Lattice dynamics and symmetry of double wall carbon nanotubes

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Abstract. Stable configurations and full symmetry groups of double wall carbon nanotubes are determined. These are used to calculate phonon bands for commensurate tubes. In particular, the modes with rigid walls are analysed and weak interlayer interaction is confirmed. Taking infra-red measurements is found to be a suitable method for characterizing double wall tubes. The heat capacity in the low temperature region is predicted to be lower than for single wall layers.

Contents

1 Introduction 2
2 Interlayer interaction 3
3 Stable configurations and symmetry 5
4 The dynamical matrix and its reduction 8
5 Phonons and perturbative interpretation 9
6 Rigid layer modes 10
7 Concluding remarks 13
   References 14

1 http://www.ff.bg.ac.yu/nanoscience
1. Introduction

Among the many synthesized carbon nanostructures, nanotubes [1] have proved to be the most interesting from the materials science viewpoint, due to their remarkable physical properties. Single wall carbon nanotubes (SWCNs) [2] have been intensively studied during the past decade, but recently methods of producing double wall carbon nanotubes (DWCNs) have been successfully developed [3]. Resonant Raman measurements have been performed on DWCNs [4], as well as experiments that are related to wall telescoping [5]. On the other hand, theoretical investigations have been very restricted. First, the interaction between walls was estimated numerically [6] and later it was studied more precisely [7, 8]; symmetry arguments were used to explain these results [9, 10]. Also, the potential barrier to relative displacements of layers has been calculated and mechanical nanodevices based on bolt–nut pair-like motions of the layers have been proposed [11]. Recently, DWCN breathing-like (BL) phonon mode calculations have been carried out [12] and interpreted within a simple analytical model [13].

Here we present a symmetry-based study of the lattice dynamics of DWCNs. First (section 2), we review the results on the influence of symmetry on the interaction between the walls. The conclusions are applied in section 3 to find the stable relative positions of the walls and the symmetry groups of DWCNs. To this end we use a simply modelled interwall interaction of the Lennard-Jonestype, since it is known that density functional methods are not reliable in van der Waals systems, despite some recent attempts to overcome this problem [14]. Then, in section 4 we explain how the dynamical matrix is constructed and reduced with the help of symmetry, enabling one in the case of commensurate DWCNs (CDWCNs) to diagonalize it by convention); therefore, its symmetry group is a line (also called a monoperiodic or a rod) group [9]:

$$L_C = T^r_q(a)D_n = Lq_{p22}, \quad L_{2A} = T^r_{q=2n}(a)D_{nh} = L2n_a/mcm.$$  \(1a\)

The label \(C\) refers to chiral tubes, for which \(n_1 > n_2 > 0\) and the chiral angle \(0 < \theta < \pi/6\). Analogously, \(Z\) and \(A\) stand for the achiral tubes: zigzag \((n_1 > n_2 = 0, \theta = 0)\) and armchair \((n_1 = n_2 > 0, \theta = \pi/6)\). The chiral and achiral groups are given as the products of subgroups: \(T^r_q(a)\) is the helical group of translational period \(a\) and rotational axis order \(q\), generated by \((C_q)^qna/q\), while \(D_n\) and \(D_{nh}\) are the point groups, which besides pure rotations \(C_n\) also contain the horizontal \(U\) axis; also, in \(D_{nh}\) there are vertical, \(\sigma_v\), and horizontal, \(\sigma_h\), mirror planes. The symmetry parameters are functions of \(n_1\) and \(n_2\):

$$n = \text{GCD}(n_1, n_2), \quad q = 2(n_1^2 + n_1n_2 + n_2^2)/nR, \quad a = \sqrt{3}DnR.$$  \(1b\)

while the helicity \(r\) is more complicated [9]. Here, \(a_0 = 2.461\ \text{Å}, D = (n/\pi)\sqrt{qR/2na_0}\) is the tube diameter and \(R = \text{GCD}(2n_1 + n_2, n_1 + 2n_2)/n\).
If a carbon atom is put at the point \( r_{000} = (D/2, \varphi_{000}, z_{000}) \) (cylindrical coordinates) and the symmetry transformations are applied to it, the whole nanotube is generated. To be precise, the atoms of the tube are at
\[
r_{tsu} = (C_q |n a/q)^r C_n U^s r_{000} = \left( \frac{D}{2}, (-1)^s \varphi_{000} + 2\pi \left( \frac{t r}{q} + \frac{s}{n} \right), (-1)^u z_{000} + \frac{n}{q} \right),
\]
for \( t = 0, \pm 1, \ldots, s = 0, \ldots, n - 1 \) and \( u = 0, 1 \).

2. Interlayer interaction

A double wall tube \( W'@W \) is a pair of coaxially arranged SWCNs \( W = (n_1, n_2) \) and \( W' = (n'_1, n'_2) \). Raman spectroscopy results for DWCNs [3, 4], particularly the frequencies of the breathing modes, show that the distance \( \Delta = (D - D')/2 \) between the two walls in a DWCN is close [16] to that in graphite, 3.44 Å.

