References


Structure of armchair single-wall carbon nanotubes under hydrostatic pressure

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Based on the helical and rotational symmetries and Tersoff potential, the structural parameters, i.e., bond lengths and bond angles, have been investigated for armchair single-wall carbon nanotubes. The bond lengths and bond angles are determined for several radii tubes of various lengths. Results for armchair tubes show that one bond length is greater than that of the graphite while the other is smaller. Furthermore, the tube length is found to have significant effects on these bond lengths and bond angles. We have also recalculated the variation of these bonds under hydrostatic pressure. With the application of pressure, the bond lengths compress and the larger bond length decreases faster with pressure in comparison to the shorter one. As a consequence, at some critical pressure the bond lengths become equal. An analysis regarding the cross-sectional shape of the nanotubes and its pressure dependence has also been done. At some particular pressure, the first transition from circular to elliptical cross section takes place. For (10,10) tube the first transition pressure is found to be equal to 2.2 GPa.

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I. INTRODUCTION

Carbon nanotubes have excited a considerable interest in the condensed-matter and materials research communities, and much experimental and theoretical work has been devoted to them as prototype of one-dimensional ordered systems with promising technological applications. The structure of single-wall carbon nanotubes (SWNTs) is qualitatively well known through simple construction of rolling a perfect graphite sheet, where only one parameter, the lattice parameter or a bond length, has been considered. The symmetry of tube is less restrictive than in graphite and more parameters are needed to determine completely the structure. Among other things, these parameters define the differences between equivalent bonds. It is very difficult to obtain direct experimental information for the structure, although a lot of theoretical information has been available. The strong similarity of the chemistry of carbon nanotubes to graphite allows theoretical analysis to be done based on empirical methodologies imported from studies on graphite. The curvature of the tubes, however, disturbs the chemistry and causes deviation from the graphite based description, especially for small radii tubes. The first evident effect of rolling a graphite sheet is introducing two inequivalent directions (axial and radial) and thus two possible bond lengths instead of only one in contrast to the case of graphene. Significant effort has been made to calculate bond lengths in carbon nanotubes using either a model potential or ab initio molecular dynamics calculations. Robertson et al. used first principle local density functional (LDF) methods to calculate the total energies for a series of high symmetry armchair \((n,n)\) tubes. They found that the minimum energy structure of (5,5) tube by direct minimization of the total energy gives a radius of 3.47 Å with both types of carbon-carbon bonds assumed equal with a length of 1.44 Å. Sanchez-Portal et al. and Lin-Hui et al. have reported two unequal bond lengths for armchair tubes using ab initio calculations. Jiang et al. also showed two bond lengths of armchair tubes using modified Cauch-Born rule to incorporate the Brenner potential. It has been found that the circular cross sections of SWNTs are energetically favorable and beyond 30 Å diameters the collapsed form becomes favorable for all the three types of SWNTs. Calculations on many properties of single-wall nanotubes such as Young's modulus, bulk and structural properties, and thermodynamical properties have also been reported using one bond length equivalent to graphite or its modified value. Cronin et al. have calculated the electronic band structure of semiconducting and metallic nanotubes under uniaxial strain using tight-binding approximations. They used unstrained bond length equal to 1.44 Å for all the tubes. Many experimental and theoretical studies have also been done on bundles as well as isolated single-wall nanotubes under pressure. These pressure dependent studies reveal that there exists a transition pressure where either the tubes collapse or the vibrational modes change or loss of reversible deformation takes place. It has been observed that the transition pressure depends on the diameter of the nanotubes and not on its chirality.

