The strain energy and Young’s modulus of single-wall carbon nanotubes calculated from the electronic energy-band theory

Zhou Xin\(^1\), Zhou Jianjun\(^\star\) and Ou-Yang Zhong-can\(^{1,2}\)

\(^1\)Institute of Theoretical Physics, The Chinese Academy of Sciences, P. O. Box 2735, Beijing 100080, China

\(^2\)Center for Advanced Study, Tsinghua University, Beijing 100084, China

(March 21, 2022)

Abstract

The strain energies in straight and bent single-walled carbon nanotubes (SWNTs) are calculated by taking account of the total energy of all the occupied band electrons. The obtained results are in good agreement with previous theoretical studies and experimental observations. The Young’s modulus and the effective wall thickness of SWNT are obtained from the bending strain energies of SWNTs with various cross-sectional radii. The repulsion potential between ions contributes the main part of the Young’s modulus of SWNT. The wall thickness of SWNT comes completely from the overlap of electronic orbits, and is approximately of the extension of \(\pi\) orbit of carbon atom. Both the Young’s modulus and the wall thickness are independent of the radius and the helicity of SWNT, and insensitive to the fitting parameters. The results show that continuum elasticity theory can serve well to describe the mechanical properties of SWNTs.

PACS numbers: 61.48.+c, 63.20.Dj, 71.20.HK, 71.25.-s
Since their discovery in 1991, Carbon nanotubes (CNTs) have invoked considerable interest in the last decade. There are many works on both the theoretical and the experimental studies about the electronic structure of CNTs, and many exciting and novel properties have been discovered. For example, it was found that the insulating, semimetallic, or metallic behavior depends upon the radius and the helicity of CNT. On the thermal and the mechanical properties, the tubes are significantly stiffer than any material presently known. To understand these many intriguing properties, many groups have calculated the strain energy and the Young’s modulus of single-wall carbon nanotubes (SWNTs). Among these calculations, many depend on the choice of an empirical potential between the carbon atoms, such as Tersoff-Brenner potential. Lenosky et al. employed an empirical model with three parameters reducible to a continuous model with two elastic moduli. They showed that the continuum elasticity model serves well to describe the deformation of multi-wall carbon nanotubes (MWNTs). Recent theoretical studies on the Young’s moduli of SWNTs show some discrepancies coming from the adoption of different empirical potentials and different relations in the continuum elasticity theory (CET), especially, the different values of the effective wall thickness of SWNT. How to calculate the Young’s modulus of SWNT is still an open question.

Here we present a simple method for the computation of the strain energy of straight SWNTs directly from the electronic band structure without introducing any empirical potential. This method had also been extended to calculate the strain energy of bent tubes. It is found that the wall thickness of SWNTs can be calculated simply from the band electrons, and the Young’s modulus by consideration of both the repulsion energy between ions and the bond-length dependencies of the electronic energy. Our results show that CET can well describe the bending of SWNTs and that both the Young’s modulus and the effective wall thickness are independent of the radius and the helicity of the tubes, and insensitive to the fitting parameters. We obtained the Young’s modulus of SWNT about 5 TPa, 5 times larger than the value of MWNT or graphite bulk samples, and the effective wall thickness about 0.7 Å, the size of carbon atom.

Generally, the total energy of the carbon system is given by the sum:

\[ E_{total} = E_{el} + E_{rep}, \]  

(1)

where \( E_{el} \) is the sum of the energy of band electrons of the occupied states and \( E_{rep} \) is given by a repulsive pair potential depending only on the distance between two carbon atoms. They are given by

\[ E_{el} = \sum_{occ} E_k, \]  

(2)

and

\[ E_{rep} = \sum_i \sum_{j>i} \phi(r_{ij}), \]  

(3)

, respectively. Since \( \phi(r) \) is a short-range potential, only interaction between neighbor atoms needs to be considered. On account of the relaxation effect, the bond length of SWNT is slightly larger than that of graphite (\( r_0 = 1.42 \) Å). However, even in \( C_{60} \), for
which the relaxation effect is significant on account of its small radius, calculations show that the energy contribution of the bond-relaxation can still be safely ignored. The total energy can now be rewritten as:

\[ E_{total} = \frac{1}{2} \sum \mathcal{E}_0 \cdot (\delta r_{ij})^2 + E_{ang}, \]  

