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LETTER TO THE EDITOR

Chirality dependence of the radial breathing mode: a simple model

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Abstract

By a simple dynamical model it is shown that the radial breathing mode of single wall carbon nanotubes is not exactly radial: its longitudinal and circumferential components are non-vanishing and both diameter and chirality dependent. However, the radial component is only diameter sensitive; likewise the frequency.

Being highly pronounced in Raman spectra and diameter sensitive, and thus important in SWCNT characterization, the radial breathing mode (RBM) of carbon nanotubes has been studied intensively over the past decade [1]. However, it is *a priori* assumed to be exactly radial. It is more or less well established that its frequency ω decreases with the tube diameter D as $\omega = A/D$. The value of the coefficient A obtained in several calculations [2, 3] varies within a few per cent.

Recently, a careful symmetry analysis [3] has shown that this mode may have non-radial components. Indeed, RBM is one of the totally symmetric modes, with displacement vectors transforming according to the identical representation ${}_0\mathrm{A}_0^+$ of the SWCNT line group [4] (or $\mathrm{A}_{1\mathrm{g}}$ of the isogonal group). As an SWCNT is generated by the symmetry group from a single atom, any symmetric mode is completely determined by the displacement vector of a single carbon atom. In the coordinate system with z-axis along the tube, and x-axis radially passing through the singled out atom C_0, the displacement vector of C_0 is $\boldsymbol{v} = (x, y, z)$ (with length v). A purely radial mode should have $y = z = 0$. However, only in the achiral tubes all the atoms are in mirror planes, and symmetric modes cannot have a component perpendicular to this plane: in zig-zag (armchair) tubes the circumferential (longitudinal) component vanishes as atoms are in the vertical (horizontal) mirror planes.

Symmetry-based calculations [3] within the force constants model on a large number of SWCNTs (all 1280 of them with diameters 2.8–50 Å) showed that the RBM frequency is only

[1] http://www.ff.bg.ac.yu/nanoscience.

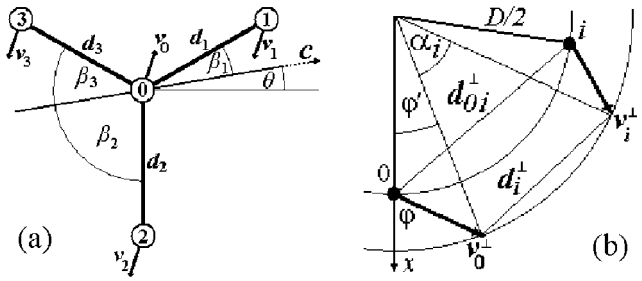

Figure 1. Geometry of the model (defining parameters β_i, d_i, φ, φ', α_i and d_{0i}): (a) atom C_0 and its neighbours (denoted as 0, 1, 2, 3). (b) Horizontal projections of equilibrium (internal arc) and by RBM displaced (outer arc) positions of C_0 and C_i; the projections of distances and displacements are indicated by $\perp$.

diameter dependent ($A = 2243$, ω in cm^{-1}, D in Å). Nevertheless, its longitudinal (z) and circumferential (y) components make up only a few per cent of the displacements, depending both on the diameter and chiral angle θ as

$$\begin{aligned} z(D,\theta) &= v(Z_1 D^{-1} + Z_3 D^{-3} + \cdots)\cos 3\theta, \\ y(D,\theta) &= v(Y_1 D^{-1} + Y_3 D^{-3} + \cdots)\sin 3\theta, \end{aligned} \tag{1}$$

with the leading coefficients $Z_1 \approx Y_1 \approx -0.2$.

In contrast, in the frozen phonon method calculations [5] a slight dependence of the RBM frequency on the tube chirality is found. Within this model it is explicitly assumed that the RBM is strictly radial, while the square root of the element $\mathcal{D}_{vv}$ of the dynamical matrix is interpreted as the RBM frequency. Consequently, if the RBM is not radial, this square root is not an eigenvalue and necessarily depends on θ.