As regards isolated SWNT, resonant Raman scattering has been used to measure the vibrations stemming from tubes of different diameters by looking at the \(A_1\) breathing mode that exhibits a strong dependence on the diameter. This provides a technique to experimentally measure the effect of pressure on the tube. The structural change was studied by Raman spectroscopy techniques. Pressure dependence of the radial and tangential vibrational modes indicated that the radial mode intensity decreases beyond 1.5 GPa for diameters associated with (10,10) nanotube bundle, suggesting that the system undergoes a phase transformation, from circular to elliptical cross section. Peters et al. have also measured experimentally a structural phase transition at 1.7 GPa for (10,10) tube in nanoropes. The behavior of vibrational modes across the transition has been very recently analyzed by Balzaur et al. using a classical molecular dynamics calculation for finite capped SWNTs. Their results show that before the phase transition which is located at 1.2 GPa for (10,10) and at 8 GPa for (5,5) tubes, peaks in vibrational spectra are found at values close to the experimental radial breathing and axial modes. Above the...
structural transition pressure, those peaks related to the circle-oval cross section are reduced or suppressed for both (5,5) and (10,10) tubes. Zang et al.\textsuperscript{23} have investigated the structural and mechanical properties of (10,10) tube under hydrostatic pressure using constant-pressure molecular dynamics simulations with Tersoff potential. They found that the tube cross section transforms into an elliptical shape at 1.55 GPa. Merlen et al.\textsuperscript{25} have performed high pressure resonant Raman experiments on well characterized purified SWNT bundles. No clear sign of phase transformation up to the highest pressure studies of 40 GPa. The short range Tersoff’s potential with the extensive molecular dynamics simulations has been successfully applied to study the structural characteristics of the lattice SWNTs.\textsuperscript{26}

In order to have an insight into such pressure induced structural transformation, it is preferable to have a detailed study based on established model potentials. Furthermore, it is necessary to understand the behavior of bond lengths and bond angles under pressure for which no detailed study exists. This paper reports results of such a calculation on armchair carbon nanotubes.

II. THEORETICAL PRELIMINARIES

A. Helical and rotational symmetries

We can visualize an infinite tube as a conformal mapping of a two-dimensional honeycomb lattice to the surface of a cylinder that is subject to periodic boundaries both around the cylinder and along its axis. A typical tube of armchair single-wall nanotubes is shown in Fig. 1, where we also show the bond lengths $b_1$ and $b_2$, and bond angles. The bond length $b_1$ is perpendicular to the tube axis, whereas $b_2$ forms an angle with it. We also see in the same figure two equivalent bond angles $\alpha$ and $\gamma$ and the third angle is $\beta$. First we assume that the cross section of the SWNT has a circular shape. The helical and rotational symmetries\textsuperscript{27} are used in this study to construct high symmetry armchair $(n,n)$ SWNTs (with $\theta=30^\circ$). However, in this both bond lengths have been taken to be equal. We simplify this procedure to obtain atomic coordinates using the two different bond lengths. This is done by first mapping the two atoms in the $(0,0)$ unit cell to the surface of cylindrical shape. The first atom is mapped to an arbitrary point on the cylindrical surface, and the second atom is found by rotating this point by $\theta=2\pi/3n$ about the cylinder axis. These first two atoms can be used to locate $2(n-1)$ additional atoms on the cylindrical surface by $(n-1)$ successive $2\pi/n$ rotations about the cylinder axis. Altogether, these $2n$ atoms complete the specification of the helical motif which corresponds to an arm on the cylindrical surface. This helical motif can then be used to tile the reminder of the tube by repeated operation of a single screw operation $S(b,\alpha_0)$ representing a translation and rotation of the cylinder axis and rotation $\alpha_0$ about this axis, where $b=2\pi r/2$ and $\alpha_0=2\pi/n$.

If we apply the full helical motif, then the entire structure of armchair SWNT is generated. This structure provides the atomic position for all atoms in terms of bond lengths and bond angles. The bond lengths and bond angles are determined by minimization of the energy of the tube, assuming atoms interact via Tersoff potential.

B. Tersoff potential

One of the commonly used empirical interaction potentials of a covalent system is the Tersoff Potential which has the following form,\textsuperscript{28,29}

$$E = \sum_i f_i(r_{ij})[(A e^{-r_{ij}} - B r_{ij} e^{-c r_{ij}})],$$

(1)

