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

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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 $5 \text{cm}^{-1}$ to $60 \text{cm}^{-1}$. Using a non-orthogonal tight-binding approximation for describing the covalent intra-tube bonding in addition, we confirm a slight chiral dependence of the breathing mode frequency and we found that the breathing mode frequency increase by $\sim 10\%$ if the nanotube lies inside a bundle as compared to the isolated tube.

31.70.Ks - 33.20.Tp - 61.48.+c - 78.20.Bh

Research in carbon nanotubes is now a very active field both because of their fascinating cylindrical structure and potential applications (see \([4]\)). 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 \([1,2]\)). On the characterization side, the direct measurement of atomic structure is frustrated by the geometrical property in nanotube bundles is frustrated by the geometrical

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 non-orthogonal tight-binding parametrization \([6]\), 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 $V_{cc} = -\frac{C_6}{a^6} + \frac{C_12}{a^{12}}$, where $d$ is the carbon-carbon distance and $C_6$ and $C_12$ are constants fitted to reproduce the structural properties of graphite \([2]\). Despite its intrinsic simplicity, the present approach is widely used to simulate van der Waals interactions between molecules (see \([10]\)). 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 $\sigma$. 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 ($a > R$):

$$V_{CT}(a) = \frac{3}{4} \pi R \sigma \left\{ \frac{C_6}{a^6} F \left[ 5/2, 5/2, 1, (R/a)^2 \right] + \frac{21 C_{12}}{32 a^{11}} F \left[ 11/2, 11/2, 1, (R/a)^2 \right] \right\}, \quad (1)$$

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 pos-
sibilities 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 & the C60 fullerene [13]. Within this simplified model the van der Waals interaction energy per unit length between two carbon nanotubes, V_{TT}, follows immediately 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 \[\frac{V}{N}\]. Then, the intertube vibrational modes (eigenvalues and eigenvectors) are deduced from the diagonalisation of the dynamical matrix constructed from a numerical evaluation of the second derivatives of the total energy with respect to the tube center coordinates \[\frac{V}{N}\]. As a practical remark, we have built the finite-size bundles enforcing the 6-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 inter-tube vibrational spectra can be sorted according to the C6v point group. In particular we find 3\(i\) Raman active modes and 2\(i\) infrared (IR) active modes.

In Fig. 1 we show the Raman and IR active modes of a finite size bundle of (10,10) (\(R=6.8\,\text{Å}\)) armchair nanotubes as a function of the number of tubes \(N\). Inter-tube modes are found between \(5\,\text{cm}^{-1}\) to \(60\,\text{cm}^{-1}\). 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 deconvolute 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 inter-tube vibration energy range [14]. For comparison between our simulation and future experimental work, we show by the solid curves in figure 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 \(16\,\text{cm}^{-1}\) [18] and are likely to interfere with intertube modes. This last mode is expected to play a role in temperature dependent conductivity of nanotube bundles since it can induce temperature dependent hopping conductivity. The intertubes mode described here could have similar behaviour.

![FIG. 1. Intertube mode frequencies of C60 bundle of infinitely long nanotubes of radius R=6.8Å as a function of the number of tubes. Only Raman active (A1 and E2) modes and IR modes (E1) are represented by fill/open circles. The total vibrational density of states, using a gaussian broadening of 0.8cm^{-1}, for a bundle with 55 tubes is also given.](image)

After presenting the new 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 inter-tube) for a 0.1% change of the tube radius. One of the limitation of the frozen phonon calculation for the BM in bundles is the fact that the pure radial mode is no more 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 C60 in [19]. Here we do not take this symmetry lowering in consideration but we believe that 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 sample.
FIG. 2. Breathing mode \((A_1)\) frequencies as a function of the tube radius. This work: Circles are for armchair tubes, squares for zig-zag and diamond for chiral tube. Solid symbols are for isolated tubes within tight-binding approach and open symbols are for tubes in a bundle (see text). + are estimated from force field approach, \(*\) and \(\times\) come from ab-initio calculations.

