The geometry and the radial breathing mode of carbon nanotubes: beyond the ideal behaviour

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New Journal of Physics 5 (2003) 125.1–125.21 (http://www.njp.org/)
Received 1 July 2003
Published 3 October 2003

Abstract. First principles calculations using density functional theory were carried out to obtain the geometrical properties and the radial breathing mode (RBM) frequency of 40 different single-walled carbon nanotubes with small diameter. Fourteen chiral nanotubes with diameters less than 0.8 nm were considered, for which the number of atoms in the unit cell is not larger than 200. From the achiral (zigzag, armchair) nanotubes all those having a diameter less than 1.6 nm were considered. The geometrical parameters deviate from the values obtained from simple wrapping of a perfect hexagonal sheet. The deviation from the ideal behaviour increases with increasing curvature. The most prominent change is the increase of the diameter with respect to its ideal value. The lattice constant along the tube axis exhibits a slight shrinking. The RBM frequency does not follow the usually assumed $1/d$ behaviour; there is a general softening with increasing curvature. The softening of the RBM frequency cannot be described by a simple function of the diameter; it also depends on the chiral angle and the metallicity of the tube. In addition to this, the coupling of the totally symmetric radial motion with the totally symmetric tangential motion(s) has a non-negligible effect.
1. Introduction

Single-walled carbon nanotubes (SWCNTs) are tubes made of carbon atoms, having a diameter in the nanometre range, whereas their length can even be much larger than 1 µm [1]. The end cap of a nanotube contains hexagons and pentagons but the mantle of a nanotube consists of only hexagons. An infinitely long SWCNT can be imagined as a rolled up piece of a graphene sheet (two-dimensional graphite plane), in other words a cylinder, formed by wrapping up a regular hexagonal lattice. The rolling up of the honeycomb lattice is characterized by the wrapping (chiral) vector ($\vec{C}_h$), connecting two carbon atoms of the graphene sheet which coincide after folding. Each SWCNT is uniquely given by the two chiral indices, $n$ and $m$ ($n \geq m$), which are the two integer coefficients in the expression of the chiral vector in terms of the primitive vectors of the hexagonal lattice: $\vec{C}_h = n \cdot \vec{a}_1 + m \cdot \vec{a}_2$. The directions of the inequivalent wrapping vectors fall within a 30° region (see figure 1). The borderline cases are the zigzag ($m = 0$) and the armchair ($n = m$) tubes. The remaining cases are the chiral tubes.

The ultimate goal of researchers would be to synthesize SWCNTs of pre-determined $(n, m)$ indices. While being still far away from controlling the $(n, m)$ indices during the production of SWCNTs, the first successful attempts in at least identifying the chiral vectors of individual tubes have already been reported recently [2]–[4]. A crucial role is played in these identifications by the position of the simplest and most characteristic vibrational mode in the Raman spectrum of the nanotubes, the radial breathing mode (RBM). It is commonly assumed that there is a simple one-to-one correspondence between the diameter of an SWCNT and its RBM frequency. Its functional form is taken as $\omega_{\text{RBM}} \sim 1/d$, based on simple arguments according to the continuum elastic theory [1, 5, 6, 7]. This is a good approximation for large diameters. In general, the properties of nanotubes with large enough diameters can be described by the ‘graphene folding’ approximation; we call this the ideal behaviour. However, deviations from the ideal behaviour can be expected for small diameters (large curvatures) where the discreteness of the atoms cannot be neglected. The accurate theoretical investigation of the tubes with small diameters has become important recently, because such tubes have been produced by several methods. SWCNTs with diameters down to about 0.7 nm are produced by the HiPCO method [8]. Annealing of peapods (C$_{60}$ @SWCNT) at high temperatures results in double-walled carbon nanotubes (DWCNTs) where the diameter of the inner tube can be as low as 0.5 nm [9]. SWCNTs with extremely small diameter of about 0.4 nm can be produced inside AFI-zeolite channels [10]. The position of these small diameter tubes on the ‘chirality map’ is shown in figure 1.
In our theoretical study, we examined the geometrical parameters and the RBM frequencies of the tubes. Calculated results show that significant deviations from the ideal behaviour are observed for SWCNTs with small diameters.

2. Theoretical method

First principles calculations on the density functional theory (DFT) [11] level have been carried out, using the ‘Vienna ab initio simulation package’ (VASP, parallel version of 4.6) [12]. The local density approximation (LDA) [13] was used. Several calculations with generalized gradient approximation (GGA) using PW91 [14] or PBE [15] functionals were also performed to check the sensitivity of the results to the applied approximation. A plane-wave basis set was employed and we used the most recent version of VASP where the interaction between the electrons and ions is described by the projector augmented-wave (PAW) method [16] instead of pseudopotentials. In order to get accurate results, the plane-wave cut-off was set to a high value of 500 eV (18.4 au). To avoid any ‘wrap-around errors’ a sufficiently large Fourier grid was used, including all wavevectors up to twice the cut-off wavenumber. A Gaussian smearing for the occupations was used with a smearing width of 0.1 eV. Several test calculations showed the insensitivity of the results with respect to the actual value of this smearing parameter. Fifteen irreducible $k$-points ($1 \times 1 \times 30$ Monkhorst–Pack grid centred around the Γ-point) were used in the one-dimensional Brillouin zone (BZ) of achiral (zigzag, armchair) nanotubes. For chiral tubes the number of irreducible $k$-points along the tube axis was less (15, 5, 3, or 1), depending on the number of atoms in their primitive cell. One $k$-point in the two perpendicular directions was enough because the distance between the individual tubes was chosen so large that the interaction between them was negligible (see below).
Geometry optimization was carried out until all the forces acting on all atoms decreased below 0.003 eV Å$^{-1}$ ($6 \times 10^{-5}$ au). Due to the plane-wave basis set, the system must be periodical in all three dimensions. In order to obtain the properties of isolated individual tubes an artificial tetragonal arrangement (or hexagonal for test purposes) of the tubes was used as shown in figure 2, with a sufficiently large distance $l$ between the tubes, in order to minimize the interactions between them. $l$ was set to 0.6 nm in all calculations. Several test calculations were also done with $l = 1.3$ nm (to check the sensitivity of the results to this distance). Simultaneously with the ionic relaxation, the lattice constant (unit cell length) along the tube axis ($c$) was optimized as well, whereas the artificial perpendicular lattice constants were kept fixed.