Because of the coaxiality, there are two parameters completely determining the configuration of a DWCN (figure 1): the angle \( \Phi \) and length \( Z \) by which the outer tube is rotated around \( z \) and translated along \( z \) from the position with coinciding \( x \) and \( x' \) axes of the walls. For each wall we fix the coordinate system with the \( x \) axis coinciding with the \( U \) axis (the one passing through the centre of the carbon hexagon). Accordingly, the atomic positions of the inner and outer wall are given by equation (2) with
\[
\varphi'_{000} = \frac{n'_1 + n'_2}{\pi D^2} a_0^2; \quad z'_{000} = \frac{n'_1 - n'_2}{2\sqrt{3}\pi D} a_0^2;
\]
\[
\varphi_{000} = \frac{n_1 + n_2}{\pi D^2} a_0^2 + \Phi; \quad z_{000} = \frac{n_1 - n_2}{2\sqrt{3}\pi D} a_0^2 + Z.
\]

For the fixed configuration \((\Phi, Z)\) the potential between walls is given as the sum of the interactions \( v(r_{i's'u'}, r_{tsu}) \) between the atoms at \( r_{i's'u'} \) in the inner and at \( r_{tsu} \) in the outer wall:
\[
V(\Phi, Z) = \sum_{i's'u'} \sum_{tsu} v(r_{i's'u'}, r_{tsu}).
\]

The stable configuration \((\Phi_0, Z_0)\) is determined by finding the minimum of this potential. At first sight this appears not to be an easy task: the sum is infinite, the pairwise potential should be known etc. Some approximations may substantially change the results. However, the symmetry enables one to solve the problem of finding minima safely. It will be used within two different arguments.
Firstly, symmetry gives rise to a powerful topological argument [17]: the extremes of an invariant function are in the positions of maximal symmetry. The potential equation (5) is obviously invariant under the symmetries of both walls and therefore under the total DWCN symmetry group, which is their intersection. The consequence is that the nonequivalent possible stable configurations are well separated, since there are only a few maximal symmetry groups. This makes many of the details of the computations inessential, giving a clear bound for the computational precision: each calculation which makes a difference between these discrete possible minima is acceptable.

Secondly, symmetry provides a very efficient way to calculate the potential equation (5) in two steps [10]. In fact, the sum over the inner tube, for the fixed position \( r = (D/2, \varphi, z) \) on the outer one, can be performed first, giving

\[
V(\Phi, Z) = \sum_{tsu} V_{in}(r_{tsu})
\]

where the potential \( V_{in}(r) \) may be understood as the potential emitted by the inner wall, in which the outer one is moving:

\[
V_{in}(r) = \sum_{t's'u'} v(r'_{t's'u'}, r).
\]

A technical advantage is that \( V_{in}(r) \) needs to be calculated only once and then the various configurations \((\Phi, Z)\) can be scanned with this potential, reducing the computational time to the square root of that required for the double summation in equation (5). Still the most substantial advantage is that \( V_{in}(r) \) is an invariant function of the symmetry group of the inner tube. This enables one to expand it over the basis of invariant functions:

\[
V_{in}(r) = \sum_{M \geq 0, \omega} a^M_{\omega}(D) C^M_{\omega}(\varphi, z),
\]

where the basis of invariant functions for the chiral tubes is

\[
C^M_{\omega}(\varphi, z) = \cos(M \varphi + 2\pi \omega z), \quad M = 0, 1, \ldots; \omega \text{ real}.
\]

For the achiral tubes, the basis is formed by the combinations

\[
A^M_{\omega}(\varphi, z) = C^M_{\omega}(\varphi, z) + C^{-M}_{\omega}(\varphi, z), \quad M, \omega \geq 0.
\]

Thus, due to the symmetry, a precise algorithm for finding \( V_{in} \) is at our disposal. Due to the invariance of this potential it is sufficient to determine it at \( r = D/2 \), for the intervals \( \varphi \in [0, 2\pi] \) and \( z \in [-a'/2, a'/2] \) (the period of the inner tube). This is done by scanning the potential at sufficiently many points; then the fast Fourier transform immediately gives the amplitudes in the expansion equation (8). The contribution of the inner tube atoms which are far from \( z = 0 \) is negligible, since the reasonable potentials rapidly decrease.

The interatomic potential is taken to be the fitted Lennard-Jones one [18]:

\[
v(r) = -\frac{18.5426}{|r|^6} + \frac{29 000.4}{|r|^12}.
\]

It should be noted that for fixed \( \varphi \) and \( z \) the potential \( V_{in}(\rho, \varphi, z) \) varies very slowly for \( \rho \) in the vicinity of 3.44 Å, making relaxation in the interlayer distance inessential for the walls with diameter differences of \( 2\Delta = (6.88 \pm 0.5) \) Å. In fact, for fixed \( \Phi \) and \( Z \), in the vicinity of the nonrelaxed configuration (purely folded layers) the total potential \( V \) has almost zero slope as
Figure 2. The interlayer interaction $V(\Phi, Z)$. Top: 2D plots for one of the coordinates fixed in the stable position. Bottom: a 3D plot. Note the longitudinal smoothness for the incommensurate $ZA$ DWCN and very weak circumferential roughness for the commensurate $AA$ DWCN.