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 tube concerns, 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 \((\nu)\), in particular the fit of our data to \(\nu = C/R\) give the following values: \(C=1307\text{cm}^{-1}\) Å for armchair tubes and \(C=1282\text{cm}^{-1}\) Å for zigzag tubes. Chiral tubes BM mode lie between armchair and zigzag lines. Recent ab-initio results showed \(C=1180\text{cm}^{-1}\) Å and \(C=1160\text{cm}^{-1}\) Å for armchair and zigzag tubes, respectively and force field data are reproduced by \(C=1111\text{cm}^{-1}\) Å \(\beta\) or \(C=1147\text{cm}^{-1}\) Å \(\beta\) irrespective of tube chirality. Considering that tight-binding methods usually overestimate vibrational frequencies by 5-10\% \(\beta\), the results presented above are not surprising. We emphasize that our tight-binding calculation reproduce well the slight difference between armchair and zigzag tubes found by ab-initio methods \(\beta\). The reason for this success is connected with the non-orthogonality of our tight-binding method that correctly describe the re-hybridization of carbon-carbon bonds when the nanotube breathe. Moreover, the low computational cost of the TB approach compared to 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 relevant considering actual produced nanotubes), the frequency shift is evaluated to be of the order of 10\%. Very recently, Venkateswaran et al. \(\beta\), using a similar model to study the pressure dependance of nanotube bundles Raman modes, found a 8\% increase of the BM of \((9,9)\) tube when they are packed compare to isolated tube. This is consistent with the present result and the difference (we found 10\% increase for a \((9,9)\) tube) is likely to come from slight difference in parameters used both for the tight binding and for the pair van der Waals potential.

Focussing on 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 vibrationnal energies, our results are inclined to conclude that the experimental Raman peak at 180\text{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\text{cm}^{-1} (force field \(\beta\)) and 194\text{cm}^{-1} (this work) or at 178\text{cm}^{-1} for the ab-initio evaluation in \(\beta\). If we consider those results as 10\% under-evaluation of the BM of tube in a bundle, we get frequencies higher than 180\text{cm}^{-1} (except for the less sophisticated force field model) and the key frequency of 180\text{cm}^{-1} is associated with tube with diameter larger than 6.8Å. This conclusion is consistent with X-rays \(\beta\) and neutron \(\beta\) diffraction if the tube-tube distance is taken to be 3.2Å (and not the graphite interlayer distance 3.35Å) since the diameter polydispersity required for diffraction spectra fit \(\beta\) implies the presence of tube larger than the \((10,10)\) tube in bundles. Moreover, electron diffraction \(\beta\) on single nanotube rope lead to the conclusion that 6.8Å < \(R < 7.5\) Å and then to a mean radius larger than the the \((10,10)\) radius.

As the BM concerns, we have only considered bundles made of a 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 6 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 \(\beta\) and electron diffraction \(\beta\) experimental studies of carbon nanotubes concluded that all tube chiralities can be found in samples with a very narrow diameter distribution. This will not change drastically our conclusions, even more, if tube chirality are randomly distributed whitin 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.

**TABLE I.** Breathing Mode (BM) frequencies for various carbon nanotubes. The first column defined 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) | \( \nu_{\text{isol}} (\text{cm}^{-1}) \) | \( \nu_{\text{bundle}} (\text{cm}^{-1}) \) | 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   |

In conclusion, we have presented the first study of the inter-tube 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 showed the first 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.

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For an infinite 2D-packing of (10,10) tubes with radii of $R=6.8\ \text{Å}$ the relaxed intertube distance is found to be $3.14\ \text{Å}$. Note that the value for the interlayer distance between two flat carbon sheets within the continuous model is $3.27\text{Å}$ and for an infinite layer stacking (graphite) is $3.23\text{Å}$. This distance correspond to the actual interlayer distance in graphite $3.34\ \text{Å}$. The ~0.1Å difference is a measure of the graphene layer thickness. Then, we have confirmed the assumption that curvature reduces the intertube distance in the bundle as compare to graphite by more than 0.1 Å.

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 [19]. This last part of the potential was added empirically to reproduced the relative orientation of $C_{60}$ molecules in the solid. In the case on nanotube-bundles there is no evidence of such orientation and we do not include such bond charge model in our calculation.

For a review on neutron experiments on nanotubes, see S. Rols, E. Anglaret and J.L. Sauvajol Submitted.

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