To obtain the deviations from the ideal behaviour, the reference parameters of a planar honeycomb lattice were calculated as well. In order to simulate an isolated graphene sheet, a large vacuum of 0.7 nm between the graphene layers was kept fixed and the geometry optimization was carried out only within the hexagonal plane. Sixty-five irreducible $k$-points ($25 \times 25 \times 1$ Monkhorst–Pack grid, centred around the $\Gamma$-point) were used in the BZ of graphene. The optimized carbon–carbon bond length and the cohesive energy per carbon atom of graphene (with respect to a non-spin-polarized carbon atom) were found to be $r_0 = 0.1413$, 0.1424, and 0.1425 nm, and $E_0 = -10.091$, $-9.238$, and $-9.221$ eV, for three different DFT calculations: LDA-PAW, GGA-PW91-PAW, and GGA-PBE-PAW, respectively.

### 3. Geometry

The geometrical parameters, e.g. the diameter ($d_0$), the chiral angle ($\theta_0$), or the lattice constant ($c_0$), of an SWCNT can be expressed as a function of the $n$, $m$ chiral indices and can be found in many papers or textbooks, e.g. in [1]:

$$d_0 = |\vec{C}_h|/\pi = r_0\sqrt{3(n^2 + nm + m^2)}/\pi$$  \hfill (1a)

$$\tan \theta_0 = \sqrt{3}m/(2n + m)$$  \hfill (1b)

<figure>
  <center>
    ![Figure 2. Hexagonal (a) or tetragonal (b) arrangement of SWCNTs.](image)
  </center>
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\[ c_0 = \sqrt{3} |\vec{C}_h| / d_R = 3r_0 \sqrt{n^2 + nm + m^2} / \text{gcd}(2n + m, 2m + n) \]  

\[(1c)\]

(here gcd denotes the greatest common divisor of two integers).

It is usually not emphasized but it is quite obvious that these formulae (which we will refer to as the formulae for the ideal case, denoted by the zero index) are valid under the assumption that the geometrical relations within the hexagonal sheet do not change due to the wrapping. This corresponds to the wrapping of a continuous sheet with a hexagonal lattice painted on it. This means that the distance between two neighbouring carbon atoms measured along the arc on the surface of the cylinder is assumed to remain the same as the original bond length in the planar graphene sheet \(r_0\). Therefore, the true bond length measured along the straight line in three dimensions between the two carbon atoms of an SWCNT is of course always less than \(r_0\) due to the trivial curvature effect, unless the bond is parallel with the tube axis, in which case they are equal.

In principle, one could start from another assumption, for example requiring that all the carbon–carbon bond lengths remain \(r_0\). This corresponds to the wrapping of a ball-and-stick model (which we may refer to as a discrete skeleton with fixed bond lengths). It is easy to show that the two approximations give the same geometrical parameters for large enough diameters and even for small diameter tubes they differ only slightly from each other. To illustrate this let us compare the diameter calculated by both methods for achiral tubes. For \((n, 0)\) zigzag tubes the continuous wrapping results in \(d_0/r_0 = \sqrt{3n}/\pi\) whereas the skeleton wrapping results in \(d_0/r_0 = \sqrt{3}/(2 \sin(\pi/2n))\). The ratio of the two types of calculation is 1.001 for \(n = 20\) and even for \(n = 4\) it is only 1.026, the diameter for the skeleton wrapping being the larger one. For \((n, n)\) armchair tubes the continuous wrapping results in \(d_0/r_0 = 3n/\pi\) whereas the skeleton wrapping results in \(d_0/r_0 = \sqrt{1 + \left((\cos(\pi/2n) + 1/2)/\sin(\pi/2n)\right)^2}\). The ratio of the two types of calculation is 1.001 for \(n = 10\) and even for \(n = 3\) it is only 1.015, the diameter for the skeleton wrapping being the larger one.

However, both assumptions are merely approximate. The interactions between the carbon atoms are different for a planar and a curved hexagonal sheet. Therefore, there is no physical reason that the bond lengths remain unchanged, either measured three dimensionally or measured on the surface of the cylinder. In fact, as we will show, deviations from the ideal structure described by the formulae \((1a)\)–\((1c)\) occur. These deviations increase with increasing curvature, as expected.