3. Stable configurations and symmetry

After calculating the potential $V_{in}$, the interaction between the walls is found with the help of equation (6). It turns out that two classes of DWCNs should be distinguished. If the DWCN is incommensurate (an IDWCN), i.e. the ratio $a'/a$ of the wall periods is irrational, $V_{in}$ is $z$ independent and therefore the interwall interaction is a function of $Z$ only (figure 2). Therefore, the minima of $V(\Phi)$ are lines along $Z$, singling out periodic stable relative positions only ($s = 0, \ldots, Q_B - 1$):

$$\Phi_s = \Phi_0 + s \frac{2\pi}{Q_B}.$$  \hspace{1cm} (12a)
Otherwise, i.e. for commensurate tubes (CDWCNs), the minima are discrete, giving diperiodic stable positions \( t = 0, \pm 1, \ldots; s = 0, \ldots, N_B - 1 \):

\[
Z_t = Z_0 + t \frac{A_B N_B}{Q_B}, \quad \Phi_{ts} = \Phi_0 + 2\pi s \frac{Q_B}{Q_B} + t R_B.
\] (12b)

These observations and particularly the values of \( N_B, R_B \) and \( Q_B \) (positive integers) and \( A_B \) (positive real) are readily explained in terms of the symmetry groups.

The symmetry group \( L_{W} \) of a DWCN is the intersection of the symmetry groups \( L_W \) and \( L_{W'} \) of its layers. That is, only the symmetries common to the two layers leave the DWCN invariant. Due to the assumption of coaxial walls, the DWCN symmetries involving rotations around the \( z \) axis and translations along it are independent of \( \Phi \) and \( Z \). In contrast, on varying \( \Phi \) one changes the position of the \( U \) axis and vertical mirror/glide planes of the outer tube, while translations along the \( z \) direction change the \( U \) axis and the horizontal mirror/roto-reflection planes. Thus only for special values of \( (\Phi, Z) \) do some of the parities coincide; they should thus be included in the DWCN symmetry. Consequently, the roto-translational part \( L_{W'}^{RT} = L_W^{RT} \cap L_{W'}^{RT} \) of the intersection is independent of the relative wall positions, and can be directly calculated from equation (1b). For most of the relative positions this is the full symmetry group \( L_{W' \ast W} \) of the DWCN. Only in the special positions with coinciding parities of the walls are these added to \( L_{W' \ast W}^{RT} \) to get \( L_{W' \ast W}^{RT} \). These special positions are the only candidates for providing stable configurations, as revealed by the anticipated topological theorem [17].

The roto-translational subgroup of DWCN, which is the intersection of the layers’ roto-translational subgroups, has been found [9, 19]. In the incommensurate cases, there are no common translational symmetries and this group reduces to

\[
L_{W' \ast W}^{RT} = C_N.
\] (13a)

Otherwise, for commensurate walls, the DWCN is periodic and the \( L_{W' \ast W}^{RT} \) group is the line group

\[
L_{W' \ast W}^{RT} = T_{\Phi_1}^R(A)C_N.
\] (13b)

The parameters of the symmetry groups are

\[
A = \hat{\alpha}' a = \hat{\alpha}a', \quad Q = N \sqrt{\bar{q} \bar{q}'}/\tau, \quad R = (r \hat{\alpha} + s \bar{q})Q/q, \quad N = \text{GCD}(n, n').
\] (14)

Here, \( \bar{q} = q/n, \bar{q}' = q'/n', \hat{\alpha} = \sqrt{\bar{q}/\text{GCD}(\bar{q}, \bar{q}')}\), \( \hat{\alpha}' = \sqrt{\bar{q}'/\text{GCD}(\bar{q}', \bar{q}')}\), while \( \tau = \sqrt{\bar{q} \bar{q}'}/\text{GCD}(r'\hat{\alpha}' q - r' \hat{\alpha} q'/n', \sqrt{\bar{q} \bar{q}'}) \). Further, the equation for the helicity \( R \) involves

\[
s = \tau (r' \hat{\alpha}' q - r' \hat{\alpha} q')(n' \phi(\hat{\alpha}'))/n' q q',\text{ where } \phi \text{ is the Euler function. In place of } R, \text{ any integer } R + j Q/N(\text{mod } Q) (j = 1, \ldots, N) \text{ may be used; as for SWCNs, we chose the unique one which is non-negative, co-prime with } Q \text{ and less than } Q.
\]

Due to the summations over the atoms, the interaction potential equation (5) is clearly invariant under all the transformations generated by the symmetries of both \( L_W \) and \( L_{W'} \). In particular, the roto-translational transformations of the two walls commute and together form the breaking group \( L_{B}^{RT} \).

In the incommensurate case, mutually incommensurate translations by \( a \) and \( a' \) generate the translational group \( T(0) \) containing all the translations \( t a + t' a' \) for all integers \( t \) and \( t' \). Using this, the breaking group is

\[
L_{B}^{RT} = C_{Q_0} T(0).
\] (15a)

\[New Journal of Physics 5 (2003) 148.1–148.15 (http://www.njp.org/)]
Note that \( T(0) \) is a quasi-continuous group: for each given number \( x \) and arbitrary \( \epsilon \), there is a choice of the integers \( t \) and \( t' \) such that \( ta + t'a' \) differs from \( x \) by less than \( \epsilon \). Therefore, the invariance of \( V(\Phi, Z) \) under this group means mathematically that for fixed \( \Phi \) the potential is constant almost everywhere along \( Z \). On the other hand, discontinuity of the potential is physically unacceptable, meaning that \( V(\Phi, Z) \) is \( Z \) independent, as observed numerically. The remaining invariance \( C_{Q_b} \) leads directly to equation (12a). In the commensurate cases, the breaking group is the line group \([19] \):

\[
L_{B}^{RT} = T_{Q_b}^{R_B}(A_B) C_{N_B}.
\]

The parameters in the last equation are

\[
N_B = \frac{mn'}{N}, \quad Q_B = \frac{qq'}{\text{GCD}(q, q')}, \quad A_B = \frac{aa'Q_bQ}{ANqq'}, \quad R_B = \frac{(r'\hat{a}q - r\hat{a}'q')a^{\phi(\hat{a})} + r'q'a'}{\hat{a}\hat{a}'} \quad (\text{mod GCD}(N\bar{q}\bar{q}', r'\hat{a}q - r\hat{a}'q'))
\]

\((R_B)\) is the minimal co-prime of \( Q_B \) solving the last equation.

