RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 60, NUMBER 12 15 SEPTEMBER 1999-II

van der Waals interaction in nanotube bundles: Consequences on vibrational modes

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(Received 7 June 1999)

We have developed a pair-potential approach for the evaluation of van der Waals interaction between carbon nanotubes in bundles. Starting from a continuum model, we show that the intertube modes range from 5 cm^{-1} to 60 cm^{-1}. Using a nonorthogonal tight-binding approximation for describing the covalent intratube bonding in addition, we confirm a slight chiral dependence of the breathing mode frequency and we found that this breathing mode frequency increases by $\sim$10% if the nanotube lies inside a bundle as compared to inside the isolated tube. [S0163-1829(99)50536-5]

Research in carbon nanotubes is now a very active field both because of their fascinating cylindrical structure and potential applications (see Refs. 1 and 2). On the characterization side, the direct measurement of atomic structure is now possible by means of scanning tunneling microscopy (STM) experiments.[3] This technique gives information on both the local atomic structure as well as electronic properties. However, it is too time-consuming for routine sample characterization. Thus one has to resort to more macroscopic techniques, which are able to handle the whole as-grown sample. One of the most popular alternative experimental tools is the measurement of the vibrational spectrum by Raman spectroscopy (see, e.g., Ref. 4). Since the suggestion was made[4] that the vibrational frequency of the fully symmetric A_g breathing mode (BM) of an isolated nanotube could be used to determine the nanotube diameter, given its marked frequency dependence on the diameter of the tube, this idea has been widely used as a characterization tool. But it should also be noted that a small chiral dependance of BM frequency was recently found by *ab initio* calculations.[5,6]

However, for developing useful technological applications, it is of primary importance to refine the characterization techniques of nanotube samples, taking into account the local environment in which the nanotubes find themselves. Surprisingly, theoretical studies of the resonance frequency have largely focused on isolated tubes, and no such studies have been reported for bundles of tubes, which is the form in which the majority of the nanotubes are to be found in experimental samples. The aim of the present paper is to show how the tube-tube interactions can be taken into account for the characterization of the BM. Due to its radial character, the BM is likely to be the most influenced mode by the nanotube packing and therefore it is necessary to quantify this effect. But before we address this question, we will present an evaluation of the intertube vibrational modes, which could also allow the characterization of samples by inelastic neutron scattering experiments.

The theoretical model we have developed to deal with the tube-packing effects in the vibrational spectra combines a description of the covalent bonds inside each nanotube via a nonorthogonal tight-binding parametrization,[7] which has proved to work very well for the structural and mechanical properties of carbon nanotubes,[8] with a pair-potential approach to deal with the van der Waals interaction between carbon nanotubes. The long-range dispersion interaction is described by a carbon-carbon Lennard-Jones potential V_{cc} given by $V_{cc}=-C_6/d^6+C_{12}/d^{12}$, where d is the carbon-carbon distance and C_6 and C_{12} are constants fitted to reproduce the structural properties of graphite.[9] Despite its intrinsic simplicity, the present approach is widely used to simulate van der Waals interactions between molecules (see Ref. 10). In all the calculations described below we consider infinitely long tubes. Let us also note that, although *ab initio* descriptions are in general more accurate and reliable, they are very computationally demanding and are limited in the size of the system.[6,11]

First, to study the intertube modes, we simplify further the model and we consider carbon nanotubes as continuous cylindrical surfaces of density σ. In this case we can compute analytically the potential felt by a carbon atom situated at a distance a from the center of the nanotube of radii R. The potential reads ($a>R$)

$$V_{cT}(a)=\frac{3}{4}\pi^2R\sigma\left\{\frac{C_6}{a^5}F[5/2,5/2,1,(R/a)^2]+\frac{21C_{12}}{32a^{11}}F[11/2,11/2,1,(R/a)^2]\right\}, \qquad (1)$$