where $E$ is the total energy of the system. The indices $i$ and $j$ run over the atoms of the system, and $r_{ij}$ is the distance between atom $i$ and atom $j$. The parameters $A$, $B$, $\lambda_1$, and $\lambda_2$ are all positive definite quantities. Other parameters and function are defined elsewhere in literature.\textsuperscript{28,29} $b_{ij}$ is a complicated function involving bond angles, $\theta_{ij}$, defined as angles between bonds $ij$ and $ik$. For graphite, $\theta_{ij}$ is always $120^\circ$ (ideal value). In general, for single-wall nanotubes, bond angles are given by $\theta_{ij} = \cos^{-1}(\langle \hat{r}_i, \hat{r}_j \rangle)$. The vectors $\hat{r}_{ij} = (\hat{r}_i - \hat{r}_j)$ and $\hat{r}_{ij} = (\hat{r}_i - \hat{r}_j)$ are between atom $i$ and nearest neighbor $j$ on the cylindrical surface; $\hat{r}_i$, $\hat{r}_j$, and $\hat{r}_k$ are the position vectors for atoms as shown in Fig. 1(b). The bond-angle forces are introduced in the potential $E_p$.

The nine parameters reported by Tersoff are: $A(eV)=1.3036 \times 10^9$, $B(eV)=3.467 \times 10^9$, $\lambda_1=3.8049 \times 10^4$, $\lambda_2=3.8049 \times 10^4$, $\alpha=3.8049 \times 10^4$, $\alpha=3.8049 \times 10^4$, $\beta=3.8049 \times 10^4$, $\gamma=3.8049 \times 10^4$, and $\delta=3.8049 \times 10^4$.

The values of these parameters, given by Tersoff, give bond length of the graphite equal to 1.46 Å.\textsuperscript{30} However, the experimental value of the bond length of graphite is equal to 1.42 Å.\textsuperscript{31} Since these parameters chosen by Tersoff do not reproduce the bond length in graphite accurately, we modified two parameters $A$ and $B$ to give a good agreement of bond length of the graphite which is 1.42 Å. The new values of the parameters $A$ and $B$ thus are taken 1206.7090 and 315.9640 eV, respectively, and all other parameters have been kept the same as in the Tersoff potential.

III. NUMERICAL PROCEDURE

By using the helical and rotational symmetries and the Tersoff potential with modified values of the parameters $A$ and $B$, we have investigated the variations of bond lengths associated with minimum energy of single-wall nanotubes.
In general, two bond lengths $b_1$ and $b_2$, and three bond angles as shown in Fig. 1 determine the structure of a carbon nanotube. A given $(n,n)$ SWNT can be constructed from the bond lengths. The atom coordinates of all the atoms of an $(n,n)$ tube are thus obtainable in terms of $b_1$, $b_2$, and $n$. We allow variation in $b_1$ and $b_2$ to obtain the position coordinates of a given length of armchair $(n,n)$ tube and then use Tersoff potential to obtain its total energy. The bond lengths are then varied one by one, and atom coordinates reobtained and so also the total energy of assumed $(n,n)$ tube. The bond lengths that result in minimum energy are retained and refined by successive adjustments to $b_1$ and $b_2$. In this way, a set of $b_1$ and $b_2$ for armchair $(n,n)$ tubes was obtained. In this way, bond lengths for all $(n,n)$ tubes reported in this paper were obtained.

All calculations were made using this set of minimized bond lengths. The energy lowers by 0.14% on choosing $b_1 \neq b_2$, as compared to that when $b_1 = b_2 = b$ was chosen for (7,7) tube. For large radius carbon nanotubes, we would expect that the bond lengths and bond angles approach to that of graphite. With this procedure all the atoms in nanotubes are constrained to remain on the same cylindrical surface thereby preserving the chemical environment in the final step of minimizing energy of tube.

We apply this procedure to different $(n,n)$ SWNTs, where $n = 3$, 5, 7, 10, 15, 30, 40, and 50, and hence having different radii. The length $L$ of tube is determined by taking the fixed number of unit cells, $N$, and then which make the length of all tubes approximately equal. We can calculate the length of armchair SWNTs in this work in terms of bond length $b_2$ by $L = \frac{3(2N-1)b_2}{\pi}$. The number of atoms in each tube then equals $4N/\pi$ for $(n,n)$ tubes, which is different for different radii. We have taken $N = 50$ for our calculation in this work.