It is remarkable that the roto-translational symmetry of the DWCN is greatly reduced in comparison to those of the walls, while, in contrast, the breaking group is much greater. In fact, the orders of the groups satisfy the relation

\[
L_{w/w}^{RT} | L_{B}^{RT} | L_{w}^{RT} = L_{w/w}^{RT} | L_{B}^{RT} | L_{w}^{RT}
\]

naturally, showing that the greater symmetry remaining in the DWCN, the less the breaking. In other words, the periods, \( A_B \) along \( Z \) and \( 2\pi/N_B \) along \( \Phi \), of the interaction potential decrease with the periods \( A \) and \( 2\pi/N \) of the DWCN. An incommensurate tube can be viewed as the limiting case: \( \tau = 0 \) and \( A = \infty \) (thus \( A_B = 0 \)), while, due to the \( Z \) independence, the fractional translations do not affect the potential and \( Q_B \) takes the role of \( N_B \).

These considerations confirm the results of numerical calculations. Finally, the stable configurations obtained are given by equation (12a) with

IDWCN

\[
\Phi_0 = 0, \quad Z_0 \text{ arbitrary}; \quad (17a)
\]

CDWCN, with \( C \) wall

\[
\Phi_0 = 0, \quad Z_0 = 0; \quad (17b)
\]

\((9, 0)@ (18, 0) \) and \((5, 5)@ (10, 10) \)

\[
\Phi_0 = \frac{\pi}{4N}, \quad Z_0 = \frac{A}{4}; \quad (17c)
\]

\((n \neq 9, 0)@ (n + 9, 0), (n \neq 5, n)@ (n + 5, n + 5) \)

\[
\Phi_0 = 0, \quad Z_0 = \frac{A}{4}. \quad (17d)
\]

All of these positions are special. For an IDWCN with both walls achiral, a vertical mirror plane is present. Further, the choice \( Z_0 = 0 \) includes also the \( U \) axis and (for both walls achiral) a horizontal mirror/roto-reflection plane (depending on \( n \) and \( n' [9] \)). For CDWCNs the symmetry groups are unique. Altogether, the resulting groups are

IDWCN; at least one \( C \) wall, \( L_{w/w} = D_{Q} \), \( \bar{Z}A, A\bar{Z}, L_{w/w} = D_{Q4}, D_{Qh}; \quad (18a) \)

CDWCN with \( C \) wall

\[
L_{w/w} = T_{Q}^{R}(A) D_{N}; \quad (18b)
\]

\((9, 0)@ (18, 0) \) and \((5, 5)@ (10, 10) \)

\[
L_{w/w} = T_{o}(A) S_{2N}; \quad (18c)
\]

\((n \neq 9, 0)@ (n + 9, 0), (n \neq 5, n)@ (n + 5, n + 5) \)

\[
L_{w/w} = T(A) D_{Nd}. \quad (18d)
\]

New Journal of Physics 5 (2003) 148.1–148.15 (http://www.njp.org/)
The isogonal point groups for commensurate tubes are

\[
\begin{align*}
\text{CDWCN with C wall} & \quad P_{W'W} = D_{Q'}; \\
(n, 0) @ (n + 9, 0), (n, n) @ (n + 5, n + 5) & \quad P_{W'W} = D_{N\delta}.
\end{align*}
\]

(19a) (19b)

4. The dynamical matrix and its reduction

After the stable configurations are fixed, the atomic positions are readily found from equation (2). This enables us to look for the dynamical matrix \( D \). For each pair of atoms \( \alpha \) and \( \beta \), there is a 3 × 3 submatrix \( D_{\alpha\beta} \) of \( D \). Adopting the convention that the atoms of the wall \( W' \) are counted first and after them the atoms of the wall \( W \), \( D \) takes on the block structure

\[
D = D_W^0 + D_W', \quad D_W^0 = \begin{pmatrix} D_W^0 & 0 \\ 0 & D_W' \end{pmatrix}, \quad D_W' = \begin{pmatrix} d_W & D_{WW}' \\ D_{WW}' & d_W \end{pmatrix}.
\]

(20a)

Here, \( D_{W'W} \) consists of the submatrices \( D_{\alpha'\beta} \) comprising the intralayer coupling, and analogously the transposed matrix \( D_{WW}' \). The dynamical matrix \( D_W^0 \) of the isolated wall \( W \) contains submatrices \( D_{\alpha\beta} \), while \( d_W \) is the matrix with zero elements apart from the diagonal submatrices

\[
d_{aa} = -\sum_{\beta} D_{\alpha\beta}.
\]

In fact, according to the translational sum rule, \( D_W^0 = -\sum_{\beta (\neq a)} D_{\alpha\beta} \), while \( D_{aa} = D_W^0 - d_{aa} \) depends on the intralayer coupling. The same holds for the layer \( W' \).

