cm^3 (or a SWNT/$H_2C{=}C$ weight ratio of 35.08), 0.10 g/cm^3 (or a SWNT/$H_2C{=}C$ weight ratio of 17.54), and 0.20 g/cm^3 (or a SWNT/$H_2C{=}C$ weight ratio of 8.77).

The bending of the CNT is achieved by using a three-point bend test, as illustrated in Fig. 1. The reverse bending forces are applied to the center region and both tube ends of the CNT. The entire force on the center region is equivalent and opposite to the summation of the

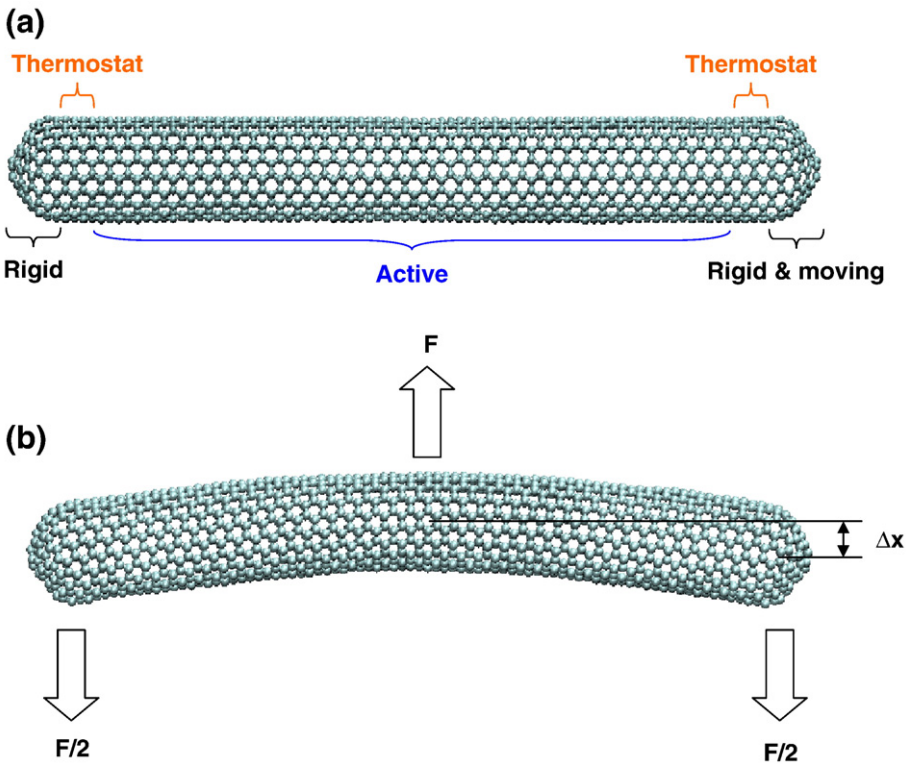

Fig. 1. Snapshots of 10 nm (10, 10) hollow CNT for (a) compression and (b) bending. The rigid, thermostat, and active regions are designated on the CNT. All atoms in CNT are active during the bending test.

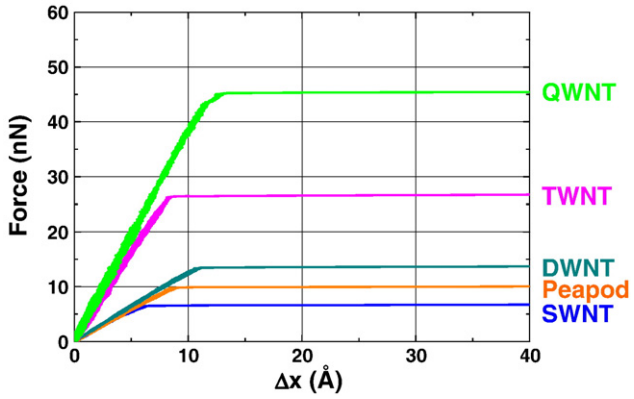

Fig. 2. Force versus deflection of various 10 nm (10, 10) hollow and filled CNTs during bending.