### IV. RESULTS AND DISCUSSION

#### A. Effect of tube radius on the structure

We present, in Table I, the results of our calculations for two different bond lengths as obtained by the procedure described above for several armchair SWNTs. The normalized values of the bond lengths (i.e., $b_1$, $b_2$, where $b_0$ is the bond length of the graphite) and bond angles have also been plotted as a function of the tube radius $(n$ or of $(n,n)$ tubes), in Figs. 2(a) and 2(b). The difference between these bonds in SWNTs from that in graphite is significant. From Fig. 2(a), we notice that $b_1$ is always greater than that of graphitic bond length whereas $b_2$ is always less than that. These results for larger radii tubes resemble those given by Lin-Hui et al., qualitatively. They also found two bond lengths for armchair SWNT structure, in which one bond length elongates as compared to that in graphite, whereas the other shrinks, but for very small tubes this tendency reverses. The work of Sanchez-Portal et al. also reports results of two bond lengths, however, showing different behaviors of bond lengths. They found that both bond lengths in armchair SWNTs have values greater than that in graphite. It should be noticed that the calculation of Ref. 6 did not reach a satisfactory graphite bond length from the beginning. Form our results we obtained the bond length of 1.42 Å for graphite which agrees quite well with the experimental value while Ref. 6 obtained 1.436 Å which deviates largely from the experimental results. Jiang et al. also found that two bond lengths for armchair tubes have values greater than that in graphite. For (5,5) tube, they found that the bond lengths equal to 1.4553 and 1.4568 Å and at the same time, they calculated the bond length of graphite equal to 1.4507 Å.

It is possible to compare our results for some of the data presented in Table I with other calculations for bond length and radius. For example, our results of (5,5) tube show that the tube has a radius of 3.43 Å and has two bond lengths equal to $b_1 = 1.44$ Å and $b_2 = 1.41774$ Å. The value of the bond length $b_1$ is in good agreement with the calculations done by Robertson et al. We have also compared our results with local density approximation calculations of 4 Å diameter SWNTs by Machon et al. They calculated relaxed geometry for SWNTs and showed that there are significant deviations from the ideal rolled graphite sheet configuration. For (3,3) tube, the radius obtained for relaxed configuration is 2.10 Å. This value is in a good agreement with our result of 2.11 Å obtained by using the procedure described in previous section.

In general, it is observed that with increase in the tube radius, $b_1$ decreases and $b_2$ increases, both approaching $b_0$. 

### Table I. Bond lengths, bond angles, radius (Å), and energy $E$ (eV at.) of armchair $(n,n)$ SWNTs.

<table>
<thead>
<tr>
<th>SWNT $(n,n)$</th>
<th>Bond lengths (Å)</th>
<th>Bond angles (deg)</th>
<th>Radius</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(3,3)$</td>
<td>1.4340 1.41765</td>
<td>116.3166 116.2655</td>
<td>3.11134</td>
<td>-6.9614</td>
</tr>
<tr>
<td>$(5,5)$</td>
<td>1.4000 1.41774</td>
<td>118.6663 118.6663</td>
<td>3.43774</td>
<td>-7.1958</td>
</tr>
<tr>
<td>$(7,7)$</td>
<td>1.3110 1.41895</td>
<td>119.50705 119.3906</td>
<td>4.78276</td>
<td>-7.2557</td>
</tr>
<tr>
<td>$(10,10)$</td>
<td>1.2555 1.41942</td>
<td>119.6350 119.6350</td>
<td>6.80626</td>
<td>-7.2665</td>
</tr>
<tr>
<td>$(15,15)$</td>
<td>1.2320 1.41976</td>
<td>119.8218 119.8218</td>
<td>10.1914</td>
<td>-7.3026</td>
</tr>
<tr>
<td>$(20,20)$</td>
<td>1.2220 1.41991</td>
<td>119.8832 119.8832</td>
<td>13.5970</td>
<td>-7.3082</td>
</tr>
<tr>
<td>$(30,30)$</td>
<td>1.2120 1.42000</td>
<td>119.9542 119.9542</td>
<td>20.3543</td>
<td>-7.3122</td>
</tr>
<tr>
<td>$(40,40)$</td>
<td>1.2120 1.42100</td>
<td>119.9535 119.9535</td>
<td>27.1391</td>
<td>-7.3155</td>
</tr>
<tr>
<td>$(50,50)$</td>
<td>1.2120 1.42100</td>
<td>119.9535 119.9535</td>
<td>33.9238</td>
<td>-7.3142</td>
</tr>
</tbody>
</table>
In order to see the influence of two bond lengths in comparison to those with one bond length structures, we also use our models for armchair SWNTs to calculate the energy assuming that these are equal (i.e., $h_1 = b_2 = b_3$), where $b$ is obtained in minimum energy configuration. The result of the normalized bond length has also been plotted as a function of the tube radius in Fig. 2(a) along with the results of tubes having unequal bond lengths. We observe that for these tubes, the radius with equal bond length structure is less than that with unequal bond length structure. As an example, in (5,5) tube, the corresponding value of the radius is 3.437 Å, whereas with equal bond lengths this value comes out to be equal to 3.411 Å. The minimized energy is lower using two bond lengths as compared to using one bond length. This indicates that two bond length structure is the structure of minimum energy.