We calculate the interlayer interaction by means of the force constant model, used recently for SWCNs [20]. In fact, we start from the graphite force constants [21] and adjust them to the tubular geometry: first the dynamical correction is made to describe approximately the change of the local force between each atom pair \( \alpha \) and \( \beta \) (induced by the folding of the graphite layer) and then a fine improvement is performed to accommodate the kinematical rotational sum rule. Denoting by \( S_{\alpha\beta} \), \( O_{\alpha\beta} \) and \( I_{\alpha\beta} \) the stretching, out-of-plane and in-plane force constants, one gets the intralayer submatrix

\[
D_{\alpha\beta} = U_{\alpha\beta} D_{\alpha\beta} U_{\alpha\beta}^T, \quad D_{\alpha\beta} = \begin{pmatrix} S_{\alpha\beta} & 0 & 0 \\ 0 & O_{\alpha\beta} & 0 \\ 0 & 0 & I_{\alpha\beta} \end{pmatrix}.
\]

(20b)

where \( U_{\alpha\beta} \) is the orthogonal matrix relating the laboratory frame to the local stretching, out-of-plane and in-plane frames of \( \alpha \) and \( \beta \). The force constants used include the interaction up to fourth-level neighbours (i.e. the nearest 18 neighbours of each atom), while for all other pairs of atoms \( D_{\alpha\beta} = 0 \). For the atoms from different walls the potential equation (11) gives directly the corresponding interlayer submatrices in the Hessian form:

\[
D_{\alpha'\beta'} = \frac{\partial^2 v(r_\alpha' - r_\beta')}{\partial x_i^{\alpha'} \partial x_j^{\beta'}}.
\]

(20c)

The dynamical matrix obtained in this way is invariant under the symmetries of the DWCN, which are further used to reduce it to facilitate the diagonalization. As for the incommensurate DWCNs, the point group symmetry equation (18a) is to be applied. The finiteness of the groups prevents very efficient reduction and (depending on the hardware capabilities) only tubes with very small numbers of atoms, i.e. short ones, can be studied. In contrast, in the commensurate cases, the symmetry of the infinite line groups enables consideration of perfect infinite CDWCNs.
Therefore, we restrict the phonon spectra calculations to the CDWCNs. To this end we use the polymer symmetry simulation package POLSym (E) [15], fully incorporating the symmetry of quasi-1D crystals in calculations of electron and phonon bands. The modified group projector technique [22] implemented exactly reduces consideration to the atoms generating the whole CDWCN by means of transformations of its symmetry group only; their number will be denoted by \( Y \) (for SWCNs \( Y = 1 \), while for CDWCNs it is larger, but finite). Then for each irreducible representation \( \Gamma \) (its dimension \( |\Gamma| \) is 1, 2 or 4) of \( L'_{WW} \) the ‘pulled down’ \( 3|\Gamma|Y \) dimensional dynamical matrix \( D'_{\Gamma} \) is constructed. Its eigenvalues are the same as the \( \Gamma \) assigned eigenvalues of \( D \), while the eigenvectors of \( D'_{\Gamma} \) give displacements of the \( Y \) generating atoms. Using simple transformation rules [22, 20], one easily finds the displacements of the other atoms in the generalized Bloch form. Thus, the complete solution of the eigenvalue problem—phonon dispersions and normal displacements—is found when this task is performed for all irreducible representations of \( L'_{WW} \).

5. Phonons and perturbative interpretation

After the dynamical matrix has been constructed and reduced, the phonon dispersions are easily calculated. Some common characteristics of CDWCN phonon bands can be seen in figure 3, presenting the branches of the tube \((5, 5)\oplus(10, 10)\). As in all quasi-1D crystals, there are four acoustic modes: longitudinal acoustic (LA), twisting acoustic (TWA) and doubly degenerate transverse acoustic (TA). The phonon branches starting at \( k = 0 \) with these modes are twofold, except that the TA branch is fourfold for \( ZZ \) and \( AA \) CDWCNs (other tubes have two almost degenerate TA branches, sticking together at \( k = 0 \)). The acoustic branches are linear in \( k \) near \( k = 0 \), with the slope almost independent of the tube (the differences are less than 1%) and close to that for SWCNs, giving the sound velocities \( v_{LA} = 9.54 \text{ km s}^{-1} \), \( v_{TA} = 20.64 \text{ km s}^{-1} \) and \( v_{TW} = 15.18 \text{ km s}^{-1} \). The bending of the high energy branches is notable, as is for SWCNs. The density of states typically has many singularities (figure 4). The heat capacity is similar to that for SWCNs, giving the sound velocities \( 9 \), \( 15 \text{ km s}^{-1} \) and \( 20 \text{ km s}^{-1} \), except for the low temperature range, where it is considerably below that of SWCNs (figure 5).