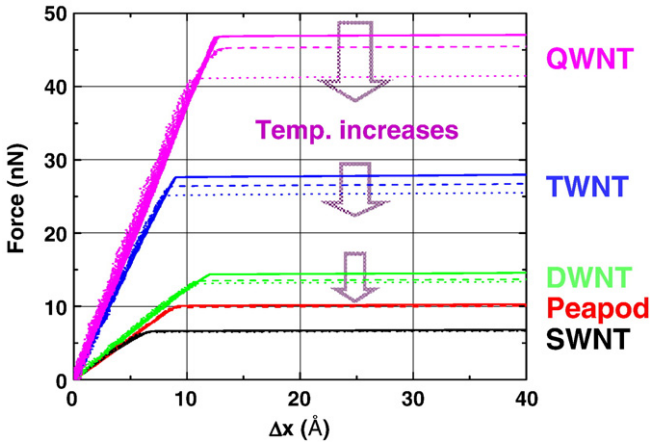

Fig. 4. The plot of forces versus deflections of various 10 nm (10, 10) hollow and filled CNTs during the bending test at different temperatures (solid line = 100 K, dashed line = 300 K, and dotted line = 600 K).

forces applied on both ends of the CNT. The bending force is increased gradually at a rate that increases deflection by 0.1 nm every 100,000 MD time steps. In the bent CNT all the atoms are subjected to classical Newtonian equations of motion along with a velocity rescaling thermostat instead of the Langevin thermostat. This is to avoid the restraint effect of the Langevin thermostat [37] that can disturb the movement of atoms as a result of the stochastic force term.

3. Results and discussion

The predicted force versus deflection of various (10, 10) hollow and filled CNTs during the bending tests are illustrated in Fig. 2. Nanotube deflection, Δx, increases linearly with the bending force in the low force region. Both hollow and filled CNTs undergo buckling with increasing bending force, beyond which they cannot support the external bending force. It is further predicted that the bending force of the (10,10) peapod is larger than that of the (10,10) SWNT in agreement with the MD simulation results of Zhu et al. [38]. In addition, the bending force of the (5,5)@(10,10) DWNT is larger than that of the peapod, such that the order of bending deflections is $\Delta x_{DWNT} > \Delta x_{Peapod} > \Delta x_{SWNT}$.

This result illustrates the manner in which filling can make nanotubes more resistant to external bending forces and the way in which the degree of resistance can be engineered by optimizing the filling material. The increased resistance to buckling on the part of the filled nanotubes is caused by the inability of the walls of the filled tubes to collapse as they are able to do when the nanotube interior is empty. The inner CNTs in the multi-walled nanotubes are able to sustain higher external forces than the fullerenes, so higher forces are required to deflect them. In addition, the fullerenes in the peapod are able to move slightly away from the deflection point in a way that the inner CNTs are not, which ultimately lowers the bending force of the peapods. Consequently, the highest external buckling force is required for the DWNT, and the second highest is observed for the peapod.

Fig. 2 also indicates that the bending forces increase as the number of nanotube shells increase, with the maximum bending deflection exhibiting dependence on the number of shells present in the system. This is due to the extra force required to deflect the additional nanotubes in the MWNT as the number of shells increases. This prediction is consistent with experimental observations [39] that SWNTs are substantially more flexible than MWNTs.

Fig. 3 shows snapshots from the MD simulations of the SWNT, peapod, DWNT, and TWNT just after buckling occurs. It illustrates the way in which the deformed region is spread along a longer region near the center of the SWNT, whereas it is more concentrated at the center of the peapod, DWNT and TWNT. This is consistent with the fact that the peapod, DWNT and TWNT are more resistant to bending than the SWNT.

