Theoretical phonon dispersion of armchair and metallic zigzag carbon nanotubes beyond the adiabatic approximation

ARTICLE *in* PHYSICA STATUS SOLIDI (B) · DECEMBER 2010

Impact Factor: 1.49 · DOI: 10.1002/pssb.201000112

2 AUTHORS:

Valentin N. Popov
Sofia University "St. Kliment Ohridski"
114 PUBLICATIONS **3,844** CITATIONS
SEE PROFILE

Philippe Lambin
University of Namur
295 PUBLICATIONS **7,911** CITATIONS
SEE PROFILE

pss-Header will be provided by the publisher

Theoretical phonon dispersion of armchair and metallic zigzag carbon nanotubes beyond the adiabatic approximation

Valentin N. Popov [*,1] and Philippe Lambin[2]

[1] Faculty of Physics, University of Sofia, 5 James Bourchier Blvd, 1164 Sofia, Bulgaria
[2] Research Center in Physics of Matter and Radiation, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium

Received ZZZ, revised ZZZ, accepted ZZZ
Published online ZZZ (Dates will be provided by the publisher.)

Keywords nanotube, Kohn anomaly, dynamic corrections, non-orthogonal tight-binding model

* Corresponding author: e-mail vpopov@phys.uni-sofia.bg, Phone: +359 2 8161833, Fax: +359 2 9625276

The dynamic corrections to the phonon dispersion of armchair and metallic zigzag carbon nanotubes are studied systematically within a non-orthogonal tight-binding model. These corrections were found to be important in the vicinity of the Kohn anomaly of the phonon dispersion at two points of the Brillouin zone. The first point is the zone-centre and the dynamic corrections are large for the longitudinal optical phonons, which give rise to the G^--band in the Raman spectra. The obtained frequencies of these phonons for a large number of metallic nanotubes are in good agreement with previous estimations and available experimental data. The second point is inside the zone for armchair nanotubes and at the zone centre for zigzag nanotubes. In this case, the dynamic effects are also studied and discussed in view of their importance for modelling of double-resonance scattering processes.

1 Introduction The prospects for industrial application of carbon nanotubes have triggered an avalanche of experimental and theoretical works [1]. The single-walled carbon nanotubes are structures with a honeycomb arrangement of carbon atoms on a cylindrical surface. The quasi-one-dimensionality of the nanotubes determines their unique electronic and vibrational properties. On average one-third of the nanotubes are zero- or tiny-gap semiconductors (often called "metallic" nanotubes) and two thirds are moderate-gap semiconductors. Many nanotube applications rely on either metallic or semiconducting nanotubes, which requires efficient monitoring of the nanotube content in the samples.

The Raman spectroscopy is a direct method for identification of the nanotube type and determination of the nanotube population in the samples [2]. The Raman spectra of carbon nanotubes exhibit a few features, the most intense being the radial-breathing mode (RBM) in the frequency region below 400 cm^{-1} and the G-band observed in the region between 1500 – 1600 cm^{-1} [3]. The frequency of the RBM is inversely proportional to the nanotube radius, which is used in the assignment of the low-frequency Raman lines to specific nanotube types. The *G*-band is only slightly dependent on the nanotube radius but generally has three subbands, which can be attributed to metallic (M) and/or semiconducting (S) nanotubes and denoted as G^+, G^-(S), and G^-(M).

The correct description of the observed *G*-subbands requires the explicit account of the electron-phonon interactions, which is usually done in the linear response approximation [4,5]. The strong electron-phonon interactions yield characteristic behaviour of the phonon dispersion of metallic nanotubes in certain points of the Brillouin zone, called the Kohn anomaly. In nanotubes, these anomalies are present at the Γ point and in two mirror points inside the Brillouin zone. This explains the separate *G*-subbands for metallic and semiconducting nanotubes.

However, the calculated G^-(M) subband does not agree well with the experimental data [3]. The reason for this is that the adiabatic approximation, used to separate the electronic and dynamic problems, fails in the regions of the Kohn anomaly of metallic nanotubes. This is supported by

many experimental observations [6–10]. Agreement of theory with experiment can be achieved by considering perturbative corrections to the phonon frequencies, so-called dynamic corrections [5]. The existing estimations of the dynamic effects have been performed within the density-functional theory (DFT) using the zone-folding (ZF) method. While DFT yields accurate phonon dispersion, the use of the ZF method may not be justified in the small-radius region of the nanotube distribution.

Here, we study the dynamic effects on the phonon dispersion of metallic carbon nanotubes by use of a perturbative approach [4] within a density-functional-based non-orthogonal tight-binding (NTB) model [11]. The paper is organized as follows. The general theoretical background is given in Sec. 2. The calculated phonon dispersion is presented and discussed in Sec. 3. The paper ends up with conclusions (Sec. 4).