B. Effect of tube length on the structure

We also investigate the effect of length of SWNT on bond lengths and bond angles. Rochefort et al.\textsuperscript{23} have studied theoretically the influence of finite length on the electronic properties of (6,6) armchair carbon nanotubes. They found that, unlike the infinite tube, which is metallic, very short (<100 Å) nanotubes have an energy band gap.

For this study, we choose three armchair (5,5), (15,15), and (30,30) single-wall nanotubes. We compare the structure of these tubes as a function of aspect ratio of $L/R$, where length $L$ has been measured in unit of radius $R$. Figure 3(a) shows the variations of bond lengths plotted as a function of the aspect ratio of $L/R$. We observe, as the tube length increases, the larger bond length value $b_1$ decreases toward graphitic value whereas the shorter bond length $b_2$ increases. For (5,5) tube having small radius, although the values of bond lengths move toward that in the graphite with increasing length but the difference between them is always significantly large, even for large $L/R$. For reasonably long lengths of the tubes, $b_1/b_2$ approach a constant value which depends on the tube radius. We denote this $L/R$ ratio as $(L/R)_c$. The actual value of this $(L/R)_c$ depends on the tube radius, but it is practically closer to 10, as can be seen from Fig. 3(a). We present these data of $b_1/b_2$ for these tubes in Table I. It can be noticed that for $(L/R)_c$, the values of bond lengths are closer to each other as compared to the case when $L/R = 1$.

The length also has an important effect on the value of energy of nanotubes. As we see from Fig. 3(c), increase of tube length tends to decrease the curvature energy. Similarly the length also has a very important effect on the values of bond angles. We observe from Fig. 3(b), for larger radii tubes as the length of tube increases the bond angles approach to that of graphite while for very short tube the two equal bond angles become slightly greater than the ideal value. For small radii tubes, the difference between them and graphite is very significant.

C. Pressure effect

I. Circular cross section

SWNTs are flexible fibers and can be 100 times stronger than steel.\textsuperscript{31} Pressing the tip of the nanotube will cause it to
bend without damage to the tip or the whole SWNT. When the force is removed, the tip of nanotube recovers to its original shape. Under a hydrostatic pressure the total potential energy of armchair SWNTs changes. According to the first law of thermodynamics,

\[ E = E_0 + P \Delta V, \]

where \( \Delta V = V_P - V_0 \) is the volume reduction, \( V_P \) the volume under applied pressure \( P \), and \( V_0 \) and \( E_0 \) are the volume and energy at zero pressure. We search about the suitable value of the bond lengths \( b_{1p} \) and \( b_{2p} \) leading to the minimum energy under pressure \( P \), as obtained from Eq. (2). For this, we first fix a new \( b_{1p} \) (corresponding to some equivalent pressure \( P \) obtainable from \( \Delta E/\Delta V \)), and obtain \( b_{2p} \) by successive minimization procedure. In this way, we calculate a set of values of \( b_{1p} \) and \( b_{2p} \) at any pressure \( P \). The bond angles are also obtained at each pressure from the final minimized set of atomic positions. The volume \( V_\text{p} \) at each pressure is obtained by assuming those solid tubes have a circular or an elliptical cross section, where radius and length are governed by \( b_{1p} \) and \( b_{2p} \).