The bending simulations are repeated at different temperatures to determine the effect of variations in thermal fluctuations on the CNT mechanical responses. The predicted forces versus deflection are given in Fig. 4. The results indicate that the maximum bending forces of the nanotubes decrease with temperature regardless of whether the CNTs are filled or not. This is because the higher temperatures increase the flexibility of the nanotubes, which lowers the force needed to achieve deflection. Similar decreases in bending strength were predicted by Jeng et al. [40] in MD simulations where peapods were indented with proximal probe tips over a range of temperatures. The extent of the deflection force decrease is predicted to be largest for the QWNT and to decrease as the number of shells decrease. This trend

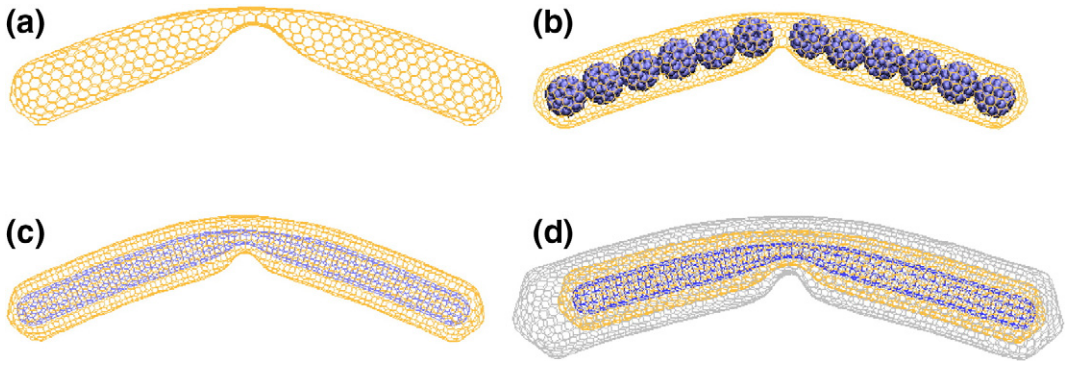

Fig. 3. Snapshots of 10 nm long (a) SWNT, (b) C_{60} filled SWNT, (c) DWNT, and (d) TWNT after the buckling events given in Fig. 2.

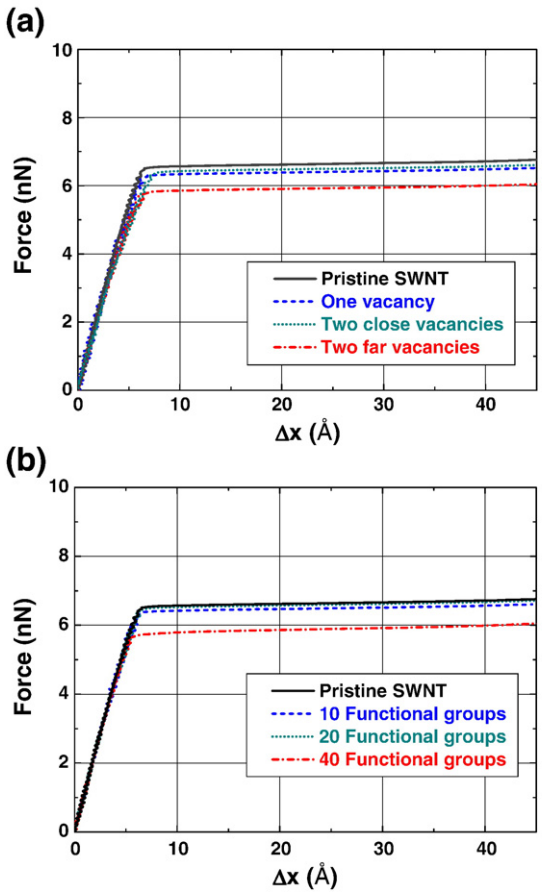

Fig. 5. Force versus deflection of 10 nm (10, 10) hollow pristine CNTs and CNTs having various densities of (a) vacancy defects and (b) functional groups.

is due to the fact that more nanotubes are softened in the QWNT than the other MWNTs considered, and so the cumulative decrease is largest for the multi-walled nanotubes with the largest number of shells.