(4)

where the first term on the right hand side of \( E_{total} \) is the sum of the repulsion energy between ions and the electronic energy contribution of the bond length change with \( \delta r_{ij} \) as the change of the distance between the \( i \)th and the \( j \)th atoms in SWNT from that in graphene. The second term is the electronic energy contribution of the angular change of the bond, when rolling from graphene to SWNT. The positions of the atoms of straight SWNTs are located on the cylindrical surface of the tube when the relaxation effect of the bonds is neglected. \( \delta r_{ij} \) is proportional to \( \rho^{-2} \), where \( \rho \) is the cross-sectional radius of SWNT, and the first term of Eq. (4) can be ignored, since it is of \( \rho^{-4} \) order. Therefore, the strain energy of straight SWNTs comes from the curvature-induced electronic energy change, and can be obtained by taking account of the electronic energy of all the occupied bands.

In order to calculate the electronic energy bands of SWNTs, we use a simple nearest-neighbor tight-binding (TB) model. This model contains nine TB parameters of graphite: Four hopping including, \( V_{ss\sigma} = -6.679, V_{sp\pi} = -5.580, V_{pp\pi} = 5.037, V_{pp\sigma} = -3.033 \) in unit of eV; four overlapping integration including, \( S_{ss\sigma} = 0.212, S_{sp\pi} = 0.102, S_{pp\sigma} = -0.146, S_{pp\pi} = 0.129 \) and an energy difference between the 2s orbit and the 2p orbit of the carbon atoms \( \Delta \mathcal{E} = (\mathcal{E}_{2s} - \mathcal{E}_{2p}) = -8.868 \) eV. The model has been used widely for the calculation of the electronic properties of both graphenes and SWNTs. In general, these TB parameters depend upon the bond-length in the way

\[ V_{\lambda'\mu}(r) = V_{\lambda\mu}(r_0) \cdot \exp(-\gamma(r - r_0)). \]  

(5)

However, in case of straight SWNTs, the \( \rho^{-2} \) order dependence of the strain energy will not be affected even if we ignore simultaneously these dependencies and the repulsion energy.

With the notation used by White et al., each SWNT is indexed by a pair of integers \((n_1, n_2)\) corresponding to the lattice vector \( R = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \) on the graphene, where \( \mathbf{a}_1, \mathbf{a}_2 \) are the unit cell vectors of the graphene. The tube structure is obtained by a rotation operation \( C_N \) and a screw operation \( S(h, \alpha) \). The operation \( C_N \) is a rotation of \( \frac{2\pi}{N} \) about the axis, where \( N \) is the largest common factor of \( n_1 \) and \( n_2 \). The \( S(h, \alpha) \) operation is a rotation of an angle \( \alpha \) about the axis of SWNT in conjunction with a translation of \( h \) units along the axis, which both \( h \) and \( \alpha \) depending on the tube parameters. Let \([m, l]\) denote a primitive unit cell in the tube generated by mapping the \([0, 0]\) cell to the surface of the cylinder first and then translating and rotating this cell by \( l \) applications of the rotational operator \( C_N \) followed by \( m \) applications of \( S(h, \alpha) \). Because \( S(h, \alpha) \) and \( C_N \) commute with each other, we can generalize the Bloch sums, and obtain the Hamiltonian matrix:

\[
\mathcal{H}_{ij}^{AA}(k, n) = \mathcal{H}_{ij}^{BB}(k, n) = \mathcal{E}_i \delta_{ij}, \\
\mathcal{H}_{ji}^{BA}(k, n) = (\mathcal{H}_{ij}^{AB}(k, n))^* , \\
\mathcal{H}_{ij}^{AB}(k, n) = \sum_r \exp[\frac{2\pi i}{N} \Delta l(r) + i k \Delta m(r)] V_{ij}^{AB}(r),
\]