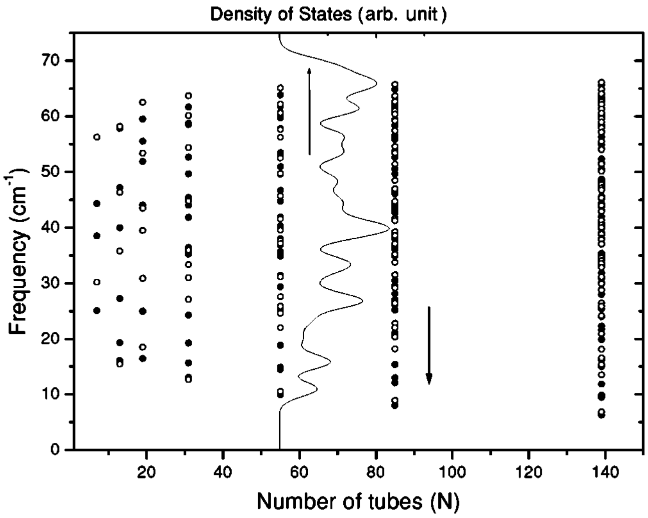

FIG. 1. Intertube mode frequencies of a C_{6v} bundle of infinitely long nanotubes of radius $R=6.8$ Å as a function of the number of tubes. Only Raman active (A_1 and E_2) modes and IR modes (E_1) are represented by filled/open circles. The total vibrational density of states, using a Gaussian broadening of 0.8 cm^{-1}, for a bundle with 55 tubes is also given.

where F is the hypergeometric function.[12] This model cannot distinguish between different layer-stackings in multilayer compounds, nor can it take account of the tube chiralities when applied to bundles of nanotubes. We feel that this is a good approximation as the registry property in nanotube bundles is frustrated by the geometry of the bundle. Our model thus can be considered to represent an average over the different stacking possibilities in a bundle of tubes of similar diameter having chiralities compatible with that diameter. In this sense we expect the continuous model potential to be able to give a realistic description of the intertube modes. This approach is similar to the one developed by Girifalco for the C_{60} fullerene.[13] Within this simplified model the van der Waals interaction energy per unit length between two carbon nanotubes, V_{TT}, follows immediatly by numerical integration of $V_{cT}(a)$ over the surface of the second nanotube. Now, the total energy of a bundle with N tubes, V_B, is obtained by summing V_{TT} over all tube pairs. Before the computation of the vibrational spectra, the total energy for a given bundle is minimized with respect to the tube positions.[14] Then, the intertube vibrational modes (eigenvalues and eigenvectors) are deduced from the diagonalization of the dynamical matrix constructed from a numerical evaluation of the second derivatives of the total energy with respect to the tube center coordinates.[15] As a practical remark, we have built the finite-size bundles enforcing the six-fold symmetry in the section of the bundle, which has one nanotube at its center (the number of tubes is $N=6i+1$ with i being the number of hexagonal shells in the bundle). In this case, all the intertube vibrational spectra can be sorted according to the C_{6v} point group. In particular we find $3i$ Raman active modes and $2i$ infrared (IR) active modes.

In Fig. 1 we show the Raman and IR active modes of a finite size bundle of (10,10) ($R=6.8$ Å) armchair nanotubes as a function of the number of tubes N. Intertube modes are found between 5 cm^{-1} to 60 cm^{-1}. To the best of our knowledge, no experimental evidence of the observation of Raman active modes in this energy range have been reported. The origin of these lack of observational evidences is probably a low scattering cross section and difficulties to deconvoluate the elastic-scattering peak. Inelastic neutron scattering experiments should also be able to probe such modes even if the difficulty of rigid displacement of long, massive cylinders could reduce the excitation probability. However, such experiments require a large quantity of highly purified nanotube powder and at present no data is available for the intertube vibration energy range.[16] For comparison between our simulation and future experimental work, we show by the solid curves in Fig. 1 the total vibrational density of states of a bundle consisting of 55 tubes. Note also that the squashing mode of isolated tubes and the libration mode[17] are predicted at about 16 cm^{-1},[18] and are likely to interfere with intertube modes. This last mode is expected to play a role in temperature dependant conductivity of nanotube bundles since it can induce temperature dependent hopping conductivity. The intertubes mode described here could have a similar behavior.

After presenting the data on intertube vibrational modes, we look at the influence of packing in the BM. The calculations were performed in a frozen phonon approach using the hybrid tight-binding plus continuous Lennard-Jones potential described above. We use a conjugate-gradient relaxation scheme to determine the geometry of the isolated tube before making the full relaxation of the tube bundle. After relaxation, we applied the frozen phonon approach to evaluate BM frequencies by computing the total energy (intra- and intertube) for a 0.1% change of the tube radius. One of the limitations of the frozen phonon calculation for the BM in bundles is the fact that the pure radial mode is no longer an eigenmode of the bundle system since packing breaks the symmetry of isolated tubes. This will lead, in addition to the frequency shift, to a degeneracy lift. These effect were study for C_{60} in Ref. 19. Here we do not take this symmetry lowering into consideration but we believe that the frozen phonon approach catches the essential feature on the packing effect on BM modes and gives a first good evaluation of the resonance frequency increase that will be useful for Raman spectroscopy analysis of nanotube samples.