The only geometrical property which we assume also to remain valid in the non-ideal case is the screw-axis rotational symmetry of the tubes. This means that any SWCNT contains only two independent carbon atoms (similarly to the planar hexagonal lattice); all the other atoms can be generated by applying the appropriate screw-axis rotations [1]. We checked the validity of this assumption numerically (see later).

In addition to the screw-axis rotational symmetry, all SWCNTs (even the chiral ones) possess \(C_2\) axes perpendicular to the tube axis and going through the centres of carbon–carbon bonds (from this and the screw-rotational symmetry it already follows also through the centres of the hexagons) as pointed out by Damnjanović et al [17]. A \(C_2\) axis is shown in figure 3 for the \((4, 2)\) chiral tube. It should be mentioned that this is not the case for boron nitride tubes, where no \(C_2\) symmetry axis exists due to the inequivalency of the B and N atoms. This results in a ‘buckling’ for BN-NTs; that is, the B and N atoms lie on two cylinders with different radii [18]. In contrast,
Figure 3. Inequivalent bond lengths and bond angles for the (4, 2) chiral tube. Also shown is a $C_2$ symmetry axis.

there is no such buckling for carbon NTs. The uniformity of the diameter of SWCNTs was checked in our calculations numerically (see later).

As a consequence of the screw-rotational axis plus the $C_2$ axis symmetries all carbon atoms of any given SWCNT are equivalent. This allows in the general case that there are three different bond lengths and three different bond angles, as shown on the example of the (4, 2) chiral tube in figure 3. The achiral tubes also have mirror planes going through the tube axis (zigzag) or perpendicular to it (armchair). This reduces the number of independent bond lengths and bond angles. For zigzag tubes, the two bonds ($r_2$, $r_3$) which are not parallel with the tube axis are equivalent. For armchair tubes, the two bonds ($r_1$, $r_3$) which are not perpendicular to the tube axis are equivalent. Similar equivalencies are true for the bond angles.

The various geometrical parameters of a given SWCNT are not independent from each other. The number of degrees of freedom is four for chiral and three for achiral tubes. Two parameters, the diameter ($d$) and the translational lattice constant ($c$), determine the repeating unit cell of the tube. The remaining parameter(s) describe the ‘building block’ within the unit cell, that is the length and the orientation of one particular (either) carbon–carbon bond. For achiral tubes the orientation is not a free parameter: one kind of bond has to be parallel (zigzag) or perpendicular (armchair) to the tube axis. All the remaining geometrical parameters of a tube with a given $(n, m)$ chirality (other bond lengths, bond angles, chiral angle, even the components of the screw-axis symmetry operation, etc) are already determined by the parameters mentioned above.

It should be emphasized that these geometrical parameters can differ from their ideal values, e.g. from those obtained from equations (1a) to (1c). The general case is illustrated in figure 4 by
unwrapping the real cylindrical hexagonal lattice back into a plane and comparing it with an ideal hexagonal lattice. The left part shows the ideal case of a perfect, undistorted hexagonal lattice (where all the bond lengths are equal and all the bond angles are 120°). The middle part shows the effect of the deformation of the unit cell, in this case an increase of the diameter and a shrinking along the tube axis. Note that the pairs of bonds pointing outwards from two opposing carbon atoms within a hexagon are not only parallel but also lie within the same straight line. Finally, changing the length and orientation of a particular type of bond (which, at the same time, involves a change for all the other types of bond, as well) results in the the red–green–blue coloured lattice on the right-hand side. Here, the aforementioned bonds are already misaligned; that is, while they remain parallel, they no longer fall on the same straight line. It should be mentioned that the misalignment is exaggerated in the figure, for clarity. In fact, as it will be shown below, it turned out from our calculations that whereas the distortion of the unit cell (increase of the diameter and decrease of the translational parameter) is significant for small diameter tubes, the misalignment angle ($\beta_1$) is small even for the tubes with the smallest diameters. One of the three misalignment angles ($\beta_1$) is shown in figure 4.

We emphasize that the deviation from the ideal case shown in figure 4 has a physical reason: the interactions are different when the atoms are arranged on a curved surface instead of being arranged on a plane. This effect should be clearly distinguished from the trivial geometrical fact that even in the ideal case, when a perfect hexagonal lattice is rolled up to a cylinder, the bond lengths and angles in three dimensions are different from their ideal values measured within the surface, especially when the diameter of the cylinder is small.

After these general considerations we present the results of our DFT (LDA-PAW) calculations. We studied the properties of 40 different SWCNTs, shown in figure 1. All zigzag tubes from (4, 0) to (20, 0) (red circles), and all armchair tubes from (3, 3) to (11, 11) (blue circles), were considered. The diameters of these tubes fall into the 0.3–1.6 nm interval. From the chiral tubes only those which fall within the 0.3–0.8 nm diameter range and for which the number of the atoms in the unit cell is less than 200 (green circles) were investigated.

In the first step, the geometries were optimized without taking into account the true symmetries of the tubes (VASP cannot handle screw-rotational axis symmetry). It turned out that in the optimized geometries both the screw-rotational and the $C_2$ symmetries hold with only very small random scattering in the bond lengths, bond angles, and the diameter, due to numerical errors. The scatterings in these parameters were found to be less than 0.0002 nm, 1°, and 0.33%, respectively, for the (5, 3) SWCNT. After that, we symmetrized the geometry by averaging the
symmetry-equivalent parameters. In the last step we fixed the unit cell length and minimized the total energy 'by hand' in the two- (achiral case) or three- (chiral case) dimensional space of the remaining degrees of freedom.

