Study of collective radial breathing-like modes in double-walled carbon nanotubes: combination of continuous two-dimensional membrane theory and Raman spectroscopy

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Abstract. Radial breathing modes (RBMs) are widely used for the atomic structure characterization and index assignment of single-walled carbon nanotubes (SWNTs) from resonant Raman spectroscopy. However, for double-walled carbon nanotubes (DWNTs), the use of conventional $\omega_{\mathrm{RBM}}(d)$ formulas is complicated due to the van der Waals interaction between the layers, which strongly affects the frequencies of radial modes and leads to new collective vibrations. This paper presents an alternative way to theoretically study the collective radial breathing-like modes (RBLMs) of DWNTs and to account for interlayer interaction, namely the continuous two-dimensional membrane theory. We obtain an analytical $\omega_{\mathrm{RBLM}}(d_o, d_i)$ relation, being the equivalent of the conventional $\omega_{\mathrm{RBM}}(d)$ expressions, established for SWNTs. We compare our theoretical predictions with Raman data, measured on individual index-identified suspended DWNTs, and find a good agreement between experiment and theory. Moreover, we show that the interlayer coupling in individual DWNTs strongly depends on the interlayer distance, which is manifested in the frequency shifts of the RBLMs with respect to the RBMs of the individual inner and outer tubes. In terms of characterization, this means that the combination of Raman spectroscopy data and predictions of continuous membrane theory may give additional criteria for the index identification of DWNTs, namely the interlayer distance. [DOI: 10.1117/1.JNP.10.103599]

Keywords: individual double-walled carbon nanotubes; radial breathing-like modes; interlayer coupling; Raman spectroscopy.

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1 Introduction

A double-walled carbon nanotube (DWNT) has two concentric carbon layers. This structure makes it an ideal system for studying the effects of interwall coupling on the physical properties of carbon nanotubes (CNTs). Compared with single-walled carbon nanotubes (SWNTs),

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DWNTs have higher mechanical strength and thermal stability and also possess interesting electronic and optical properties.[1,2] A DWNT can have one of the four possible electronic configurations with each wall being either semiconductor (S) or metallic (M): S@S, M@S, M@M, and S@M (inner-tube@outer-tube). Every configuration may have different electronic properties.

The Raman scattering is the main analytical tool to study intrinsic properties of DWNTs. Spectroscopic experiments on DWNTs have been initially performed on solution-based samples or in bundles.[3–5] Recently, more evolved experiments using combinations of different complementary techniques (e.g., atomic force microscopy, electron diffraction (ED), and resonant Raman spectroscopy) were performed by our and other groups to measure Raman spectra of individual DWNTs and to study the effects of van der Waals interaction.[6–11]

In our recent work, combining high-resolution transmission electron microscopy (HRTEM), ED, and resonant Raman spectroscopy on individual free-standing DWNTs,[11] we have shown that the strength of this "inner" tube–"outer" tube interaction, which is dependent on the interlayer distance in DWNTs, strongly affects the out-of-phase radial breathing-like mode (RBLM) frequencies. We thus proposed that the positions of the radial breathing-like modes (RBLMs) and the difference between experimental and theoretical calculations within atomistic valence force field model[12] can be used as criteria to evaluate diameters of the inner and outer tubes in nonindex-identified DWNTs.

This paper presents an alternative theoretical way to study low-frequency collective modes of DWNTs based on the two-dimensional (2-D) continuous membrane theory. We show that this approach provides a new and straightforward way to quantitatively analyze RBLMs of coupled systems.

2 Experimental Details

The individual double-walled carbon nanotubes were synthesized by the catalytic chemical vapor deposition directly onto commercial TEM grids (with holes up to 3 μm in diameter).[13,14]

To study individual single- and multiwalled carbon nanotubes, we developed an experimental procedure based on the combination of resonant Raman spectroscopy, ED, and HRTEM. This approach provides an unambiguous way to identify the chiral indices of CNTs.[6,15,16] In this work, TEM, HRTEM, and electron diffraction patterns (EDPs) were obtained in an FEI Titan microscope operating at 80 kV to reduce damages induced by electron irradiation.[14] TEM images and EDPs were recorded within an average 5-s acquisition times.

Resonant Raman scattering measurements were carried out using a Jobin Yvon T64000 spectrometer equipped with a liquid nitrogen-cooled, silicon charge-coupled device detector. The scattered light was collected through a microscope using a backscattering configuration. In all the measurements, both incident and scattered light polarizations are along the nanotube axis (// // polarized Raman spectrum). Incident excitations from Ar+ and Kr+ lasers, dye laser, and tunable Ti/sapphire laser were used. To avoid heating effects, the laser power impinging the sample was kept below 50 μW with a 100× objective (numerical aperture of 0.95). The low-frequency part (RBM region) of Raman spectra was fitted following standard procedures with a set of two Lorentzians in an OriginPro package.