In reality, for such a finite system, this way of calculating energy by using \( \Delta V \) is an approximation because volume change assumes a continuous distribution of atoms. Figure 4 shows the results of our calculations of the bond lengths at various pressures for (5,5), (10,10), (15,15), and (30,30) SWNTs. We observe that the bond lengths \( b_1 \) and \( b_2 \) decrease under pressure. The larger bond length \( b_1 \) decreases faster with pressure as compared to the shorter bond length \( b_2 \). The behavior of bond angles is different. The larger bond angle \( \beta \) increases with pressure while the two

<table>
<thead>
<tr>
<th>SWNT</th>
<th>Radius (Å)</th>
<th>( b_1/b_0 )</th>
<th>Radius (Å)</th>
<th>( b_1/b_0 )</th>
<th>( b_1/b_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,5)</td>
<td>3.449234</td>
<td>1.0204</td>
<td>3.437746</td>
<td>1.01408</td>
<td>1.4490</td>
</tr>
<tr>
<td>(15,15)</td>
<td>10.21297</td>
<td>1.0035</td>
<td>10.19041</td>
<td>1.00200</td>
<td>1.0056</td>
</tr>
<tr>
<td>(30,30)</td>
<td>20.49756</td>
<td>1.0014</td>
<td>20.36864</td>
<td>1.00070</td>
<td>1.0025</td>
</tr>
</tbody>
</table>
equal bond angles $\alpha$ and $\gamma$ decrease with pressure (Fig. 5).

At some critical values of pressure ($P_c$), both bond lengths become equal to each other ($b_1 = b_2 = b_c$). The value of this critical pressure and corresponding critical bond length ($b_c$) are dependent on tube radius (see Fig. 6). Above this critical pressure, the shorter bond length changes to larger bond length and vice versa. It emerges that the value of $P_c$ reduces with increasing tube radius. By observing Fig. 4 we found that for large radius, $P_c$ approaches to zero and $b_c$ approaches to that of graphite, as expected. The critical values of pressure for (5,5) and (10,10) are found to be 10.52 and 1.55 GPa, respectively. We can also observe clearly the effect of tube radius on the bond angles at zero pressure in the same figure.

The variation of the extensive parameters of the tube such as tube length and radius with pressure has also been plotted in Fig. 7(a) for (10,10) tube. We observe that the compressions of the tube radius and length are different in rigidity. This result indicates that the single-wall nanotubes are extremely rigid along the tube axis than in radial direction as proposed by Reich et al.\textsuperscript{3} A better estimate about the rigidity of tubes is provided by the results of bulk modulus obtained from $B = -\frac{V}{dP/dV}$. The slope $\Delta P/\Delta V$ is obtained by extrapolating the $P$-$V$ curve by a quadratic fit up to zero pressure. These results are plotted in Fig. 7(b). At zero pressure, the values of the bulk modulus for (10,10), (15,15), and (30,30) tubes with a circular cross section are 129.0, 90.0, and 46.51 GPa, respectively. The bulk moduli for all radii tubes increase with pressure. There is a strong radius dependence of the bulk modulus.

2. Elliptical cross section

We also examine the existence of the shape transition under pressure of armchair tubes. Firstly, we investigate the shape of the tubes at zero pressure. Following similar proce-
FIG. 8. Energy as a function of $n$ for armchair $(n, n)$ SWNTs having circular cross section ($e = 1.0$) and various elliptical cross sections.

FIG. 9. (a) Energy with pressure for (10,10) tube. AB and CD curves are corresponding to circular and elliptical cross section, respectively. First transition pressure $P_T$ as a function of (b) tube radius with elliptical aspect ratio equal to 0.99 for armchair SWNTs and (c) elliptical aspect ratio for (10,10) tube. (d) Bulk modulus versus $n$ for armchair $(n, n)$ SWNTs. Similar curves are obtained for other radii tubes.
To study the existence of the shape transition of armchair SWNTs under pressure, we choose three armchair (10,10), (15,15), and (30,30) SWNTs. Under pressure, the cross section was assumed to collapse to elliptical cross section, with elliptical aspect ratio $b_r/a_c$ as parameter, varying from 0.98 to 0.99. Above this value of elliptical aspect ratio, the energy of the tube is practically identical to that from circular cross section.