The total energy per carbon atom increases when a graphene sheet is folded to an SWCNT; the difference is called the folding energy. This is plotted in figure 5, where the armchair tubes are depicted by blue circles, the zigzags by red circles, and the chiral ones by green circles. According to continuum elastic theory this increase is proportional to the square of the curvature [19]. Figure 5 shows that this is indeed the case for large enough diameters. The slope of the fit for tubes with diameters larger than 1 nm is 0.078 eV nm$^2$. However, for small...
diameters the folding energy increases faster than the inverse square of the diameter as can be more clearly seen in figure 6. A similar trend was obtained in [20], but only for zigzag tubes. Figure 5 serves as the first example which points out the different behaviour of a cylinder formed of discrete atoms with respect to a continuous cylinder. The scattering of the points is out of the numerical errors; that is, one can draw the conclusion that the folding energy is not a simple function of the diameter alone but it depends also on the chirality of the tube. As we will show, similar behaviour can be observed for all other parameters, too.

Figure 7 shows that the geometry optimization results in blowing up the tubes in the radial direction: the diameters of the tubes increase with respect to the ideal values calculated by equation (1a). The smaller the diameter of the tube the larger the relative change. It should be mentioned that the increase is larger than would be expected from a simple argument based on the difference between curved and straight lines (see above). From that simple argument the increase would be only 1.5% and 2.6% for (3, 3) and (4, 0) SWCNTs, respectively, whereas the DFT calculated increase is more than twice as large.

The lattice constant also deviates from the ideal behaviour. Figure 8 plots the relative deviation as a function of the inverse diameter, showing that the deviation is significant, though smaller than that of the diameter itself. The general trend is a definite shrinking of the lattice constant, yet not as a uniform function of the diameter, but as one which also depends on the chirality. Furthermore, even for tubes of the same chirality, some additional modulation can be seen. In particular, the zigzag tubes all have the same chiral angle, yet their lattice constant shows a clear periodic pulsing, where the repeating period is formed by a group of three consecutive zigzag nanotubes. The origin of this behaviour is discussed in detail in [21, 22]. To briefly summarize: $n = 3k$ zigzag nanotubes are metallic, while the rest (except for the very small diameter tubes) are all non-metallic. The position of the gap in the band structure for the zigzag tubes always lies on the $\Gamma$–K–M straight line of the BZ, where $\Gamma$ is the centre of the BZ, K is the trigonal symmetry point of the BZ, where the HOMO and LUMO bands of graphene touch each other, and M is the midpoint between two neighbouring K points. However the gap may lie either on the $\Gamma$ side of the K point, or the M side of the K point, for the non-metallic tubes. The
two sides are inequivalent due to the anisotropy around the K point (trigonal warping). For the metallic tubes, there is no bandgap, because its position would be exactly in the K point. The location of the gap periodically moves from one side of the K point to the other as we decrease the diameter. This causes the ‘triad’ structure of the lattice constant (and just about all other parameters) for the zigzag tubes.

The bond lengths also deviate from the ideal behaviour. Figure 9 shows the relative change of the individual bond lengths as a function of the inverse diameter, for $r_1$, $r_2$, and $r_3$. Most of the bonds elongate with decreasing diameter. The only exceptions are the $r_1$ bonds (which are the most parallel to the tube axis) for the zigzag and the majority of the chiral tubes. The behaviour of $r_1$ for the zigzag tubes is surprising. This phenomenon is clearly a physical effect, which does not follow from simple graphene folding, for in the case of zigzag tubes, the $r_1$ bond—being the only bond which is exactly parallel to the tube axis—is not influenced by the curvature of the tube and, as such, it should remain completely unchanged. The scattering of the points in figure 9 clearly shows that the change in the bond lengths is not merely diameter dependent, but also chirality dependent. The zigzag tubes show the same triad structure as can be observed for the lattice constant. The armchair tubes exhibit the smallest change in the bond lengths. To illustrate the typical absolute values of the bond lengths we show the case of the very small diameter tubes grown in zeolite: the $(r_1−r_2−r_3)$ bond lengths (in Ångström) are (1.397–1.440–1.440), (1.421–1.421–1.430), and (1.409–1.432–1.428), for the (5, 0), (3, 3), and (4, 2) tubes, respectively.

The calculated bond angles are plotted in figure 10 as a function of the inverse diameter, for $\theta_1$, $\theta_2$, and $\theta_3$. All three bond angles decrease as compared to the ideal 120° for all kinds of tube with decreasing diameter. The largest decrease arises for $\theta_1$ of zigzag tubes. However, this is not surprising, as this is the angle which is most sensitive to the folding of the graphene sheet.

A more appropriate parameter to characterize the curvature effect is the pyramidalization angle [23], plotted against the inverse diameter in figure 11. This angle characterizes the $\sigma−\pi$ rehybridization effect [24], and measures the deviation from the planarity of the three bonds of a given carbon atom. Its value is 0° for a pure sp² and 19.47° for a pure sp³ carbon atom.