Further, it is obvious that the \( W'W \) branches resemble the union of branches of \( W \) and \( W' \) (figure 3) which would be obtained in the case of noninteracting walls. This is a consequence of the considerably lower interlayer interaction, equation (11), with respect to the intralayer one described by the force constants. This means that the elements of submatrices \( D_{\alpha'\beta'} \) are much less than those of \( D_{\alpha'\beta} \) (unless \( \alpha = \beta \)). Therefore, the perturbative approach may be applied to interpret the CDWCN modes obtained in terms of the isolated layers’ ones and to indicate some novel features. Obviously, in this context equation (20a) shows that the intralayer interaction matrix \( D'_W \) is a perturbation of the noninteracting wall dynamical matrix \( D^0_{WW} \). The transition to the basis \( |a'\rangle, |a\rangle \) (\( a' \) and \( a \) enumerate modes of \( W' \) and \( W \)) of the normal modes of noninteracting walls makes \( D_{WW}^0 \) diagonal, with eigen-energies \( \omega_{a'}^2 \) and \( \omega_a^2 \), while the perturbation retains the same structure. However, the off-diagonal matrix elements \( \kappa_{a'a'} = \sqrt{m'(|a'|D_{WW}^0|a\rangle)\sqrt{m}} \) take on the meaning of the coupling between the oscillators, i.e. modes \( |a'\rangle \) and \( |a\rangle \). Recall that the normal mode basis is weighted by square roots of the length mass densities of the walls: \( m = cD \) and \( m' = cD' \), where \( c = 14.375 \text{ amu Å}^{-1} \). If these two modes are not coupled to the others, they form a two-dimensional invariant subspace of \( D_{WW} \), which can be diagonalized independently of the rest of \( D_{WW} \). This submatrix is precisely the dynamical matrix [13] of the oscillators with frequencies \( \omega_{a'}^2 \) and \( \omega_a^2 \), and masses \( m' \) and \( m \), coupled by the oscillator with
Figure 3. Phonon bands of (5, 5)@(10, 10) (black). See the movie to compare with bands of the noninteracting layers (coloured).

Thus, whenever mixing with other modes is negligible, the two coupled isolated wall modes give two DWCN modes with frequencies

$$\Omega_{\pm}^2 = \frac{1}{2} \left[ \omega_a^2 + \omega_{a'}^2 + \frac{\kappa_{a'a}}{\mu_+} \pm \sqrt{(\omega_a^2 - \omega_{a'}^2)^2 + 2 \frac{\kappa_{a'a}}{\mu_+} (\omega_a^2 - \omega_{a'}^2) + \frac{\kappa_{a'a}^2}{\mu_+^2}} \right],$$

(22) where $\mu_\pm = \frac{mm'}{(m \pm m')}$. The higher frequency $\Omega_+$ corresponds to the out-of-phase oscillations of the walls and the other one to the in-phase ones. The symmetry gives a hint as regards the applicability of the perturbative model. In fact, due to the invariance of the interaction potential under the symmetry groups of both walls (i.e. under the breaking group), the coupling of modes with same quantum numbers will be much stronger than the mixing with differently assigned modes; therefore the candidates for producing the perturbative interpretation are the pairs of modes assigned in the same way, which are well separated energetically from the other modes with the same symmetry. Further, it is clear that the coupling of two modes (chosen in this way) is stronger for the low unperturbed frequencies, as the interaction field is effectively averaged in the rapid oscillations and thus partly cancelled.

For example, the perturbative model [13] applies well to the totally symmetric radial breathing modes of the walls, giving in-phase and out-of-phase breathing-like modes of the DWCN, in accordance with earlier predictions [12] and matching the experimental results [4]. Also, the calculations show that the other pair of totally symmetric modes, high energy ones, are almost unperturbed.

6. Rigid layer modes

The translational acoustic modes correspond to the displacements for the same polar vector of all atoms. Consequently, under the symmetry operations they transform as the components of
Figure 4. The phonon density of states. Left: entire frequency range. Right: enlarged low frequency region, with solid and dashed curves denoting RL mode peaks.

Figure 5. Heat capacities of three double wall tubes (black) and their layers (coloured).

Figure 6. TRL (see movieTRL), LRL (see movieLRL) and TWRL (see movieTWRL) modes.
Table 1. Symmetries of the acoustic and rigid layer modes. Each mode (second row) is assigned to irreducible representations of the isogonal/line group. The values of the isogonal group principal axis order $Q$ found for various tubes are given in column 1. Rows 3–5 and 6, 7 refer to CDWCNs with at least one chiral wall and both walls achiral, respectively (isogonal groups $D_Q$ and $D_{Qd}$; for $Q = 1$, instead of $D_1$ and $D_{1d}$, the groups $C_2$ and $C_{2h}$ are used).

| $Q$  | $TA_x, TRL_x$ | $TA_y, TRL_y$ | $LA, LRL$ | $TWA, TWRL$ |
|------|----------------|---------------|-----------|-------------|
| 1    | $A_0A_0^+$    | $B_0A_0^-$   | $B_0A_0^-$| $B_0A_0^-$  |
| 2    | $B_0A_0^+$    | $B_0A_1^+$   | $B_1A_0^+$| $B_1A_0^+$  |
| 3, 5, 9, 14 | $E_0E_1$     | $A_1A_0^+$   | $A_1A_0^+$| $A_0B_0^+$  |
| 1    | $B_1B_0^+$    | $B_0A_0^-$   | $A_1A_0^+$| $A_2B_0^-$  |
| 3, 5, 9 | $E_{1u}E_1^+$| $A_{2u}A_0^-$| $A_{2g}A_0^-$| $A_{2g}B_0^+$|

the polar vector (momentum). Analogously, the TWA mode corresponds to the rotations around the tube axis and it is assigned as the $z$ component of the axial vector (angular moment). Thus, these modes are assigned to $k = 0$ and the corresponding momentum quantum numbers of the isogonal group. The irreducible representations of the isogonal groups of SWCNs and DWCNs associated with these modes are presented in Table 1.