In Fig. 2 and Table I we present the results for the BM modes of isolated tubes of different radii and chiralities as well as the values for the corresponding infinite bundles. As far as isolated tubes and concerned, we see that armchair (n,n) and zigzag $(n,0)$ tubes do not follow exactly the same scaling law with diameter. We reproduce the known $1/R$ scaling of the BM frequency (ν), in particular the fit of our data to $\nu=C/R$ give the following values: $C=1307$ cm^{-1} Å for armchair tubes and $C=1282$ cm^{-1} Å for zigzag tubes. Chiral tubes BM mode lie between armchair and zigzag lines. Recent *ab initio* results[5] showed $C=1180$ cm^{-1} Å and $C=1160$ cm^{-1} Å for armchair and zigzag tubes, respectively, and force field data are reproduced by $C=1111$ cm^{-1} Å (Refs. 20 and 21) or $C=1147$ cm^{-1} Å (Ref. 22) irrespective of tube chirality. Considering that tight-binding methods usually overestimate vibrational frequencies by 5–10 %,[23,24] the results presented above are not surprising. We emphasize that our tight-binding calculation reproduce well the slight difference between armchair and chiral tubes found by *ab initio* methods.[6] The reason for this success is connected

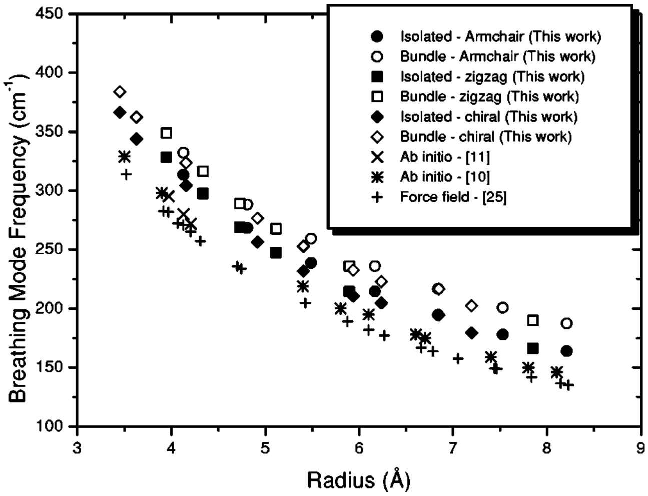

FIG. 2. Breathing mode (A_1) frequencies as a function of the tube radius. This work: Circles are for armchair tubes, squares for zigzag, and diamond for chiral tubes. Solid symbols are for isolated tubes within the tight-binding approach and open symbols are for tubes in a bundle (see text). + are estimated from the force field approach (Ref. 20), × (Ref. 6), and ⋆ (Ref. 5) come from *ab initio* calculations.

TABLE I. Breathing mode (BM) frequencies for various carbon nanotubes. The first column defines the tube, the second one is the radius of the relaxed structure. The frequencies of the isolated tubes and tubes in bundle are given in the next two columns. The last column is the relative increase of the BM frequency when bundles are packed.

(n,m)	R (Å)	ν_{isol} (cm^{-1})	ν_{bundle} (cm^{-1})	shift (%)
(6,4)	3.45	366	384	4.8
(8,2)	3.63	344	362	5.3
(7,4)	3.81	313	330	5.2
(10,0)	3.91	328	349	6.2
(6,6)	4.07	313	332	6.0
(10,1)	4.16	304	323	6.3
(11,0)	4.34	297	316	6.4
(12,0)	4.70	269	289	7.4
(7,7)	4.81	268	288	7.4
(10,4)	4.92	256	276	7.9
(13,0)	5.11	247	268	8.3
(12,3)	5.41	232	253	9.1
(8,8)	5.49	239	259	8.6
(15,0)	5.90	214	236	10.1
(14,2)	5.93	211	233	10.4
(9,9)	6.17	214	236	10.1
(12,6)	6.23	205	227	10.7
(10,10)	6.85	195	217	11.4
(16,4)	7.19	179	202	12.8
(11,11)	7.53	178	201	12.9
(20,0)	7.84	166	190	14.2
(12,12)	8.21	164	187	14.4

with the nonorthogonality of our tight-binding method that correctly describes the rehybridization of carbon-carbon bonds when the nanotube breathes. Moreover, the low computational cost of the tight-binding (TB) approach compared to density-functional theory (DFT) allowed us to perform a more systematic study of chiral and achiral nanotubes (see Table I).