Figure 8. Relative change of the lattice constant from its ideal value as a function of the inverse diameter (zigzag, armchair, chiral tubes).
Figure 9. Relative change of the $r_1$ (top), $r_2$ (middle), and $r_3$ (bottom) bond lengths from their ideal values as a function of the inverse diameter (● zigzag, ● armchair, ● chiral tubes).
Figure 10. Decrease of the \( \theta_1 \) (top), \( \theta_2 \) (middle), and \( \theta_3 \) (bottom) bond angles from their ideal values as a function of the inverse diameter (\( \bullet \) zigzag, \( \bullet \) armchair, \( \bullet \) chiral tubes).
Pyramidalization angle (see [23]) against inverse diameter. This angle is $0^\circ$ for a pure sp$^2$ and $19.47^\circ$ for a pure sp$^3$ carbon atom (zigzag, armchair, chiral tubes).

Table 1. Reliability of the calculations illustrated for the relative changes in diameter, lattice constant, and bond length parallel with the tube axis (all in %) for (9, 0) and (5, 0) zigzag tubes with three different DFT parametrizations.

|       | $(d - d_0)/d_0$ | $(c - c_0)/c_0$ | $(r_1 - r_0)/r_0$ |
|-------|-----------------|-----------------|------------------|
| (9, 0) LDA-PAW | 1.06 ± 0.01 | $-0.050 \pm 0.009$ | $-0.315 \pm 0.004$ |
| PW91-PAW | 1.11 ± 0.01 | $-0.061 \pm 0.012$ | $-0.344 \pm 0.006$ |
| PBE-PAW | 1.08 ± 0.01 | $-0.057 \pm 0.015$ | $-0.332 \pm 0.006$ |
| (5, 0) LDA-PAW | 3.79 ± 0.02 | $-0.252 \pm 0.022$ | $-1.121 \pm 0.005$ |
| PW91-PAW | 3.98 ± 0.02 | $-0.295 \pm 0.040$ | $-1.194 \pm 0.008$ |
| PBE-PAW | 3.92 ± 0.01 | $-0.280 \pm 0.015$ | $-1.166 \pm 0.008$ |

This angle characterizes quantitatively the increasing chemical reactivity of the SWCNTs with increasing curvature. For the smallest diameters it reaches, even exceeds, the pyramidalization angle of C$_{60}$, which is $11.6^\circ$.

The calculated misalignment angles are plotted in figure 12 as a function of the inverse diameter, for $\beta_1$, $\beta_2$, and $\beta_3$. Though these angles are small, they are not negligible for tubes with small diameters. $\beta_1$ for zigzag tubes and $\beta_2$ for armchair tubes are exactly zero for symmetry reasons.

Finally, we discuss the reliability of our calculations. In order to estimate the errors of the geometrical parameters, we extended our calculations on the (9, 0) and (5, 0) zigzag tubes, applying various arrangements: with the distance $l$ between the tubes set to 0.6 nm as well as 1.3 nm, both in tetragonal and hexagonal arrangements (see figure 2). Table 1 summarizes the average values and the errors obtained from these different calculations for some of the most relevant geometrical parameters. As can be seen, the errorbars are smaller than the size of the circles on the figures. For comparison, the whole procedure was repeated with two more DFT
Figure 12. $\beta_1$ (top), $\beta_2$ (middle), and $\beta_3$ (bottom) misalignment angles against inverse diameter ($\bullet$ zigzag, $\bullet$ armchair, $\bullet$ chiral tubes).
parametrizations: GGA-PW91 and GGA-PBE. Whereas the average values differ slightly from those of the LDA results, the errors remain of the same order of magnitude.

4. Radial breathing mode (RBM)

The RBM, as pointed out in the introduction, plays a crucial role in the experimental determination of the chiral indices of isolated SWCNTs. Therefore, it is very important to know the precise behaviour of the RBM frequency of different nanotubes. It is a common assumption in the literature that the RBM frequency is proportional to the inverse diameter of the nanotube (just as one would expect from the continuum limit): \( \omega_{\text{RBM}} = C/d \). Different groups have used different values for the constant \( C \) (218 [5], 223.75 [25], 234 [6], 232 [7], 248 [2], and 223.5 [3], all in \( \text{cm}^{-1} \text{nm} \)). An additional constant of 10–15 \( \text{cm}^{-1} \) is sometimes used to approximately describe the effects of interaction with the environment (a substrate for isolated tubes, the outer nanotube for the inner tubes of double-wall carbon nanotubes, or neighbouring nanotubes for a sample of bundled tubes); see e.g. [3, 26, 27].

In order to investigate the RBM mode of the SWCNTs we carried out first principles calculations, using DFT. We used the same LDA-PAW method as described above. Starting from the optimized geometries, we calculated the total energies of each nanotube with fixed lattice constant \( c \) and with increased and decreased diameter, thus treating the problem as a one-dimensional oscillator. The maximum relative change in diameter was \( \pm 2\% \) in order to remain in the harmonic range. For all tubes, a good quadratic fit was obtained. The case of the (5, 3) tube—which has the largest number of atoms (196) in the unit cell of all the tubes that we considered—is illustrated in figure 13. The quadratic fit gives us the force constant, which straightforwardly determines the frequency.