It is important that the isolated layers’ acoustic modes in achiral tubes have mutually different quantum numbers, which are the same for all SWCNs. Further, their zero frequency is much less in comparison to the other modes, making them suited to perturbative analysis. Since both unperturbed frequencies vanish in this case, equation (22) becomes

$$\Omega_+ = 0, \quad \Omega_+(D) = \sqrt{\frac{2\kappa}{c} \frac{D - \Delta/2}{D(D - \Delta)}}. \quad (23)$$

In this way, two coupled isolated layer acoustic modes of the same type give one DWCN acoustic and one optic mode. In both modes the layers vibrate as rigid bodies: acoustic modes and optic modes are in-phase and out-of-phase combinations of acoustic modes of the layers. The optic modes will be denoted like the corresponding acoustic ones: transverse rigid layer (TRL), longitudinal rigid layer (LRL) and twisting rigid layer (TWRL) modes (figure 6).

The coupling constant $\kappa$ is itself a function of the tube diameter and the interlayer distance. It is obvious that the number of interacting atoms per unit length increases with $D$, yielding an increase in $\kappa$ as well. Therefore we propose a polynomial function $\kappa(D)$. It appears that for LRL and TWRL modes the first order polynomial fits well to numerical data [23], while for TRL modes an additional term quadratic in $D$ is necessary. Taking the coupling constant in the suitable form $\kappa(D) = c\omega_{\infty}^2(\delta_0 + D + \gamma D^2)/2$ we get finally

$$\Omega_+(D) = \omega_{\infty} \sqrt{\frac{(D + \delta_0 + \gamma D^2)(D - \Delta/2)}{D(D - \Delta)}}. \quad (24)$$

This expression, with the parameters $\omega_{\infty}$, $\delta_0$ and $\gamma$ taken from Table 2, describes the numerical results nicely (figure 7). For LRL and TWRL modes, when $\gamma = 0$, the large $D$ limit of $\Omega_+(D)$ is

New Journal of Physics 5 (2003) 148.1–148.15 (http://www.njp.org/)
Figure 7. Frequencies of rigid layer modes as functions of the tube diameter. The calculated frequencies (symbols) are compared to the fitted ones (curves) (by equation (24) with parameters given in table 2).

$\omega_\infty$, which is close 35 cm$^{-1}$ for both modes and for both types of achiral DWCN. In fact, the two modes become two degenerate perpendicular modes of graphite [24] at the A point ($k_z = \pi/c$, $k_x = k_y = 0$), with the adjacent planes moving rigidly in the plane in opposite directions. The frequency limit obtained corresponds very well to the lowest frequency at the A point of the graphite modes. For TRL modes (due to the $D^2$ term) $\Omega_\omega(D)$ vanishes in the large $D$ limit. These results may be of experimental interest, since TRL and LRL modes are IR active (TWRL is IR active for tubes with at least one chiral wall). Corresponding to the singularities in the phonon density of states, figure 4, intensive spectral lines may be expected.

The appearance of rigid layer modes in CDWCNs affects the low temperature heat capacity. In fact, if there was no interlayer interaction, the heat capacity of a DWCN would be the same as those of the walls (since it would be an average of almost identical quantities). However, as was explained, the coupling of the wall acoustic modes (altogether eight modes) produces, besides four DWCN acoustic modes, another four optical modes. Therefore, in the low temperature region, where only the acoustic modes contribute, the specific heat of the DWCN is significantly lower (figure 5) and this agrees nicely with the available experimental data [25].

7. Concluding remarks

Within the model of Lennard-Jones interwall interaction, the stable configurations of layers and the corresponding symmetry groups have been studied. For perfect infinite walls with incommensurate periods, the relative wall translations along the tube axis do not affect the interaction potential: such motion becomes a superslippery degree of freedom. For commensurate walls (only approximately 0.5% of DWCNs with the proposed interlayer distance $\Delta = 3.44 \pm 0.2$ Å are commensurate!), using the symmetry, the phonon dispersions are found and assigned using the complete set of quantum numbers. It turns out that the symmetry of a CDWCN is very small in comparison to that of the walls, which has important physical consequences. In particular, low $Q$ means that many of the $k = 0$ modes have angular momentum $m = 0$, New Journal of Physics 5 (2003) 148.1–148.15 (http://www.njp.org/)
Table 2. Parameters of equation (24) fitted to numerical calculations. The frequencies are in cm$^{-1}$ when the diameter of the outer wall is given in Å.

| $(n, 0)@(n + 9, 0)$, $\Delta = 7$ Å | $(n, n)@(n + 5, n + 5)$, $\Delta = 6.78$ Å |
|-----------------------------------|-----------------------------------|
| $\omega_{\infty}$ | $\delta_0$ | $\gamma$ | $\omega_{\infty}$ | $\delta_0$ | $\gamma$ |
| LRL | 34.7 | −4 | 0 | 37.4 | −4 | 0 |
| TWRL | 33.8 | 1.33 | 0 | 36 | 1.33 | 0 |
| TRL | 62.5 | −4.67 | −0.0068 | 61.7 | −4.39 | −0.006 |

with well defined $U$ parity, even with chiral layers. Knowing that this implies a van Hove-like singularity in the phonon density of states, this explains the increased number of peaks.