Importantly, the slopes of the curves are roughly constant regardless of the temperature, which is consistent with the finding that the Young's modulus of the CNTs remains approximately constant during compression as the temperature increases. Jeng et al. [41] suggested that the mechanical properties of CNTs are insensitive to the thermal state of the system at small deformations during tensile testing, but are sensitive under large deformation. This means that the mechanical properties of CNTs, such as Young's modulus, are insensitive to thermal conditions but the thermal motion of the atoms may be important for obtaining the correct maximum buckling force.

During the synthesis or purification of CNTs defects, such as vacancies, can be introduced into the nanotube walls. CNTs also can be treated to covalently attach chemical groups to the sides [42] or ends [43]. In these cases the sp^2-hybridization of the carbon atoms around the defects and functional groups are altered. To investigate the effect of wall defects on the mechanical responses of the CNTs, two types of defects, vacancies and H_2C=C functional groups, are introduced on the CNT surface and the effects of these defects on the bending of the CNTs are considered. Fig. 5 indicates that the maximum bending forces decreases as the number of wall defects and the density of the functional groups increase. The reason for this decrease is attributed to the disruption in the fidelity of the graphene lattice that makes up the nanotube walls. In the case of bent SWNTs, the vacancy defects are located at the ends of the buckles. In addition, the buckles always occur in the middle of the SWCNTs during bending because the forces are applied to the middle and ends of CNTs.

4. Conclusions

The simulations discussed here predict that filling SWNTs increases their maximum deflection during bending. MWNTs are predicted to support higher external loads than SWNTs and peapods because the inner CNTs sustain higher external forces than the fullerenes, and the fullerenes are mobile enough to slightly remove themselves from the point of nanotube collapse during deflection. This mechanical behavior of hollow or filled CNTs is predicted to deteriorate at high temperatures, with a greater deterioration predicted for multi-walled nanotubes than peapods or SWNTs. The chemical modification of the CNT wall through the generation of vacancies or the attachment of functional groups is also predicted to weaken the ability of CNTs to withstand bending because of disruptions in the graphene lattice structure that makes up the CNT walls.