2 Theoretical part The calculations of the phonon dispersion of armchair and zigzag metallic nanotubes in the adiabatic approximation were performed within a lattice-dynamical model [4] based on the symmetry-adapted non-orthogonal tight-binding model [11]. In essence, the dynamical matrix is derived by considering the change of the total energy of the nanotube due to a static perturbation (a "frozen" phonon) up to second order in the atomic displacements. This change of the total energy contains the electronic response to the perturbation in the linear-response approximation. The obtained phonon dispersion corresponds well to the available experimental data except for the overestimation of the LO and TO branches. In this paper, all phonon frequencies were downscaled by a factor of 0.9 for better agreement with experiment. All calculations are done for temperature of 300 K.

The phonon dispersion of a nanotube can be understood in comparison with that of graphene. Indeed, a nanotube can be viewed as obtained by cutting out from graphene an infinite strip with a rectangular unit cell with N carbon pairs. The allowed wavevector values for the strip lie in a rectangle in the reciprocal space of graphene. The nanotube is then obtained by rolling up the strip into a seamless cylinder. This imposes rotational boundary conditions on the electron wavefunctions and phonon eigenvectors, which restrict the allowed wavevectors only to values on N parallel lines (so-called cutting lines) along the strip. It can be proven that for 1/3 of the nanotubes one of the cutting line passes through the K point of the Brillouin zone of graphene. At this point, cone-like conduction band and valence bands of graphene touch each other at the Fermi energy. Similarly, linear conduction and valence bands touch each other at the Fermi energy at two mirror points with wavevectors q^* and $-q^*$ in the Brillouin zone of 1/3 of the nanotubes characterizing them as metallic.

The presence of touching cone-like bands at the Fermi energy is responsible for the Kohn anomalies in the phonon dispersion of graphene [12] and metallic nanotubes [4,5] as a result of scattering of electrons between states at the Fermi energy. In graphene, there are two non-equivalent K points leading to Kohn anomalies at the Γ and K points of the Brillouin zone. Similarly, the Kohn anomalies in the phonon dispersion of metallic nanotubes are at the Γ point and at two mirror points in the Brillouin zone of the nanotube, $2q^*$ and $-2q^*$ (up to a reciprocal lattice vector) [4].

The strong electron-phonon interactions close to the Kohn anomalies make the adiabatic approximation inapplicable and require dynamic corrections to the phonon dispersion. The latter were estimated here in the lowest order of the perturbation theory. The account of the dynamic corrections leads to modification of the Kohn anomalies.

3 Results and discussion The calculated phonon dispersion of armchair nanotube (5,5) in the adiabatic approximation (see Fig. 1) exhibits well-expressed Kohn anomalies at two points of the Brillouin zone. The affected phonon branches correspond to cutting lines through the Γ and K points of the Brillouin zone of graphene and are drawn by solid and dashed lines, respectively. Largest anomalies have the branches, arising from the LO and TO branches of graphene, and for this reason we shall keep this notation for the corresponding branches of nanotubes.

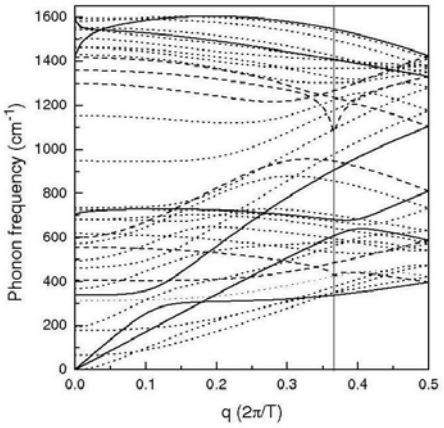

Figure 1. Phonon dispersion of nanotube (5,5). The position of the Kohn anomaly at wavevector $2q^*$ is denoted by a vertical line. T is the nanotube translation period. The phonon branches for cutting lines through the Γ and K points of the Brillouin zone of graphene are drawn by solid and dashed lines, respectively. The branches for all other cutting lines are given by dotted lines.

The Kohn anomalies of the LO and TO branches in the adiabatic approximation and with dynamic correction in the vicinity of the Γ point of nanotube (5,5) are shown in Fig. 2. The TO phonon does not change at the Γ point but has divergence at two points with wavevectors $q_{1,2} = \hbar\omega/\beta_{1,2}$, where ω is the Γ point phonon frequency and $\beta_{1,2}$ are the slopes of the electronic bands at the K point [5]. The LO phonon has a significant upshift at the Γ point, reaches a minimum, and then tends to the adiabatic branch with the increase of the wavevector.

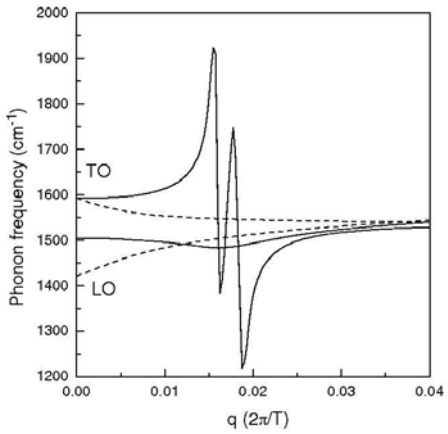

Figure 2 LO and TO phonon branches of nanotube (5,5) close to the Γ point of the Brillouin zone. The branches in the adiabatic approximation are given by dashed lines and those with dynamic corrections are given by solid lines.

