phys. stat. sol. (b) **237**, No. 2, R7–R10 (2003) / **DOI** 10.1002/pssb.200301825

Rapid Research Note

The radial breathing mode frequency in double-walled carbon nanotubes: an analytical approximation

E. Dobardžić[1], **J. Maultzsch**[2], **I. Milošević**[1], **C. Thomsen**[*, 2], and **M. Damnjanović**[1]

[1] Faculty of Physics, University of Belgrade, P.O. Box 368, 11001 Belgrade, Serbia
[2] Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Received 8 May 2003[**], accepted 14 May 2003
Published online 16 May 2003

PACS 63.22.+m, 78.30.Na

We study the breathing-like phonon modes of double-walled carbon nanotubes in a simple analytical model by considering the tube walls as coupled oscillators. The force constant of the oscillator coupling is found to be proportional to the inner tube diameter. Thus, only for small-diameter tubes, the shift of the breathing-like phonon mode frequencies (relative to the radial breathing modes of the isolated layers) scales with the tube diameter D. For tubes with larger diameter the in-phase breathing-like phonon mode frequency is inversely proportional to the diameter (like the radial breathing modes of the single wall carbon nanotubes), while the out-of-phase mode approaches asymptotically, as $1/D^2$, the graphite B_{2g} phonon mode frequency.

Due to the remarkable physical properties and potential applications carbon nanotubes (CNTs) have been investigated intensively since their discovery by Iijima [1]. In particular, the vibrational properties of single-wall carbon nanotubes (SWCNTs) [2] have been studied extensively by many research groups [3–5]. More recently, experimental studies of double-walled CNTs have appeared [6, 7] focussing on the role of the wall-to-wall interaction for the so-called radial breathing mode of the tubes. For isolated single-walled tubes this frequency is generally taken to be a good indicator of the tube diameter D. For double-walled tubes the simple $1/D$ dependence of the frequency is modified by the presence of the additional wall-to-wall interaction. Popov and Henrard [8] studied the breathing-like phonon modes (BLMs) of double- and multi-walled CNTs within a valence-force field model and a continuum model, showing clearly the effect of this additional interaction. Here we present a very simple, analytically solvable model of two coupled oscillators by which we are able to explain the main features of the BLMs of double-walled carbon nanotubes (DWCNTs) as predicted in Ref. [8]. In particular, we derive simple expressions in the small and large-diameter limit from which one may estimate the diameter of inner and outer tubes from experimental Raman frequencies.

A DWCNT consists of two co-axial SWCNTs, the walls of which are assumed to be at a distance $d/2 = 3.44$ Å and the diameters of which are $D_1 = D$ and $D_2 = D + d$. The frequency of the radial breathing mode (RBM) of isolated SWCNT scales inversely with the tube diameter ($\omega = \alpha/D$) as was originally

[*] Corresponding author: e-mail: thomsen@physik.tu-berlin.de, Phone: +49 30 314 23187, Fax: +49 30 314 27705
[**] First received as Original Paper 4 March 2003.

 0370-1972/03/23706-00R7 $ 17.50+.50/0

reported by Rao et al. [9] leading to many further estimates [3, 4, 10] of the factor of proportionality α. Here we adopt the value $\alpha = 2243$ Å cm^{-1}, which we obtained by fitting an ensemble of 200 SWCNTs of different chiralities and diameters by means of the *POLSym* code [11].

We assume that the RBMs of the layers of a DWCNT mix into the BLMs of the whole double-wall tube. (Such a simplification is a fairly good approximation as we show below by comparing our results to the more sophisticated calculations of Popov and Henrard [8]). Thus, the elementary spring geometry of coupled oscillators determines the BLMs frequencies:

$$m_1\ddot{x}_1 = -k_1 x_1 - k(x_1 - x_2)\,, \qquad m_2\ddot{x}_2 = -k_2 x_2 - k(x_2 - x_1)\,,$$

where k_i and $\omega_i = \sqrt{k_i/m_i}$ are the force constant per unit length and the RBM frequency of the corresponding isolated SWCNT ($i = 1$ for the inner, and $i = 2$ for the outer layer), while k is a force constant that characterizes the inter-layer interaction. The linear mass densities m_i of a CNT scale with the tube diameter: $m_i = cD_i$, where $c = 14.375$ amu Å^{-1}. This system of equations can be written in matrix form after introducing the weighted coordinates $X_i = \sqrt{m_i}\,x_i$:

$$\begin{pmatrix}\ddot{X}_1\\ \ddot{X}_2\end{pmatrix} = W\begin{pmatrix}X_1\\ X_2\end{pmatrix}, \qquad W = \begin{pmatrix}-\dfrac{k_1+k}{m_1} & \dfrac{k}{\sqrt{m_1 m_2}}\\ \dfrac{k}{\sqrt{m_1 m_2}} & -\dfrac{k_2+k}{m_2}\end{pmatrix}. \tag{1}$$