We show in Fig. 9(a) the energy as a function of applied pressure for (10,10) SWNT. The energy assuming circular cross section is indicated by the A to B curve, whereas, with elliptical cross section, from C to D curve. Each point on the curve C to D represents a different value of the elliptical aspect ratio $b_r/a_c$ ($b_r/a_c$ begins from the value 0.99 to 0.98 decreasing by 0.001). We observe that at some pressure, the energy of the collapsed tube is lower than the energy of the tube with circular cross section. The first transition pressure ($P_T$) comes out to be 2.2 GPa with $b_r/a_c$ equal to 0.99 for (10, 10) tube. It is found that the first transition pressure depends on the tube radius [Fig. 9(b)] in addition to the elliptical aspect ratio [Fig. 9(c)].

Our results of the first transition pressure ($P_T$) required to collapse the (10, 10) tubes are in agreement with the experimental value and other theoretical values calculated by other studies. They found that the first transition pressures are 1.55, 1.62, 1.7, and 1.0 GPa, while in other study, the first transition pressure for short (10,10) nanotubes is given to be 1.1 GPa. However, in all these studies, no mention has been made about the value of this aspect ratio. Moreover, these calculations of the first transition pressure for (10,10) tubes are in bundles or nanotubes, in which confinement affects the transition pressure. The intertube interactions with a bundle can cause considerable extrinsic and anisotropic effects on the individual nanotubes such as a polyanization of the tube cross section.

Bulk moduli, at the first transition pressure, for the collapsed armchair (10, 10), (15,15), and (30,30) SWNTs are found to be equal to 87.3, 53.13, and 30.31 GPa, respectively. We also plotted the values of the bulk modulus in Fig. 9(d); at zero pressure (curve i), at $P_T$ (curve ii), and at pressure, tube has circular cross section, equal to $P_T$ (curve iii).

V. SUMMARY AND CONCLUSION

In this paper, we have investigated the effect of radius and tube length on the values of C-C bond lengths and bond angles of armchair SWNTs. For this study, we construct the SWNT through two bond lengths. We determined these bond lengths by calculating the energy of several tubes, having various diameters and lengths, using Tersoff potential, and then minimizing it.

As a result of this work, it emerges that the structure of armchair tubes has unequal bond lengths and bond angles. The equality of bond lengths is only an asymptotic result for large diameter and long tubes. One of these bond lengths is larger than that in graphite sheet whereas the other less than it. Two of bond angles are found to be equal and less than the third one. The values of these bonds are very sensitive to radius and tube length. The larger deviation of these bonds from the corresponding values of that in graphite results from small radius tubes. Whereas this small variation in bond lengths may not generally be so important and is not unexpected, it may have significant manifestations on the experimental results that provide structural information.

We also calculated the structure of armchair SWNTs under hydrostatic pressure. The bond lengths are found to depend on pressure very significantly. The two bond lengths respond differently to the pressure; the longer one decreases faster as compared to shorter one, resulting in equality of the two at some critical pressure. Above this critical pressure, the short and long bond lengths reverse, short becoming long and vice versa. This critical pressure and equivalent bond length depend on the tube radius, approaching zero for large radius, as expected.

Results of present calculation predict the existence of the shape transition, from circular cross section to elliptical shape at some transition pressures. The onset of this transition occurs at first transition pressure which depends on the tube radius and on the elliptical aspect ratio $b_r/a_c$. Our result for the first transition pressure for (10,10) tubes is in good agreement with experimental and other theoretical values.

We believe that the results of this paper regarding two bond lengths are important. Furthermore, critical pressure at which these two become equal is much more important. The critical pressure obtained by us seem to be closer to experimentally measured transition pressure for (5,5) and (10,10) tubes. This feature is likely to be different for different chirality tubes and will be the subject of future interest by us. It is hoped that the findings of this paper will be useful for characterizing the type of the tube including its radius by experimentally correlating the critical pressure to $(n,m)$ tubes.

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