A simplified model of coupled oscillators was used to discuss some characteristics of the phonon bands. In particular, the rigid layer modes were considered. These are interesting due to their infra-red activity. Hence, obtaining precise data may serve to provide an additional routine method for CDWCN characterization, which is sensitive to both the diameter and the chirality. To this end, after reliable experimental data are obtained, the Lennard-Jones model can be more thoroughly fitted to them, to enable such precise prediction. Qualitatively, the low frequency of the RL modes confirms the predictions of weak interlayer interaction, which is important in tribology. The results are in good agreement with the predictions and measurements of telescoping [5, 6, 8, 10] of the walls. Also, the extrapolated frequencies agree with those of the corresponding graphite modes. Finally, the heat capacity is found to be, at low temperatures, considerably lower than that of SWCNs and the mechanism of this effect has been explained. The same argument applied to multiwall tubes straightforwardly explains how the graphite limit is achieved, which may be helpful in understanding heat capacity measurements on samples formed of many different tubes.

References

[1] Iijima S 1991 Nature 354 56
[2] Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, Xu C H, Lee Y H, Kim S G, Rinzler A G, Colbert D T, Scuseria G E, Tomanek D, Fischer J E and Smally R E 1996 Science 273 483
[3] Smith B W and Luzzi D E 2000 Chem. Phys. Lett. 321 169
Hirahara K, Suenaga K, Bandow S, Kato H, Okazaki T, Shinohara H and Iijima S 2000 Phys. Rev. Lett. 85 5384
Smith B W, Monthioux M and Luzzi D E 1998 Nature 396 323
Bacs R R, Laurent Ch, Peigney A, Bacs W S, Vaugien Th and Rousset A 2000 Chem. Phys. Lett. 323 566
Li W Z, Wen J G, Sennett M and Ren Z F 2002 Chem. Phys. Lett. 368 299
[4] Bandow S, Takizawa M, Hirahara K, Yudasaka M and Iijima S 2001 Chem. Phys. Lett. 337 48
Benoit J M, Buisson J P, Chauvet O, Godon C and Lefrant S 2002 Phys. Rev. B 66 075416
Bandow S, Chen G, Sumanasekera G U, Gupta R, Yudasaka M, Iijima S and Eklund P C 2002 Phys. Rev. B 66 075416
Bacs R R, Peigney A, Laurent Ch, Puech P and Bacs W S 2002 Phys. Rev. B 65 161404
[5] Cummings J and Zettl A 2000 Science 289 602
Yu M, Yakobson B and Ruoff R 2000 J. Phys. Chem. B 104 8764
[6] Charlier J-C and Michenaud J-P 1993 Phys. Rev. Lett. 70 1858

New Journal of Physics 5 (2003) 148.1–148.15 (http://www.njp.org/)
[7] Kwon Y-K and Tomanek D 1998 Phys. Rev. B 58 R16001
[8] Kolmogorov A and Crespi V 2000 Phys. Rev. Lett. 85 4727
[9] Damnjanović M, Milošević I, Vuković T and Sredanović R 1999 J. Phys. A: Math. Gen. 32 4097
        Damnjanović M, Milošević I, Vuković T and Sredanović R 1999 Phys. Rev. B 60 2728
[10] Damnjanović M, Vuković T and Milošević I 2002 Eur. Phys. J. B 25 131
        Vuković T, Damnjanović M and Milošević I 2003 Physica E 16 259
[11] Lozovik Y E, Minogin A V and Popov A M 2003 Phys. Lett. A 313 112
        Saito R, Matsuo R, Kimura T, Dresselhaus G and Dresselhaus M S 2001 Chem. Phys. Lett. 348 187
[12] Popov V N and Henrard L 2002 Phys. Rev. B 65 235415
[13] Dobardžić E, Maultzsch J, Milošević I, Thomsen C and Damnjanović M 2003 Phys. Status Solidi b 237 R7
[14] Schroder E and Hyldgaard P 2003 Surf. Sci. 532 5 880
[15] Milošević I, Damnjanović A and Damnjanović M 1996 Quantum Mechanical Simulation Methods in Studying Biological Systems ed D Bicout and M Field (Berlin: Springer) chapter 14
[16] Saito Y, Yoshikawa T, Bandow S, Tomita M and Hayashi T 1993 Phys. Rev. B 48 1907
[17] Abud H and Sartori G 1983 Ann. Phys. 150 307–72
[18] Saito R, Matsuo R, Kimura T, Dresselhaus G and Dresselhaus M S 2001 Chem. Phys. Lett. 348 187
[19] Damnjanović M, Milošević I, Dobardžić E, Vuković T and Nikolić B 2003 J. Phys. A: Math. Gen. 36 10349
[20] Dobardžić E, Milošević I, Nikolić B, Vuković T and Damnjanović M 2003 Phys. Rev. B 68 045408
[21] Jishi R A, Venkataraman L., Dresselhaus M S and Dresselhaus G 1993 Chem. Phys. Lett. 209 77
[22] Damnjanović M and Milošević I 1995 J. Phys. A: Math. Gen. 28 1669–79
        Damnjanović M, Vuković T and Milošević I 2000 J. Phys. A: Math. Gen. 33 6561
[23] Dobardžić E, Milošević I, Vuković T, Nikolić B and Damnjanović M 2003 Eur. Phys. J. B 34 409
[24] Jishi A and Dresselhaus G 1982 Phys. Rev. B 26 4514
[25] Mizel A, Benedict L X, Cohen L M, Louie S G, Zettl A, Budraa N K and Beyermann W P 1999 Phys. Rev. B 60 3264
        Popov V N 2002 Phys. Rev. B 66 153408