3 Results

The Raman spectra of 14 identified individual free-standing DWNTs have been recorded and analyzed in detail. Figure 1 shows the RBLM range of the Raman spectrum measured on one of these individual DWNTs, namely (23,5)@(22,17), with the corresponding HRTEM image and EDP. Our individual DWNTs are ultralong, clean from amorphous carbon, and have no signature of the D-band (not shown) in Raman spectra.[13,14] Only five of these 14 individual DWNTs had both RBLMs observed in the Raman spectra. All the structural parameters for these five tubes and the measured ω_{RBLMs} are listed in Table 1. In addition to our own data, we will use the results of Liu et al.[8] for the evaluation of our theoretical approach.

Recently, we have described the low-frequency dynamics of DWNTs in the framework of the continuous 2-D membrane theory (for its detailed theoretical description, applicability, and

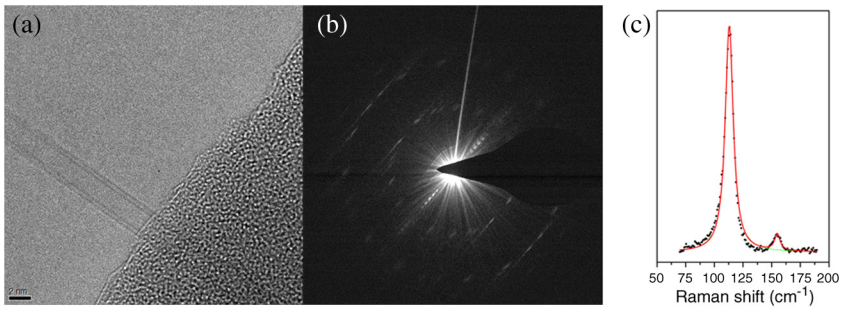

Fig. 1 (a) High-resolution transmission electron microscopy (HRTEM) image, (b) electron diffraction pattern, (c) and measured radial breathing-like modes (RBLMs) (633 nm) of the (23,5)@(22,17) double-walled carbon nanotube (DWNT) studied in this paper. Green lines correspond to the two individual Lorentzians, while red line stands for their superposition.

Table 1 The structural and vibrational information on the double-walled carbon nanotubes (DWNTs) studied in this work. The diameters d are given in nm and frequencies ω in cm^{-1}.

#	(n,m) indices	d_i	d_o	Δd	ω_L^{exp}	ω_H^{exp}
1	(12,8)@(16,14)	1.37	2.04	0.67	133	186
2	(13,9)@(24,7)	1.50	2.21	0.71	123	169
3	(18,2)@(20,12)	1.49	2.19	0.70	122	167
4	(22,11)@(27,17)	2.28	3.01	0.73	98	121
5	(23,5)@(22,17)	2.03	2.65	0.62	113	154

comparison with other models describing RBLMs, see Ref. 17). We treated each layer of DWNTs as a 2-D membrane composed of single atoms (or in other words having zero thickness) and not as a finite-thickness plate. Following this approach, we obtained the equation[17]

$$[d_i \cdot (\omega_{i,\mathrm{SWNT}}^2 - \omega^2) + 2G] \cdot [d_o \cdot (\omega_{o,\mathrm{SWNT}}^2 - \omega^2) + 2G] - 4G^2 = 0, \tag{1}$$

where ω are the RBLM frequencies of DWNT; d_o and d_i are the diameters of outer and inner layers respectively; $G = f(d_o, d_i)$ (G unit is cm^{-2} nm when the frequencies are in cm^{-1} and the diameters in nm, see Ref. 16) is a coupling function between the two layers (see below for more information); and finally $\omega_{i,\mathrm{SWNT}}^2$ and $\omega_{o,\mathrm{SWNT}}^2$ are the RBM frequencies of the isolated individual inner and outer layers.

We now further develop the ideas of the above-mentioned work. By simplifying Eq. (1), we obtain the formula

$$\omega_{\mathrm{RBLM}} = \sqrt{\frac{b \pm \sqrt{b^2 - 4c}}{2}}, \tag{2}$$

with parameters b, c being defined as

$$b = \omega_{o,\mathrm{SWNT}}^2 + \omega_{i,\mathrm{SWNT}}^2 + \frac{2G \cdot (d_o + d_i)}{d_o \cdot d_i}, \tag{3}$$

$$c = 2G \cdot \left(\frac{\omega_{o,\mathrm{SWNT}}^2}{d_i} + \frac{\omega_{i,\mathrm{SWNT}}^2}{d_o}\right) + (\omega_{o,\mathrm{SWNT}} \cdot \omega_{i,\mathrm{SWNT}})^2, \tag{4}$$

and

$$\omega_{i(o),\mathrm{SWNT}} = \frac{227}{d_{i(o)}}\sqrt{1 + C_e \cdot d_{i(o)}^2}. \tag{5}$$