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References

[1] S. Iijima, C. Brabec, A. Maiti, J. Bernholc, J. Chem. Phys. 104 (1996) 2089.
[2] B.I. Yakobson, C.J. Brabec, J. Bernholc, Phys. Rev. Lett. 76 (1996) 2511.
[3] A. Garg, S.B. Sinnott, Chem. Phys. Lett. 295 (1998) 273.
[4] B. Ni, S.B. Sinnott, P.T. Mikulski, J.A. Harrison, Phys. Rev. Lett. 88 (2002) 205505.
[5] D. Danailov, P. Keblinski, S. Nayak, P.M. Ajayan, J. Nanosci. Nanotechnol. 2 (2002) 503.
[6] H. Trotter, R. Phillips, Y. Hu, B. Ni, S.B. Sinnott, P. Mikulski, J.A. Harrison, J. Nanosci. Nanotechnol. 5 (2005) 536.
[7] B. Jeong, J.-K. Lim, S.B. Sinnott, Appl. Phys. Lett. 91 (2007) 093102.
[8] B. Jeong, J.-K. Lim, S.B. Sinnott, Nanotechnology 18 (2007) 485715.
[9] B.-W. Jeong, J.-K. Lim, S.B. Sinnott, J. Appl. Phys. 101 (2007) 084309.
[10] A. Sears, R.C. Batra, Phys. Rev. B 73 (2006) 085410.
[11] X. Wang, B. Sun, H.K. Yang, Nanotech. 17 (2006) 815.
[12] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, S.B. Sinnott, J. Phys. Condensed Matter 14 (2002) 783.
[13] J.P. Lu, X.P. Li, R.M. Martin, Phys. Rev. Lett. 68 (1992) 1551.
[14] U.D. Venkateswaran, A.M. Rao, E. Richter, M. Menon, A. Rinzler, R.E. Smalley, P.C. Eklund, Phys. Rev. B 59 (1999) 10928.
[15] L. Henrard, E. Hernandez, P. Bernier, A. Rubio, Phys. Rev. B 60 (1999) R8521.
[16] J. Tersoff, Phys. Rev. B 37 (1988) 6991.
[17] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
[18] C.F. Cornwell, L.T. Wille, Solid State Comm. 101 (1997) 555.
[19] J.A. Harrison, R.J. Colton, C.T. White, D.W. Brenner, Mat. Res. Soc. Sym. Proc. 239 (1992) 573.
[20] J.A. Harrison, D.W. Brenner, J. Am. Chem. Soc. 116 (1994) 10399.
[21] P. de_Sainte_Clare, K. Son, W.L. Hase, D.W. Brenner, J. Am. Chem. Soc. 100 (1996) 1761.
[22] B. Ni, R. Andrews, D. Jacques, D. Qian, M.B.J. Wijesundara, Y.S. Choi, L. Hanley, S.B. Sinnott, J. Phys. Chem. B 105 (2001) 12719.
[23] Y. Hu, S. Shen, L. Liu, S.-Y. Wu, C. Jayanthi, S.B. Sinnott, J. Chem. Phys. 116 (2002) 6738.
[24] I. Jang, D.L. Burris, P.L. Dickrell, P.R. Barry, C. Santos, S.S. Perry, S.R. Phillpot, S.B. Sinnott, W.G. Sawyer, J. Appl. Phys. 102 (2007) 123509.
[25] E. Albertazzi, C. Domene, P.W. Fowler, T. Heine, G. Seifert, C. Van Alsnoy, F. Zerbetto, Phys. Chem. 1 (1999,) 2913.
[26] D. Troya, S.L. Mielke, G.C. Schatz, Chem. Phys. Lett. 382 (2003,) 133.
[27] H.U. Jäger, K. Albe, J. Appl. Phys. 88 (2000) 1129.
[28] K. Nordlund, J. Keinonen, T. Mattila, Phys. Rev. Lett. 77 (1996) 699.
[29] O.A. Shenderova, D.W. Brenner, A. Omeltchenko, X. Su, L.H. Yang, Phys. Rev. B 61 (2000) 3877.
[30] P. Träskelin, E. Salonen, K. Nordlund, A.V. Krasheninnikov, C.H. Wu, J. Appl. Phys. 93 (2003) 1826.
[31] T. Belytschko, S.P. Xiao, G.C. Schatz, R.S. Ruoff, Phys. Rev. B 65 (2002) 235430.
[32] M. Sammalkorpi, A.V. Krasheninnikov, A. Kuronen, K. Nordlund, K. Kaski, Phys. Rev. B 70 (2004) 245416.
[33] B.-W. Jeong, J.-K. Lim, S.B. Sinnott, Appl. Phys. Lett. 90 (2007) 023102.

[34] M. Igami, T. Nakanishi, T. Ando, J. Phys. Soc. Jpn. 68 (1999) 716.
[35] H.J. Choi, J. Ihm, S.G. Louie, M.L. Cohen, Phys. Rev. Lett. 84 (2000) 2917.
[36] J. Ihm, A. Zunger, M.L. Cohen, J Phys. C Solid State 12 (1979) 4409.
[37] S. Heo, S.B. Sinnott, J. Nanosci. Nanotechnol. 7 (2007) 1518–1524.
[38] J. Zhu, Z.Y. Pan, Y.X. Wang, L. Zhou, Q. Jiang, Nanotech. 18 (2007) 275702.
[39] J. Muster, M. Burghard, S. Roth, G.S. Duesberg, E. Hernandez, A. Rubio, J. Vac. Sci. Technol. B 16 (1998) 2796.
[40] Y.-R. Jeng, P.-C. Tsai, T.-H. Fang, J. Chem. Phys. 122 (2005) 224713.
[41] Y.R. Jeng, P.C. Tsai, T.H. Fang, J. Phys. Chem. Solids 65 (2004) 1849.
[42] J. Chen, M.A. Hamon, H. Hu, Y.S. Chen, A.M. Rao, P.C. Eklund, R.C. Haddon, Science 282 (1998) 95.
[43] S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung, C.M. Lieber, Nature 394 (1998) 52.