(6)
where \([\Delta m(r), \Delta l(r)]\) for \(r = 1, 2, 3\) are the cell indices of the primitive unit cells located by the three nearest-neighbor atoms \(B\) of atom \(A\) in the tube. \(A\) and \(B\) are two independent carbon atoms in a primitive unit cell of SWNT. Let \(n = 0, 1, \ldots, N - 1\) represent the \(N\) sub-Brillouin Zones, \(k\) be a one-dimensional wave vector. \(\mathcal{E}_1 = \mathcal{E}_{2s}, \mathcal{E}_i = \mathcal{E}_{2p}\) for \(i = 2, 3, 4\). Taking the \(2p\) wave function as a vector and \(2s\) wave function a scalar, one can easily obtain:

\[
\begin{align*}
V_{p_i,p_j}^{AB}(r) &= (\hat{e}_{A_i} \cdot \hat{e}_{B_j(r)}) V_{pp\pi} \\
&- (\hat{e}_{A_i} \cdot \hat{u}_r)(\hat{e}_{B_j(r)} \cdot \hat{u}_r)(V_{pp\pi} - V_{pp\sigma}), \\
V_{s,p_i}^{AB}(r) &= (\hat{e}_{B_i(r)} \cdot \hat{u}_r)V_{sp\sigma}, \\
V_{p_i,s}^{AB}(r) &= -(\hat{e}_{A_i} \cdot \hat{u}_r)V_{sp\sigma}, \\
V_{s,s}^{AB}(r) &= V_{ss\sigma}.
\end{align*}
\]

(7)

where \(\hat{u}_r\) \((r = 1, 2, 3)\) be the unit vector from the atom \(A\) to its three neighboring atoms \(B\). \(\hat{e}_{A_i}\) and \(\hat{e}_{B_j(r)}\) are the unit vector of the \(2p_i\) wave function of atom \(A\) and the unit vector of the \(2p_j\) wave function of atom \(B\), respectively. The overlapping integration matrix \(\mathcal{S}(k, n)\) has the same form as the Hamiltonian matrix, with four overlapping integration parameters to replace the four hopping integration parameters, and with unit to replace the energy of \(2s\) and \(2p\) wave function \(\mathcal{E}_{2s}\) and \(\mathcal{E}_{2p}\). Thus we obtain an \(8 \times 8\) Hamiltonian matrix \(\mathcal{H}(k, n)\) and an overlapping integration matrix \(\mathcal{S}(k, n)\). By solving the secular equation \(\mathcal{H}(k, n)\mathcal{C}_i(k, n) = E_i\mathcal{S}(k, n)\mathcal{C}_i(k, n)\), we can calculate the electronic energy band \(E_i\) of SWNTs.

Taking account of the total energy of all the occupied band electrons in SWNTs relative to that in graphene, we have calculated the strain energy \(E_s\) of the straight SWNTs. With the possible bond length dependence of the TB parameters being neglected, and with the real bond length of SWNT \([\bar{u}_r]\), where \(\bar{u}_r\) represents vectors between the nearest neighbor atoms in the tube\(^2\), we have calculated the direction cosines \(\hat{e}_i \cdot \hat{u}_r\) of Eq. (7). Fig. 1 shows that \(E_s\) depends only on the radius \(\rho\) of the tubes. The characteristic behavior \(E_s=\mathcal{C}/\rho^2\) is found with \(\mathcal{C} \approx 1.44\) eV\(\cdot\)\AA\(^2\)/atom, in good agreement with previous calculated value 1.34\(^2\) or 1.53 eV\(\cdot\)\AA\(^2\)/atom\(^2\), and excellently close to the value of 1.57 extracted from the measured phonon spectrum of graphite\(^2\).