Equation (2) is an equivalent of well-known $\omega(d)$ relations established for SWNTs.[18] It provides a powerful and easy-to-use tool to analyze coupled radial breathing-like vibrations as it considers (a) all different interlayers distances Δd and (b) different environment conditions (constant C_e). For every DWNT, defined by a couple of diameters (d_o, d_i), Eq. (2) gives two frequencies corresponding to the in-phase RBLM [ω_L, sign "–" in Eq. (2)] and the out-of-phase RBLM [ω_H, sign "+" in the Eq. (2)]. The constant C_e in Eq. (5) describes different environments for the CNTs.[18]

It is also clear from Eqs. (2)–(4) that the knowledge of the coupling function $G = f(d_o, d_i)$ is necessary for the calculations of ω_{RBLM}. In the absence of the exact theoretical form, it is possible to determine it from the fit of experimental data. For instance, the empirical form of the coupling function $G = f(d_o, d_i)$ was previously determined[17] on the basis of experimental data of Liu et al.,[8] for which the absence of external interaction ($C_e = 0$) on both tubes was stated. It is expressed as $G = [A + B(d_o - d_i) + C(d_o + d_i)](d_o + d_i)$ with $A = 7210$ cm^{-2}, $B = -9670$ cm^{-2}/nm, and $C = 61$ cm^{-2}/nm.[16] The normalized intertubes coupling, G_{norm} (equivalent to unit-area force constant of Ref. 8), defined as $G/\langle d\rangle$ with $\langle d\rangle = (d_o + d_i)/2$, provides a unique way to evaluate how the van der Waals interactions vary with Δd. For the Liu et al. data, this function is plotted in Fig. 2 (black circles).

We now calculate the G_{norm} values for our individual DWNTs. It was previously found that in the framework of the atomistic model, RBLM frequencies of (12,8)@(16,14) DWNT are best described, if $C_e = 0.065$ for the outer layer and $C_e = 0$ for the inner layer are considered.[6,11] Because all DWNTs, studied in this work, were synthesized following the similar procedure, we use the same C_e values. Under this assumption, we find that the calculated G_{norm} values for our DWNTs (red rhombs in Fig. 2) wind around the G_{norm} values derived from the fit of Ref. 8. This confirms that the intertubes coupling G_{norm} mainly dependent on the interlayer distance Δd, independently of the structure and environment of the constituent outer and inner SWNTs.

Finally, we illustrate the practical use of our model on the example of the work of Liu et al.,[8] for which more experimental data are available and the G function is better established. By choosing the proper form of G (see above) and using the Eq. (2), we can calculate a set of $\omega(d)$ relations for different interlayer distances, $\Delta d = d_o - d_i$, both for in-phase ω_L and out-of-phase ω_H RBLMs. These calculated curves are shown in Fig. 3 as solid thin lines, with Δd in the range 0.60 to 0.76 nm with a step of 0.02 nm. In addition, the results of calculations are compared with the $\omega = 228/d$ relation (black-dotted dashed line) and $\omega_{\mathrm{RBLMs}}(d)$ relation, obtained from the atomistic valence force field model with $\Delta d = 0.68$ nm and without adjustable parameters, (thick black-dashed line), which was used in our previous works.[6,7,11,19]

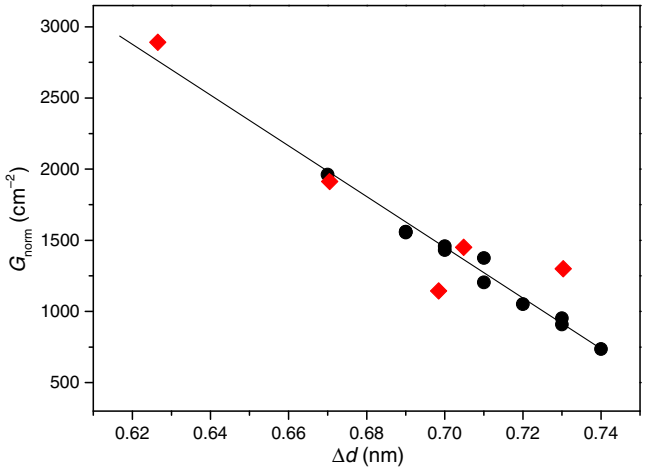

Fig. 2 The coupling G_{norm} as a function of interlayer distance calculated within continuous membrane theory using the available experimental data from Ref. 8 (black circles) and from the present work (red rhombs). The line is a guide for eyes.