Therefore, it is important to clarify whether the RBM displacements are purely radial. To this end we consider a very simple nearest neighbours dynamical model, assuming only that the RBM is totally symmetric. Nevertheless, the model transparently shows that the RBM frequency is chirality independent, while the displacements have non-radial components being both chirality and diameter dependent.

Before elaborating the model, we note that a totally symmetric displacement (x, y, z) increases the energy of the SWCNT. Then, the basic principles require that the normal mode is in the direction with extremal value of this increase. In other words, for fixed amplitude v the increase of energy E is a function, say, of y and z displacements (since $x^2 = v^2 - y^2 - z^2$) and for each SWCNT (i.e. for each D and θ) this function must have a local extremum corresponding to the RBM (i.e. close to $y = z = 0$). Essentially, each dynamical model introduces such a function, and minimization is performed within the eigenproblem resulting in phonon dispersions.

As in the radial vibrations the bond angles are almost preserved, the energy is related only to the stretching of the bonds. This inspires the simplest model we consider: the increase of energy is a function of the averaged changes in distances to the first neighbours. Each carbon atom on the tube has three nearest neighbours C_i ($i = 1, 2, 3$) (figure 1(a)). It is easy to calculate the distances d_{0i} in the SWCNT stable configuration, being a purely folded graphene layer:

$$d_{0i}^2 = e^2 \sin^2 \beta_i + D^2 \sin^2 \frac{e \cos \beta_i}{D}, \tag{2}$$

where $e = 1.42$ Å is the length of the C–C bond in graphene; the angles between the bonds

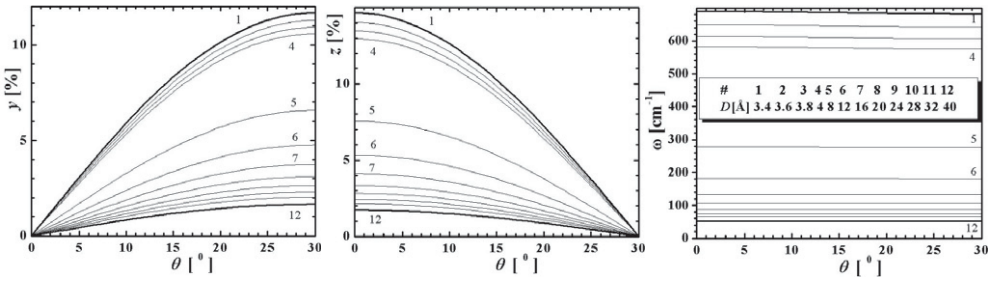

Figure 2. Chirality dependence of $\bar{y}$, $\bar{z}$ (coordinates of minimum of $E(y, z)$ in percentages of the total displacement length v) and $\omega = \sqrt{897.2E(\bar{x}, \bar{y})/Kv^2}$. The twelve curves correspond to the diameters listed in the panel at the right.

and the chiral vector $\boldsymbol{c} = (n_1, n_2)$ depend on θ as:

$$\beta_1 = \frac{\pi}{6} - \theta, \qquad \beta_2 = \frac{\pi}{2} - \theta, \qquad \beta_3 = \frac{\pi}{6} + \theta. \tag{3}$$

When the RBM is excited, each atomic position is changed by the corresponding RBM vector $\boldsymbol{v}_i$. Elementary geometry (figure 1(b)) gives new distances to the neighbours:

$$d_i^2(\varphi, z) = (e \sin\beta_i + 2\zeta_i z)^2 + (D^2 + 4v^{\perp^2} + 4Dv^{\perp}\cos\varphi)\sin^2\frac{\alpha_i}{2}. \tag{4}$$

Here, $v^{\perp} = \sqrt{1 - z^2}$ is the length of the projection of the displacement $\boldsymbol{v}_i$ to the plane perpendicular to the tube (it is the same for all atoms); the coefficients $\zeta_1 = -\zeta_2 = \zeta_3 = -1$ serve to include the fact that the positive longitudinal component z of the displacement elongates C_0–C_2, but shortens the other two bonds. Further,

$$\alpha_i = \frac{2e\cos\beta_i}{D} + 2F_i\varphi', \qquad \varphi' = \arctan\frac{v^{\perp}\sin\varphi}{\frac{D}{2} + v^{\perp}\cos\varphi}. \tag{5}$$

Again, $F_1 = -F_2 = -F_3 = 1$ provides for the positive component y (i.e. $\varphi > 0$) of the displacement to shorten the bond C_0–C_1 and elongate C_0–C_2 and C_0–C_3; $\varphi = \arctan y/x$ is the circumferential angle of displacement.