Recently, “curved SWNTs” and “torus-like SWNTs” have been found\(^2\). They still have the \(sp^2\) bond structure, but it is predicted to have pentagon-heptagon defects\(^2\). In “curved SWNTs”, the bond-length is nearly the same as that in graphite sheet, since the distortion that is created by the bending nature of the curved tube is topologically relaxed by the inclusion of fivefold and sevenfold rings. However, the application of an external force moment at the two ends of the tube gives a different deformation. The hexagonal structure of the tube will not change until it reaches a critical bending curvature\(^2\). The tube undergoes only a simple compression on the inner side, and a stretching on the outer side. In the following discussion, the word “curved SWNT” refers to the growthed SWNT with pentagon-heptagon defects, and the word “bent SWNT” refers to SWNT that bends with outer-stretching and inner-compressing deformations under external force moments applied to the two ends of the tube. Using an empirical model employed by Lenosky et al.\(^3\), Ou-Yang et al.\(^3\) have developed a macroscopic continuous elastic model to calculate for “curved SWNT”. In their work, the strain energy of “curved SWNT” come from the angular change of the bonds or the curvature of the tubes. However, in the case of “bent SWNT”, the bond
length effect will contribute the main part of the strain energy. In what follows, we will treat only the latter case.

The “bent SWNT” surface can be described by

$$\bar{Y}(s, \phi) = \bar{r}(s) + \rho [\bar{N}(s) \cos \phi + \bar{b}(s) \sin \phi]$$

where \(\bar{r}(s)\) is the position vector of the axis, and \(0 < s \leq l\), is the arc-length parameter along the bent SWNT axis. \(0 < \phi \leq 2\pi\). \(\bar{N}(s)\) and \(\bar{b}(s)\) are unit normal and unit binormal vector of \(\bar{r}(s)\), respectively. The position of each carbon atom is described by two parameters, \(s\) and \(\phi\). The two operations \(C_N\) and \(S(h, \alpha)\) can still be used to determine the positions of atoms in the SWNT. Therefore, a translation of \(h\) units along the axis of SWNT means an addition of \(h\) to \(s\), and a rotation of \(\alpha\) about the axis means an addition of \(\alpha\) to \(\phi\). However, because the rotational symmetry about the axis of the bent SWNT is broken, \(C_N\) and \(S(h, \alpha)\) are not symmetry operations. It is necessary to generalize the Bloch sums in the crystal unit cell containing \(M \times N\) primitive unit cells of SWNT. Here \(M\) is the length of the cell along the direction (unit is \(h\)). \(M = 2(n_1^2 + n_2^2 + n_1 n_2)/N^2\), for \(n_1 - n_2\) not a multiple of \(3N\), and \(M = 2(n_1^2 + n_2^2 + n_1 n_2)/(3N^2)\), for \(n_1 - n_2\) a multiple of \(3N\).

We calculate only SWNT with constant radius of curvature \(R\). It is not principal difficult to extend the present treatment to general bent SWNTs. In bent SWNT, \(V_{ij}^{AB}(r)\) depends on the position of the atom \(A\), and will be written as \(V_{ij}^{AB}(l; m; r)\), where \([m, l]\) are indices of the primitive unit cell of the atom \(A\). When SWNT is bent to a different direction \(\bar{N}(s)\), \(V_{ij}^{AB}(r)\) will be different, but the Hamiltonian matrix elements are almost independent of the bending direction. We have found that the anisotropy effect is very small. Similar to the case of the straight SWNT, it is easy to obtain the \((8 \cdot M \cdot N) \times (8 \cdot M \cdot N)\) matrices of the Hamiltonian and the overlapping integration.

Since the change of bond length \(\delta r\) in bent SWNT is proportional to \(\frac{\rho}{R}\), the energy contribution of the bond stretching and bond compressing will be of the order of \(\frac{1}{R^2}\). It is necessary to calculate both the electronic energy \(E_{el}\) and the repulsion energy \(E_{rep}\) between the ions. In order to fit the force constant of graphite, we take \(\gamma = 1.024 \text{Å}^{-1}\), \(\phi' = \frac{\partial \phi}{\partial \bar{r}} = -13.63 \gamma \text{ eV/Å}^2\) and \(\phi'' = 60.4 \text{ eV/Å}^4\). With these parameters, we arrive correctly the second derivative of the stretching energy \(E_c\) of SWNTs be \(D = \frac{\partial^2 E_c}{\partial \bar{r}^2} = 58.5 \text{ eV}\) and the Poisson ratio be \(\sigma = 0.24\), where \(\epsilon\) is the relative compression along the axis of SWNT.