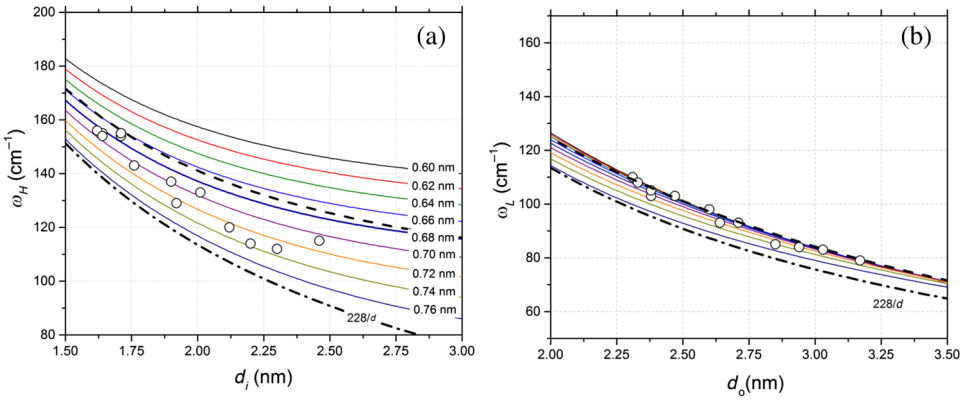

Fig. 3 Theoretical $\omega_{\mathrm{RBLM}}(d)$ relations (shown as solid thin lines), calculated using Eq. (2) for (a) out-of-phase (ω_H) and (b) in-phase (ω_L) RBLMs for different interlayer distances (with Δd in the range 0.60 to 0.76 nm with a step of 0.02 nm), and compared with the $\omega = 228/d$ relation (black dotted dashed line) and $\omega_{\mathrm{RBLMs}}(d)$ obtained from the atomistic valence force field model (thick black-dashed line).[12] The experimental data of Liu et al.[8] are represented by open circles.

The experimental data of Liu et al.[8] are represented by open circles in Fig. 3. As expected, at large Δd the $\omega_{\mathrm{RBLM}}(d)$ relations tend to $\omega = 228/d$, or in other words to the case of noninteracting layers. From the analysis of Fig. 3, we can clearly see that the out-of-phase mode, ω_H, is much more affected by the change of the interlayer distance than the in-phase mode, ω_L. Therefore, it is possible to estimate the interlayer distance of the given DWNT from the comparison between the relative position of the measured out-of-phase ω_H and the calculated $\omega_{\mathrm{RBLM}}(d)$ relations. In this way, the predictions of continuous membrane theory may give additional criteria for the index-identification of DWNTs.

4 Conclusions

We presented an alternative way to calculate low-frequency collective modes of DWNTs: 2-D continuous membrane theory. Following this approach, we have obtained a $\omega_{\mathrm{RBLM}}(d_o, d_i)$ relation being an equivalent to the conventional formulas established for individual SWNTs.

This approach was first applied to the understanding of the experimental data of Ref. 8 for which the absence of external interaction ($C_e = 0$) on both tubes was stated. A monotonic dependence of the normalized intertubes coupling, G_{norm}, with Δd is clearly stated. A close dependence of G_{norm} is found from the fit of our data meaning that the normalized intertubes coupling in DWNTs indeed depends on the interlayer distance Δd.

In terms of characterization, the combination of Raman spectroscopy data and the predictions of continuous membrane theory may give additional criteria for the index identification of DWNTs.

Acknowledgments

T. T. and D. L. performed synthesis of individual double-walled carbon nanotubes. D. L., T. M., M. P., and J.-L. S. devised and performed Raman experiments. D. L. and R. A. identified atomic structures of the nanotubes by electron diffraction and HRTEM. M. A. and S. R. devised 2-D membrane theory and made calculations of RBLM frequencies of individual DWNTs. D. L., M. A., D. R., A. O., T. M., R. A., M. P., J.-L. S., S. R., and Yu. Y. actively participated in the data analysis, discussions, and wrote the paper. D. L., M. A., D. R., and S. R. gratefully acknowledge the financial support of Russian Science Foundation (Grant No. 15-12-10004). R. A. gratefully acknowledges the support of the Spanish Ministerio de Economia y Competitividad (FIS2013-46159-C3-3-P) and funding from the European Union Seventh Framework Program under Grant No. 312483–ESTEEM2 (Integrated Infrastructure Initiative–I3). The microscopy work was conducted in the Laboratorio de Microscopias Avanzadas at the Instituto de Nanociencia de Aragon, Universidad de Zaragoza (Spain).

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