The frequencies of the BLMs of the DWCNT are square roots of the dynamical matrix W eigenvalues:

$$\Omega_{1,2}^2 = \frac{1}{2}\left\{\omega_1^2 + \omega_2^2 + \frac{k}{m} \pm \sqrt{(\omega_1^2-\omega_2^2)^2 + 2k\left(\frac{1}{m_1}-\frac{1}{m_2}\right)(\omega_1^2-\omega_2^2) + \frac{k^2}{m^2}}\right\}, \tag{2}$$

where $m = m_1 m_2/(m_1 + m_2)$ is the reduced mass (per unit length) of the DWCNT. The corresponding eigenvectors (X_1^i, X_2^i) $(i = 1, 2)$ give the displacements X_1^i of the inner and X_2^i of the outer wall within the corresponding normal mode; for $X_2^1 = X_2^2 = 2k\,\sqrt{m_1 m_2}/(m_2 - m_1)$ the inner layer radius changes to

$$X_1^{1,2} = -(k + \mu m(\omega_1^2 - \omega_2^2)) \mp \mu\sqrt{k^2 + m^2(\omega_1^2-\omega_2^2)^2 + 2k\,\frac{m}{\mu}(\omega_1^2-\omega_2^2)}\,, \tag{3}$$

where $\mu = (m_1 + m_2)/(m_2 - m_1)$. Obviously $X_1^1 < 0$ while $X_1^2 > 0$. Since both $X_2^{1,2}$ are positive, these two phonon modes are of the out-of-phase and of the in-phase type, respectively (see Fig. 1).

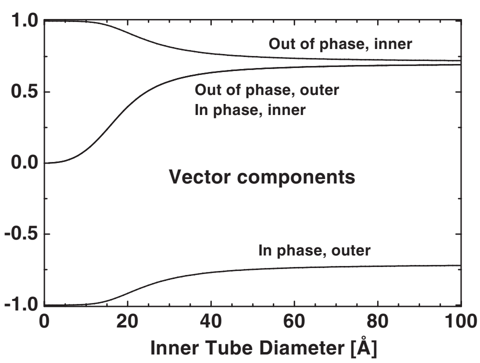

Fig. 1 Normalized coordinates x_j^i of the BLMs as function of the inner diameter D. In the $D \to \infty$ limit the values $\pm 1/\sqrt{2}$ corresponding to the displacements of the graphene transverse acoustic and the B_{2g} phonon modes (127 cm^{-1}) are obtained.

By explicitly inserting the diameter dependence of the masses and the frequencies, it can easily be noticed that in the large-diameter limit (i.e. $D_i \to \infty$) the last term under the square root in Eq. (2) prevails, which gives $\Omega_1^\infty = \sqrt{k/m}$ and $\Omega_2^\infty = 0$ as the limiting values of the BLMs frequencies. The latter, coming from the in-phase BLM, corresponds to the graphite transverse acoustic mode, while the higher frequency one (i.e. the out-of phase BLM) in the limit considered, becomes the B_{2g} graphite phonon mode with the well known frequency of 127 cm^{-1}. On the other hand, as the number of the interacting atoms (per unit length) scales with D, the BLMs energy must increase with D (approaching zero as $D \to 0$); therefore, the inter-layer force constant k can be expanded into the Laurent series over D: $k = \sum_{l=1}^{\infty} \kappa_l D^l$. In the large D limit the expression of the reduced mass (per unit length) becomes $m \approx cD/2$, i.e. it essentially scales linearly with D. Therefore, to get a finite value for $\Omega_1^\infty = \sqrt{2k/cD} = \sqrt{2\sum_{l=1}^{\infty} \kappa_l D^l/cD}$, all the κ_i but κ_1 must vanish. In particular, the experimental limit of the graphite B_{2g} mode 127 cm^{-1} is obtained for $\kappa_1 = 115927$ amu cm^{-2} Å^{-1}.

After determining all the relevant parameters, we turn to the inspection of the general behavior of the BLMs. In Fig. 2 the diameter dependence of BLMs frequencies (2) together with the RBMs of the corresponding single-wall layers are depicted. Evidently, the BLM shifts relative to the RBM frequencies of the isolated single-layer, $\Delta_{1,2} = \Omega_{1,2} - \omega_{1,2}$, are always positive. The diameter dependence of the BLM frequencies and of the frequency shifts shown in Fig. 2 agree very well with the results of Popov and Henrard [8] which were obtained within a valence force field model for double-walled nanotubes.

For very small diameters $(\omega_1^2 - \omega_2^2)^2$ is much greater than the other terms under the square root in (2); e.g. $(\omega_1^2 - \omega_2^2)^2$ is at least ten times larger than the other terms whenever the inner diameter D is smaller than 6.77 Å. Thus, it is straightforward to get:

$$\Omega_{1,2} \approx \omega_{1,2} + \frac{k}{2m_{1,2}\omega_{1,2}}. \tag{4}$$

Thus, for small diameters the shifts are linear in D: $\Delta_{1,2} \approx \kappa D/2c\alpha$.