Fig. 2(a) shows the strain energy \(E_b\) per atom of the (5,5) SWNT as a function of the bending radius \(R\). The data follow quite well with the expected behavior \(E_b = E_s + \lambda/R^2\). A least square fit to the data yields a value of \(\lambda \approx 173 \text{ eVÅ}^2/\text{atom}\). Previous studies on “curved SWNTs” give a simple formula can be given,

$$E_b = \frac{C R}{\rho^2 \sqrt{R^2 - \rho^2}} \approx \frac{C}{\rho^2} + \frac{C}{2R^2}.$$  

(9)

In comparing with our results, we find that the value of \(\lambda\) for “curved SWNT” is equal to \(C/2\), only 0.7 eVÅ²/atom. It implies that the strain energy of pentagon-heptagon defects is far less than the strain energy of the stretching and compressing of the bond length. The experimental fact that the deformations of “bent SWNT” are change of bond length rather than the pentagon-heptagon defect reveals that there is a high potential barrier between the
two deformations to prevent the change of the hexagonal structure under the addition of a moment of external force at the two end of SWNT.

By CET, we can calculate the Young’s modulus $Y$ of SWNT from three different strain energies. They are the rolling energy $E_s$, the compressing or stretching energy $E_c$ and the bending strain energy $\Delta E_b$. The three energies are given by

$$E_s = \frac{C}{\rho^2}, \quad (10)$$

$$E_c = \frac{1}{2} D \epsilon^2, \quad (11)$$

$$\Delta E_b = \frac{\lambda}{R^2}, \quad (12)$$

where $\epsilon$ is the relative stretch or compression along the axis of SWNTs, and $D$ is the second derivative of $E_c$. The three quantities $C$, $D$ and $\lambda$ are given by

$$C = \frac{\Omega}{24(1 - \sigma^2)} Y \cdot b^3, \quad (13)$$

$$D = \Omega \cdot Y \cdot b, \quad (14)$$

$$\lambda = \frac{\Omega}{4} Y \cdot b(\rho^2 + b^2/4), \quad (15)$$

respectively. Where $\Omega = 2.62 \text{ Å}^2/\text{atom}$ is the occupied area per carbon atom in SWNTs, $b$ is the effective wall thickness of SWNT. Previous calculations indicate that the value of $D$ of SWNTs is about 58 eV/atom, same as that of graphites. However, since the wall thickness is not well defined in single-layered structure, various values of $b$ are used in the studies, thus the obtained $Y$ are quite different. Lu and Hernández et al. took the interwall distance of graphite (3.4 Å) as the thickness, and obtained the average Young’s modulus of SWNT about 1 TPa, in consistency with the corresponding measurement in multiwall nanotubes and bulk graphite samples. But the average value of $Y$ can not describe all kinds of deformations of SWNTs, such as the rolling of graphene and the bending of SWNT, though it can describe the stretching and compressing deformation along the axis direction of SWNT. Yakobson et al. have given $Y = 5.5$ TPa and $b = 0.66 \text{ Å}$ by using the rolling energy formula of graphite sheet [ Eq. (14)] and the stretching energy formula of graphene or SWNT [Eq. (13)], simultaneously. The obtained value of $b$ is about the $\pi$ orbital extension of carbon atom, which corresponds to the general fact that elasticity results from the overlapping of electron cloud between atoms. However, since Eq. (13) describe the rolling of single-layered graphene, the results given by Yakobson seems to correspond to graphite sheet rather than SWNT. The Young’s modulus and the effective wall thickness of SWNT and their dependence of the tube radius and helicity still remain unknown.