Figure 14 shows the product of the diameter and the calculated RBM frequency as a function of the optimized inverse diameter. For chiral tubes, the chiral indices and the chiral angle are also depicted.
If the frequencies followed the $C/d$ rule, then ($\omega_{\text{RBM}} \cdot d$) would be constant. This approximately holds for large diameters (with $C$ being somewhere between 233 and 236 cm$^{-1}$ nm; compare with values listed earlier), yet the figure shows that there is a strong decreasing tendency of this ‘constant’ as the diameter is decreased (i.e. as the inverse diameter grows). Furthermore, this decrease is not at all smooth; the points on the figure scatter about in a rather wide range, seeming wildly on top of that. There is some order within this illusory chaos however, as both the armchair and the zigzag tubes follow a rather systematic behaviour.

The armchair tubes occupy the top region of the figure, showing the smallest average deviation (quite similar to the bond lengths). Zigzag tubes show the largest average deviation (also quite similar to the bond lengths), and on average the chiral tubes are somewhere in between. Yet individually this is no longer the case; some chiral tubes are actually slightly lower on this plot than the lowest zigzag tube, and some of the armchairs also show a greater softening than the rest of their kind. In the case of zigzag tubes a clear systematic behaviour can be recognized, reminiscent of the case of the ‘triad structure’ of geometrical parameters: non-metallic zigzag tubes tend to follow a more or less smooth curve, while the metallic ones are systematically lower than this curve.

It is worth comparing the results of figure 14 in the larger diameter region with the earlier results in [6]. Using the older version of the VASP code and ultrasoft pseudopotentials, the factor $C$ was found to be slightly different for zigzag (232 cm$^{-1}$ nm) and for armchair (236 cm$^{-1}$ nm) tubes in full agreement with our recent results, pointing out the robustness of the LDA results for the RBM frequency.

So far the RBM has been treated exactly as it was always treated in the literature: all the carbon atoms move radially inwards or outwards in phase. There is however another effect which can also influence the RBM frequency and which has never been investigated in the literature, as far as we know. The RBM is a totally symmetric $A_{1g}$ (or $A_g$) mode, but it is not the only one. In zigzag and armchair tubes, there are altogether two $A_{1g}$ modes, while in chiral tubes there are three $A_g$ modes, as pointed out recently by Damnjanović et al [17]. One is the RBM, while the other one (or other two) corresponds (correspond) to tangential movement along the
Figure 15. Calculated $\omega^{\text{RBM}} \cdot d$ against inverse diameter, by taking into account the coupling with other totally symmetric vibrational modes. The figure also shows the chiral indices and the chiral angle for chiral tubes. A general but chirality dependent softening trend can be seen as compared to the uncoupled case shown in figure 14 (zigzag, armchair, chiral tubes).

cylinder (a component of the high frequency G mode, but not the main peak of it). In principle these vibrational modes may couple to one another; the coupling is not symmetry forbidden. By treating the RBM mode together with the tangential mode(s) instead of separately, the coupling can be considered. Our results show that the coupling is small, but for smaller diameters it yields a measurable difference in the RBM frequency as compared to the un-coupled calculation. This difference is on the order of a few wavenumbers, and is most significant for the smaller tubes, such as those grown in zeolite. This may be the reason for the difference between our calculated results and those obtained by Li et al [28]. Our results for achiral tubes are in good agreement with the phonon dispersion relation study of Dubay and Kresse [29]. A more detailed study of the effect of this coupling is in progress.

In the present work we focus on the individualities of the tubes, and figure 15 shows how the individual behaviour of the RBM frequency of the nanotubes is affected by the coupling. A significant smoothening is seen as compared to figure 14.

The armchair tubes form an almost horizontal line with some small fluctuations. The zigzag tubes still show the highest deviation from the $1/d$ behaviour, suggesting that the deviation is strongest for the nanotubes with close-to-zigzag chiralities, and weakest for close-to-armchair chiralities. The chiral tubes do tend to follow this behaviour, but there are numerous exceptions as well. Some tubes with a chiral angle far from being close to zigzag fall closer to the zigzag tubes; in other words, the frequencies of some ‘weird’ chiral nanotubes are softened more than their chiral angle suggests (if we accept the argument above). However a simple explanation can be given for this phenomenon. Restricting ourselves to the zigzag tubes, we can see that they show the same behaviour as in the un-coupled calculation: the non-metallic tubes follow a more or less smooth curve, while the metallic ones systematically drop below this smooth curve, as if the metallic band structure would further contribute to the softening of the RBM mode beyond the high curvature. Now, if we examine figure 15 again, it is easy to see that all the aforementioned ‘weird’ tubes are not at all weird, they are just metallic! For example, let us consider the following series of tubes: (6, 1), (6, 2), (6, 3), and (6, 4). One would expect these
four nanotubes to show a monotonically decreasing amount of deviation in the order written above. But figure 15 shows that, while the non-metallic (6, 1), (6, 2), and (6, 4) do indeed follow a monotonically decreasing curve with decreasing diameter, the single metallic (6, 3) drops below this curve. The (5, 2) tube also falls lower than we would expect from the position of the (5, 1) and (5, 3) tubes, and (7, 1) even falls below the zigzag tubes.

In summary, we conclude the following for the behaviour of the RBM mode of small diameter nanotubes. The strong curvature effects cause a significant deviation from the simple $1/d$ rule which describes the larger diameter tubes well. This is expected, as curvature effects become more and more important at smaller diameters. Beyond this deviation, there is also a wide scattering of the RBM frequencies for tubes of nearly the same diameter but different chiralities. Thus the RBM frequency does not depend merely on the diameter, but the chiral angle as well. One more effect stands out in our results, namely that the metallic nanotubes show a greater softening of the RBM frequencies than the non-metallic ones.