We can now turn to the case of nanotube bundles. As expected, Fig. 2 and Table I show a clear increase in the BM frequencies when tubes are packed into bundles. The relative increase goes from 5% for a tube of radius $R=3.5$ Å to 15% for $R=8$ Å. For $R=6.8$ Å (that are revelant considering actual produced nanotubes), the frequency shift is evaluated to be of the order of 10%. Very recently, Venkateswaran *et al.*,[25] using a similar model to study the pressure dependance of nanotube bundles Raman modes, found an 8% increase of the BM of (9,9) tubes when they are packed compared to isolated tubes. This is consistent with the present result and the difference [we found a 10% increase for a (9,9) tube] is likely to come from a slight difference in parameters used both for the tight binding and for the pair van der Waals potential.

Focusing on the consequences on the interpretation of Raman spectra, the effect of neighboring tubes on BM frequencies can lead to misinterpretation of Raman results and to a 10% error in radius determination. Even if tight-binding calculations do not give exact numbers for vibrational energies, our results are inclined to conclude that the experimental Raman peak at 180 cm^{-1} is to be associated with tubes of diameter larger than the (10,10) tube diameter. Indeed, simulation for single-wall nanotubes predicted a BM for a (10,10) tube between 163 cm^{-1} (force field[20]) and 194 cm^{-1} (this work) or at 178 cm^{-1} for the *ab initio* evaluation in Ref. 5. If we consider those results as a 10% underevaluation of the BM of the tube in a bundle, we get frequencies higher than 180 cm^{-1} (except for the less sophisticated force field model) and the key frequency of 180 cm^{-1} is associated with tube with diameter larger than 6.8 Å. This conclusion is consistent with x-rays[26,27] and neutron[28] diffraction if the tube-tube distance is taken to be 3.2 Å (and not the graphite interlayer distance 3.35 Å) since the diameter polydispersity required for diffraction spectra fit[28] implies the presence of a tube larger than the (10,10) tube in bundles. Moreover, electron diffraction[29] on a single nanotube rope leads to the conclusion that 6.8 Å$<R<$7.5 Å and then to a mean radius larger than the the (10,10) radius.

As far as the BM is concerned, we have only considered bundles made of an infinite number of nanotubes and the study of finite bundles will obviously lead to a gradual change of the BM vibration frequency going from a frequency close to the bulk value for the central tubes (surrounded by six tubes) to a frequency close to the isolated-tube value corresponding to tubes at the bundle surface. This behavior is expected from the short-range tube-tube interaction (at the scale of tube diameter). Note that STM Ref. 3 and electron diffraction[29] experimental studies of carbon nanotubes concluded that all tube chiralities can be found in samples with a very narrow diameter distribution. This will not drastically change our conclusions, moreover, if tube chirality is randomly distributed within the rope, no registry is possible between adjacent tubes and the continuous model is well justified. Furthermore, we have checked that an increase/decrease of the tube diameter within the rope leads to a reduction/increase of the BM vibrational frequency of neighboring tubes. Then, both the surface effect and ‘‘defect'' (larger or smaller tubes) will then lead to a broadening of the experimental Raman spectra as observed experimentally.

In conclusion, we have presented a study of the intertube vibrational modes (both Raman and IR active) in bundles of single walled nanotubes and proposed neutron inelastic scattering as an experimental test of the validity of our empirical model. We have also shown computational evidence of the packing influence on the BM of nanotubes and drawn conclusions on the interpretation of the experimental Raman spectra and how to extract useful experimental information about the nanotube structure and diameter.

We have benefited from fruitful discussions with P. Senet, E. Anglaret, S. Rols, J. L. Sauvajol, A. Loiseau, and Ph. Lambin. This work was supported by the TMR contract NAMITECH [Contract No. ERBFMRX-CT96-0067(DG12-MIHT)], the Belgian Programs (PAI/UAP 4/10) and JCyL(VA28/99). L.H. was supported by the Belgian Fund for Scientific Research (FNRS).

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[15] We note that for the calculation of phonons in C_{60} solid, the Lennard-Jones carbon-carbon intermolecular potential has been successfully used together with a bond charge model (Ref. 19). This last part of the potential was added empirically to reproduce the relative orientation of C_{60} molecules in the solid. In the case of nanotube bundles there is no evidence of such a orientation and we do not include such bond charge model in our calculation.

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