With Eq. (15), from the calculation of the bending strain energy of SWNTs with various radius, one may simultaneously find $Y$ and $b$ of SWNTs. Fig. 2(b) shows the relationship between $\lambda$ and the radius of the tube in the form $\lambda = b^* \rho^2 + a^*$. In comparison with the Eq. (15), it implies that both $Y$ and $b$ are independent of the radius and helicity of SWNTs. The value of $b^* = 15.3 \text{ eV/atom}$ is consistent with the value $D/4 = 14.7 \text{ eV/atom}$. However, it is difficult to obtain the exact value of $a^*$, because the first term of $\lambda$ is much greater than the second term $a^*$, to introduce high errors in the our fitting of $a^*$. Carefully analysis of
the strain energy of “bent SWNT”, gives only that the electronic energy from the angular change of the bond can contribute to the $\rho^0$ order of the bending strain energy of SWNT. The other terms, including the repulsion energy between ions and the electronic energy from the nonzero $\gamma$ effects (Eq. (5)), depend on $\delta r$, hence on the radius of the tube $\rho$. For wall thickness, is is unnecessary to consider the bond length dependence of TB parameters and the repulsion energy. It require only to calculate $\gamma = 0$ bond angular contribution $E_{el0}$ of the electronic energy. When $\gamma = 0$, the $1/R$th order perturbation of Hamiltonian is zero, and $E_{el0} = \frac{\lambda_{el0}}{R^2}$. The $\rho^0$ order term of $\lambda$ come completely from the $\lambda_{el0}$ and the residual part of $\lambda$ affects only the value of $\rho^2$ order. The exact value of $a^*$ can be obtained by calculating $E_{el0}$. Fig. 2 (c) shows the expected relationship $E_{el0} = \lambda_{el0}/R^2$. Fig. 2(d) gives values of $\lambda_{el0}$ for some SWNTs. It lead to $a^* = 1.05r_0^2$ eVÅ$^2$/atom by fitting it to $a^* = a_1\rho + a_2\rho^2$. The wall thickness of the tube is supposed to be identical to that of graphite, then from Eq. (13) and Eq. (15), it gives $a^* = \frac{3}{2}(1 - \sigma^2)C \approx 1.0r_0^2$ eVÅ$^2$/atom. Therefore, $b$ is about 0.74 Å, and $Y$ is about 5.1 TPa. This shows that both $Y$ and $b$ are independent of the radius and helicity of the tube, and the Young’s modulus of SWNT is five times greater than the average value of MWNT. The obtained value of $b$ is independent of the fitting parameters $\gamma$ and $\phi''$, and $Y$ is also insensitive to these parameters.

In summary, our calculation shows the following results: the strain energy of the straight SWNT come mainly from the occupied bands electrons, The obtained Young’s modulus of SWNT is independent of the radius and the helicity and is much larger than the modulus of the bulk sample. The effective thickness of SWNT is about the size of the carbon atom, far less than the distance between the layers of the graphite. These results show that CET can well describe the deformation of the bent tubes.

The authors acknowledge the useful discussions in our group. We would like to thank Dr. X.-J. Bi, Mr. Y.-H. Su and G.-R. Jin for correcting an earlier version of the manuscript and thank Prof. Y.-Z. Xie and Dr. H.-J. Zhou for correcting the manuscript in English. The numerical calculations are performed partly at ITP-Net and partly at the State Key Lab. of Scientific and Engineering Computing.
REFERENCES