5. Summary

We have studied theoretically the geometry and the RBM of SWCNTs with small diameter. We have carried out first principles calculations using DFT within the LDA, applying a plane-wave basis set and PAW method. All tubes (achiral and chiral as well) were investigated within the 0.3–0.8 nm diameter range for which the number of atoms in the unit cell is less than 200 (three armchair, six zigzag, and 14 chiral tubes). In addition to that the investigations were extended for all achiral tubes with diameters less than 1.6 nm (the largest armchair and zigzag tubes considered were (11, 11) and (20, 0), respectively).

The properties of nanotubes with large enough diameters can be described by the ‘graphene folding’ approximation; we call this the ideal behaviour. All geometrical parameters of the nanotubes show an increasing deviation from the ideal behaviour with decreasing diameter. As curvature increases, the diameter becomes larger and the unit cell length becomes shorter with respect to their ideal values. The bond lengths and bond angles become different from their ideal values and they are no longer uniform. The changes of the geometrical parameters depend not only on the curvature but also on the chirality and even on the electronic structure of the tube. This can be most clearly seen for zigzag tubes. They all have the same chiral angles (zero) but their parameters show a characteristic periodicity with a period of 3. This triad structure is a consequence of the periodic change of the bandgap position combined with the trigonal warping.

The RBM frequency is usually assumed to depend on the inverse of the diameter of the tube. It turns out from our calculations that this is only true for large enough diameters. Increasing curvature leads to a softening of the RBM frequency with respect to what would follow from a simple $1/d$ behaviour. This softening depends not only on the curvature. For tubes with similar diameter, zigzag tubes have smaller RBM frequencies, armchair tubes have larger RBM frequencies, and the chiral tubes are in between. The dependence on the chiral angle is further ‘modulated’ by the dependence on ‘metallicity’: metallic tubes have systematically lower RBM frequencies than the semiconducting tubes, if we compare tubes with similar diameter and chiral angle. The ‘opening’ of the RBM frequency versus diameter plot, in other words the deviation from the ideal $1/d$ behaviour, is only a few wavenumbers for tubes with diameters around 1 nm; however, it can be as large as 20 cm$^{-1}$ for tubes with the smallest diameters.

There is one more important factor which can influence the RBM. We have shown, as far as we know for the first time in the literature, that the coupling of the RBM to the other totally
Table 2. Diameter in nm ($d_{\text{DFT}}$), relative change of the unit cell constant in % ($\Delta c/c_0$), and RBM frequency in cm$^{-1}$ without ($\omega_{\text{DFT}}$) and with coupling ($\omega^*_{\text{DFT}}$) of small diameter SWCNTs, together with some other characteristics (see text).