In the large D region (e.g. $D > 10$ Å), we approximate the BLMs frequencies by leading terms in the expansion over D^{-1}:

$$\Omega_1 \approx \Omega_1^\infty - \frac{d\Omega_1^\infty}{4D}, \qquad \Omega_2 \approx \omega_2 + \frac{\alpha d}{2D^2}, \tag{5}$$

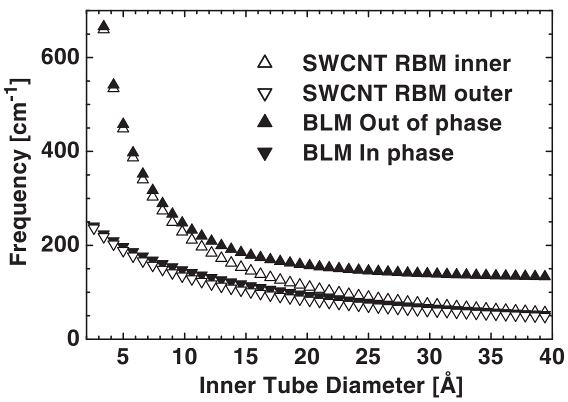

Fig. 2 The BLMs compared to the corresponding SWCNTs RBMs.

physica status solidi • Rapid Research Note

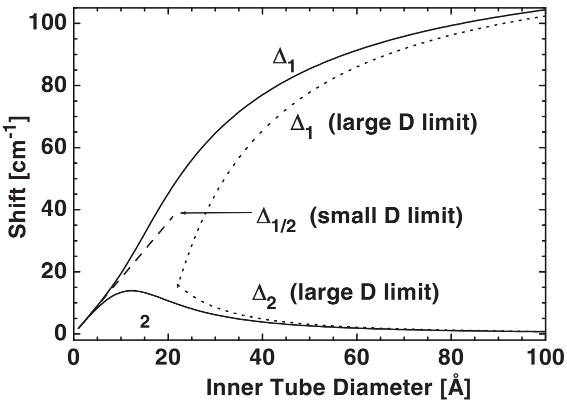

Fig. 3 The BLMs shifts relative to the corresponding SWCNTs RBMs. The analytic results are obtained directly from (2), while small and large *D* limits are given by (4) and (5).

which yield different behaviors of the shifts:

$$\Delta_1 \approx \Omega_1^\infty - (4\alpha + d\Omega_1^\infty)/4D\,, \qquad \Delta_2 \approx \alpha d/2D^2\,.$$

These approximations are depicted in Fig. 3. In the perturbation theory framework the shifts represent the corrections to the SWCNTs RBMs. Unlike the in-phase shift which is small enough for all the tubes, the out-of-phase BLM accommodates perturbation theory only for thin enough DWCNTs. Further, the coupling force constant k is not negligible with respect to the RBMs constants k_i, except for very small diameters. Even more, it exceeds the k_1 value as the inner layer diameter D exceeds 24.7 Å.

In summary, we presented an analytically solvable approach for the breathing-like phonon modes in double-walled carbon nanotubes, where the tube walls were treated as coupled oscillators. In the large-diameter limit, the in-phase and out-of-phase vibrations of the walls approach the transverse acoustic mode and the B_{2g} mode, respectively, of graphite. For small tube diameters, i.e., if the inner diameter is smaller than 10 Å, the frequency shift of the BLM with respect to the RBM of the single-wall tube is approximately linear in D and given by Eq. (4). Since the inner tube diameters of DWCNTs grown by catalytic chemical vapor deposition [6] or by heat treatment of peapods [7] were reported to be in the range of 7–10 Å, Eq. (4) can be readily used to estimate the expected BLM frequencies or to determine the tube diameters from the experimentally observed breathing-like phonon modes in double-walled tubes.

References

[1] S. Iijima, Nature **354**, 56 (1991).
[2] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smally, Science **273**, 483 (1996).
[3] D. Sánchez-Portal, E. Artacho, J. M. Soler, A. Rubio, and P. Ordejón, Phys. Rev. B **59**, 12678 (1999).
[4] V. N. Popov, V. E. Van Doren, and M. Balkanski, Phys. Rev. B **59**, 8355 (1999).
[5] O. Dubay and G. Kresse, Phys. Rev. B **67**, 035401 (2003).
[6] R. R. Bacsa, R. Peigney, Ch. Laurent, P. Puech, and W. S. Bacsa, Phys. Rev. B **65**, 161404(R) (2002).
[7] S. Bandow, G. Chen, G. U. Sumanasekera, R. Gupta, M. Yudasaka, S. Iijima, and P. C. Eklund, Phys. Rev. B **66**, 075416 (2002).
[8] V. N. Popov and L. Henrard, Phys. Rev. B **65**, 235415 (2002).
[9] A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus, and M. S. Dresselhaus, Science **275**, 187 (1997).
[10] J. Kürti, G. Kresse, and H. Kuzmany, Phys. Rev. B **58**, R8869 (1998).
L. Henrard, E. Hernandez, P. Bernier, and A. Rubio, Phys. Rev. B **60**, R8521 (1999).
[11] I. Milošević, A. Damjanović, and M. Damnjanović, Quantum Mechanical Simulation Methods in Studying Biological Systems, edited by D. Bicout and M. Field (Springer-Verlag, Berlin, 1996), pp. 295–311.