1. S. Iijima, Nature (London) 354, 56 (1991).
2. C. Dekker, Phys. Today 52, 22, (1999).
3. N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. 68, 1579 (1992); R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. 60, 2204 (1992); J. M. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. 68, 631, (1992).
4. R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B 46, 1804 (1992).
5. C. T. White, D. H. Robertson, and J. W. Mintmire, Phys. Rev. B 47, 5485, (1993); H. Yorikawa and S. Muramatsu, Phys. Rev. B 52, 2723, (1995).
6. J. W. G. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) 391, 59 (1998); T. W. Odom, J.-L. Huang, P. Kim, and C. M. Lieber, Nature (London) 391, 62 (1998).
7. M. S. Dresselhaus, Nature (London) 358, 195 (1992).
8. Daniel S., E. Artacho, and J. M. Soler, cond-mat/9811363.
9. D. H. Robertson, D. W. Brenner, and J. W. Mintmire, Phys. Rev. B 45, 12592 (1992).
10. G. B. Adams, O. F. Sankey, J. B. Page, M. O’keeffe, and D. A. Drabold, Science 256, 1792, (1992).
11. T. Lenosky, X. Gonze, M. Teter, and V. Elser, Nature (London) 355, 333, (1992).
12. J. Tersoff, Phys. Rev. B 46, 15546 (1992).
13. Z.-C. Ou-Yang, Z.-B. Su, and C.-L. Wang, Phys. Rev. Lett. 78, 4055 (1997).
14. B. I. Yakobson, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett. 76, 2511 (1996).
15. J. P. Lu, Phys. Rev. Lett. 79, 1297 (1997).
16. E. Hernández, C. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. 80, 4502 (1998).
17. J. Tersoff, Phys. Rev. Lett. 61, 2879 (1988); D. W. Brenner, Phys. Rev. B 42, 9458 (1990).
18. M. Menon, E. Richter, and K. R. Subbaswamy, J. Chem. Phys. 104, 5875 (1996).
19. J. Yu, P. K. Kalia, and P. Vashishta, J. Chem. Phys. 103, 6697 (1995); D. Tomanek, Phys. Rev. Lett. 67, 2331 (1991).
20. Approximately replacing the real length of \( \vec{u}_r \) with \( r_0 \) in calculating \( \hat{u}_r \) of the direction cosines, we found that \( C \) is about 2.34 eV Å\(^2\)/atom, larger than the results of Tersoff, Ou-Yang, and Nicklow. But it is agreement with the results of Daniel and Hernández et al.
21. R. Nicklow, N. Wakabayashi, and H. G. Smith, Phys. Rev. B 5, 4951 (1972).
22. J. Liu, H. Dai, J. H. Hafner, D. T. Colbert, R. E. Smalley, S. J. Tans, and C. Dekker, Nature (London) 385, 780 (1997).
23. S. Iijima, C. Brabec, A. Maiti, and J. Bernholc, J. Chem. Phys. 104(5), 2089 (1996).
24. R. A. Jishi, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B 47, 16671 (1993).
25. R. Al-Jishi and G. Dresselhaus, Phys. Rev. B 26, 4514 (1982).
26. the \( \rho \) order contribution of \( \lambda_{id} \) may be nonzero, although the term of the total \( \lambda \) vanishes.
27. W. W. Wong, P. E. Sheehan, and C. M. Lieber, Science 277, 1971 (1997); M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, Nature (London) 381, 678 (1996).
FIG. 1. The strain energy per atom versus the radius of \((n, m)\) tubes, where \(n = 6 \sim 13\) and \(m = 0, 1, 2\) or \(n\). The solid line corresponds to a least square fit to the \(\frac{C}{\rho^2}\) behaviors. \(C = 0.71 \cdot r_0^2 \approx 1.44\) eV\(\AA^2\)/atom. \(C\) is independent on the helicity of tubes. The \(\rho^{-\beta}\) behaviors is clearly shown in the inset (\(\beta \approx 2.03\)). Here \(r_0\) is 1.42 \(\AA\), the cohesive energy of graphite is \(-7.39\) eV.

\[E_s(eV)\]

\[\rho/d_0\]

\[E_s(eV)\]

\[\rho/d_0\]

\[E_{el0}(eV)\]

\[\rho/d_0\]

\[E_{el0}(eV)\]

\[\rho/d_0\]

FIG. 2. (a) Strain energy per atom versus the bending radius \(R\) in \((5,5)\) tube. The solid line is a fit to the \(E_s + \lambda/R^2\), where \(E_s\) is the cohesive energy of straight \((5,5)\) tube. \(\lambda = 86.1 \times 1.42^2\) eV\(\AA^2\)/atom. (b) the value of \(\lambda\) of some \((n,0)\) and \((n,n)\) tubes. The solid line is a fit to \(a^* + b^* r_p^2\), \(b^* \approx 15.27\) eV. (c) \(E_{el0}\) versus the bending radius \(R\) in \((5,5)\) tube. The solid line is a fit to \(E_0 + \lambda_{el0}/R^2\). The zero point of \(E_{el0}\) has moved. (d) The value of \(\lambda_{el0}\) of these tubes. The solid line is a fit to \(a_0 + a_1 r_p + a_2 r_p^2\), and the \(a_0 \approx 1.05\).