| n | m | N | $\theta_0$ | $d_0$ | $d_{\text{DFT}}$ | $\Delta c/c_0$ | $234/d_{\text{DFT}}$ | $\omega_{\text{DFT}}$ | $\omega^*_{\text{DFT}}$ |
|---|---|---|-----------|------|-----------------|----------------|-------------------|----------------|----------------|
| 4 | 0 | 16 | 0        | 0.3116 | 0.3341          | -1.293         | 700.4            | 651.3          | 642.3          |
| 5 | 3 | 76 | 23.4     | 0.3395 | 0.3531          | 0.277          | 662.7            | 651.1          | 648.6          |
| 4 | 1 | 28 | 10.9     | 0.3569 | 0.3732          | -0.343         | 627.0            | 589.5          | 584.1          |
| 5 | 0 | 20 | 0        | 0.3895 | 0.4043          | -0.274         | 578.8            | 544.9          | 536.1          |
| 3 | 3 | 12 | 30       | 0.4047 | 0.4176          | -0.096         | 560.3            | 541.1          | 551.4          |
| 4 | 2 | 56 | 19.1     | 0.4122 | 0.4252          | -0.196         | 550.4            | 539.5          | 536.3          |
| 5 | 1 | 124 | 8.9     | 0.4337 | 0.4462          | -0.172         | 524.4            | 487.1          | 493.2          |
| 6 | 0 | 24 | 0        | 0.4673 | 0.4793          | -0.188         | 488.2            | 463.6          | 458.5          |
| 4 | 3 | 148 | 25.3    | 0.4738 | 0.4833          | 0.101          | 484.1            | 479.4          | 476.0          |
| 5 | 2 | 52 | 16.1     | 0.4864 | 0.4970          | -0.063         | 470.8            | 451.5          | 448.8          |
| 6 | 1 | 172 | 7.6     | 0.5108 | 0.5216          | -0.192         | 448.6            | 437.8          | 432.8          |
| 4 | 4 | 16 | 30       | 0.5396 | 0.5489          | -0.028         | 426.3            | 424.3          | 419.2          |
| 5 | 3 | 196 | 21.8    | 0.5452 | 0.5546          | -0.084         | 421.9            | 417.4          | 413.5          |
| 7 | 0 | 28 | 0        | 0.5452 | 0.5546          | -0.043         | 421.9            | 411.0          | 405.3          |
| 6 | 2 | 104 | 13.9    | 0.5617 | 0.5704          | -0.008         | 410.3            | 404.5          | 400.2          |
| 7 | 1 | 76 | 6.6      | 0.5881 | 0.5971          | -0.090         | 391.9            | 374.6          | 373.1          |
| 6 | 3 | 84 | 19.1     | 0.6182 | 0.6263          | -0.038         | 373.6            | 364.5          | 363.1          |
| 8 | 0 | 32 | 0        | 0.6231 | 0.6319          | -0.119         | 370.3            | 363.6          | 358.5          |
| 5 | 5 | 20 | 30       | 0.6746 | 0.6821          | -0.058         | 343.1            | 337.3          | 338.9          |
| 6 | 4 | 152 | 23.4    | 0.6790 | 0.6864          | -0.043         | 340.9            | 336.1          | 333.4          |
| 9 | 0 | 36 | 0        | 0.7010 | 0.7084          | -0.043         | 330.3            | 317.8          | 318.2          |
| 8 | 2 | 56 | 10.9     | 0.7139 | 0.7209          | -0.021         | 324.6            | 316.5          | 314.9          |
| 7 | 4 | 124 | 21.1    | 0.7512 | 0.7580          | -0.051         | 308.7            | 307.1          | 303.7          |
| 10 | 0 | 40 | 0        | 0.7789 | 0.7852          | 0.008          | 298.0            | 294.5          | 290.7          |
| 6 | 6 | 24 | 30       | 0.8095 | 0.8158          | -0.058         | 286.8            | 284.3          | 283.6          |
| 11 | 0 | 44 | 0        | 0.8568 | 0.8629          | -0.051         | 271.2            | 268.2          | 264.6          |
| 12 | 0 | 48 | 0        | 0.9347 | 0.9401          | -0.013         | 248.9            | 242.8          | 242.2          |
| 7 | 7 | 28 | 30       | 0.9444 | 0.9499          | -0.053         | 246.3            | 246.2          | 243.4          |
| 13 | 0 | 52 | 0        | 1.0126 | 1.0172          | 0.006          | 230.0            | 228.9          | 225.5          |
| 8 | 8 | 32 | 30       | 1.0793 | 1.0843          | -0.046         | 215.8            | 216.5          | 213.1          |
| 14 | 0 | 56 | 0        | 1.0905 | 1.0951          | -0.026         | 213.7            | 212.4          | 209.7          |
| 15 | 0 | 60 | 0        | 1.1684 | 1.1725          | -0.007         | 199.6            | 196.4          | 195.6          |
| 9 | 9 | 36 | 30       | 1.2142 | 1.2186          | -0.037         | 192.0            | 192.7          | 189.4          |
| 16 | 0 | 64 | 0        | 1.2463 | 1.2501          | 0.002          | 187.2            | 186.4          | 183.7          |
| 17 | 0 | 68 | 0        | 1.3241 | 1.3281          | -0.023         | 176.2            | 175.6          | 173.0          |
| 10 | 10 | 40 | 30       | 1.3491 | 1.3531          | -0.031         | 172.9            | 173.6          | 170.7          |
| 18 | 0 | 72 | 0        | 1.4020 | 1.4054          | -0.005         | 166.5            | 164.4          | 163.5          |
| 19 | 0 | 76 | 0        | 1.4799 | 1.4831          | 0.001          | 157.8            | 157.3          | 155.1          |
| 11 | 11 | 44 | 30       | 1.4840 | 1.4874          | -0.024         | 157.3            | 158.0          | 155.2          |
| 20 | 0 | 80 | 0        | 1.5578 | 1.5613          | -0.019         | 149.9            | 149.3          | 147.1          |
symmetric modes at higher frequencies is small, but not negligible. The detailed analysis of this
effect is in progress.

Finally, we summarize the most important calculated parameters in table 2. The first two
columns show the $n$ and $m$ chiral indices; the third column shows $N$, the number of carbon
atoms in the unit cell. In the next two columns the ‘ideal’ values for the chiral angle ($\theta_0$, in
degrees) and diameter ($d_0$, in nm), obtained by equations (1b) and (1a), can be seen. For the
diameter, $r_0 = 1.413$ Å was used as the LDA-PAW optimized value for the bond length in
graphene. The next two columns show the LDA-PAW optimized diameter of the tubes ($d_{\text{DFT}}$ in
nm) and the relative change of the lattice constant ($\Delta c/c_0 = (c_{\text{DFT}} - c_0)/c_0$ in %). In the last
three columns the RBM frequencies can be seen: first, for comparison, the one calculated with
the usual inverse diameter formula, $\omega_0 = 234/d_{\text{DFT}}$, where 234 cm$^{-1}$ nm is our DFT calculated
average coefficient for large diameter tubes (without coupling); the last two columns show our
LDA-PAW calculated values, first assuming that all atoms move purely in a radial direction
($\omega_{\text{DFT}}^r$), and lastly allowing the coupling with the totally symmetric tangential mode (modes) for
achiral (chiral) tubes ($\omega_{\text{DFT}}^\ast$).

Acknowledgments

We acknowledge financial support from the grants OTKA T038014 and FKFP-0144/2000 in
Hungary, and from the National Science Foundation (grants CHEM-9802300 and CHEM-
9601976) in the USA. We thank Professor G Kresse, O Dubay and Professor P Knoll for useful
discussions. DFT calculations were performed on the Schrödinger II cluster at the University of
Vienna, using the Vienna ab initio simulation package (VASP).

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