In the considered dynamical model the vibrational energy per atom is assumed to be proportional to the squared increase of the distance to the three neighbours:

$$E(y, z) = K\sum_{i=1}^{3}(d_{0i} - d_i)^2. \tag{6}$$

Substituting here (2) and (4), $E(y, z)$ becomes an explicit function of y and z, with diameter D, chiral angle θ and elongation v as parameters. Then for each D and θ the coordinates $\bar{y}$ and $\bar{z}$ (independent of v) of its minimum, being the closest to $y = z = 0$ extreme, are looked for. Finally, the potential energy of the harmonic oscillator is proportional to frequency ω, mass m and v^2: $E = m\omega v^2/2$; thus, from (6) one gets $\omega = \sqrt{2E(\bar{y}, \bar{z})/mv^2}$.

This task is performed numerically for diameters 3.4 Å $\leqslant D \leqslant$ 40 Å and all chiralities ($0 \leqslant \theta \leqslant 30°$) in 9384 points on the rectangular grid in steps of 0.2 Å for D and 0.6° for θ. The obtained results are presented in figures 2 and 3. Clearly, the mode is not strictly radial, as the minimum of $E(y, z)$ is not at $y = z = 0$. The non-radial components of the RBM (coordinates of the minimum) depend both on the chirality and diameter of the tube (their various values give different curves). This dependence has the same form as (1), meaning that the radial component x is chirality independent. It is significant that the fit of the results gives

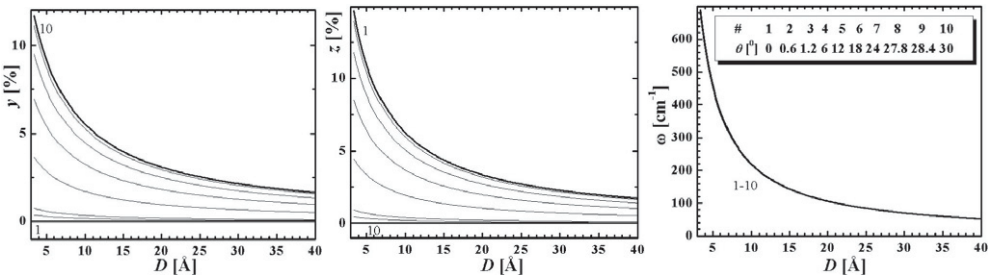

Figure 3. Diameter dependence of $\bar{y}$, $\bar{z}$ and ω (see the caption of figure 2). The ten curves correspond to the chiral angles given in the panel at the right.

$Z_1 \approx Y_1$ as in the precise force constant model (in the model presented, Z_1 and Y_1 are close to 0.07; however, the value itself is not of interest, as the model is oversimplified). Note that for zig-zag ($\theta = 0$) and armchair ($\theta = \pi/6$) tubes, symmetry conditions are automatically matched as $y = 0$ and $z = 0$, respectively, for any diameter. As for the frequency, it is chirality independent (the curves for various θ in figure 3, right panel, coincide), and obey an $\omega = A/D$ law. Obviously, the values of ω and A depend on the introduced phenomenological constants K; in figure 3 we use $2K/m = 897.2$ to get $A = 2243$ as in [3].

In conclusion, the presented analysis proves that even in the simplest models there are chirality sensitive non-radial components of the RBM. Also, in this model the frequency is independent of the chiral angle. Since the calculations are performed for all the diameters and chiral angles in quite large ranges (given above), and even for those not corresponding to the simply folded SWCNT, the results are valid for the relaxed structures as well. This makes the obtained results relevant and important for narrow carbon nanotubes for which the frozen phonon model is likely to be misleading.

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