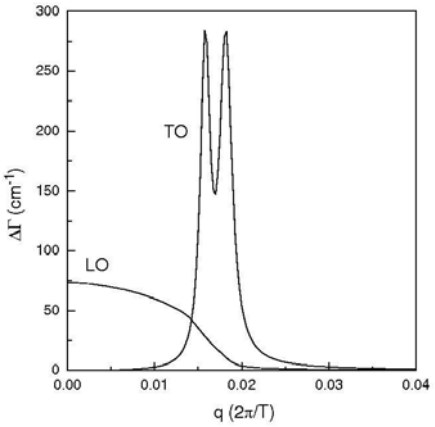

Figure 3 Damping of the LO and TO phonon branches of nanotube (5,5) close to the Γ point of the Brillouin zone.

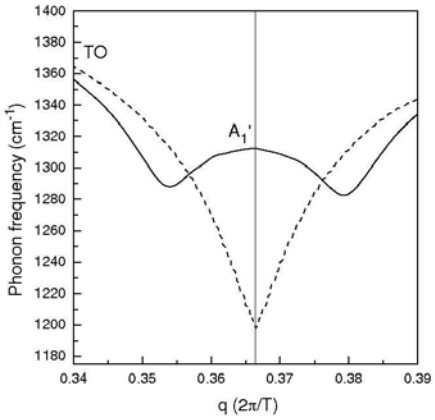

Figure 4 TO phonon branch of nanotube (5,5) close to the Kohn anomaly along the Γ*X* direction of the Brillouin zone. The position of the Kohn anomaly $2q^*$ is denoted by a vertical line.

The damping of the LO and TO branches close to the Γ point is shown in Fig. 3. The damping of the TO branch reaches maximal value at wavevectors $q_{1,2}$ and rapidly tends to zero away from these points. The damping of the LO branch is maximal at the Γ point but decreases monotonously to zero with the increase of the wavevector.

The phonon dispersion of metallic zigzag nanotubes shows similar behaviour. The main difference is the presence of a single singularity of the TO branch due to the fact that for these nanotubes the wavevector q^* coincides with the Γ point and therefore the electronic bands are symmetric with respect to it.

For Raman measurements of one-phonon scattering processes, only the Γ phonons are important. At the Γ point, the TO and LO phonons of metallic nanotubes are usually denoted by G^+ and G^-, respectively. For armchair nanotubes only the G^+ phonon is Raman-active, while for zigzag ones only the G^- is Raman-active.

The part of the TO branch with Kohn anomaly inside the Brillouin zone in the adiabatic approximation and with dynamic corrections for nanotube (5,5) is shown in Fig. 4 and the damping of this branch is shown in Fig. 5. The effect of the dynamic correction is similar to that for the LO branch at the Γ phonon. The correction is largest for the A_1' phonon of the TO branch at the $2q^*$ point. The corresponding graphs for zigzag nanotubes are similar to those in Fig. 4 and 5 with the only difference that the $2q^*$ point coincides with the Γ point.

The results for the G^+ and G^- phonons for all armchair and metallic zigzag nanotubes with radii between 3 Å and 15 Å are summarized in Fig. 6 and the damping is shown in Fig. 7. From these figures it can be concluded that, irrespective of nanotube type,

- the G^+ phonons have negligible dynamic correction and damping. The G^+ phonon frequency decreases from ≈1591 cm^{-1} to ≈1585 cm^{-1} with increasing nanotube radius.
- the G^- phonon frequencies undergo large upward dynamic correction, decreasing from ≈80 cm^{-1} to ≈20 cm^{-1} with increasing nanotube radius. The corrected G^- phonon increases from ≈1500 cm^{-1} to ≈1579 cm^{-1} with increasing nanotube radius.
- the two sets of the G^+ and G^- phonon frequencies seem to lie on two monotonous curves in the considered radius range irrespective of the nanotube type (armchair or zigzag).

As a whole, the obtained G^+ and G^- phonons are in good agreement with available experimental data [3] and other estimations of the dynamic corrections [5,9]. To illustrate this, we compare the frequencies of these phonons for two values of the radius. For radius of 5 Å the derived values for the G^-/G^+ phonon frequencies are: 1543/1591 cm^{-1} [3], 1540/1580 cm^{-1} [5], 1560/1620 cm^{-1} [9], 1536/1591 cm^{-1} (here). For radius of 12 Å the corresponding frequencies are: 1577/1591 cm^{-1} [3], 1576/1587 cm^{-1} [5], 1590/1591 cm^{-1} [9], 1576/1588 cm^{-1} (here).

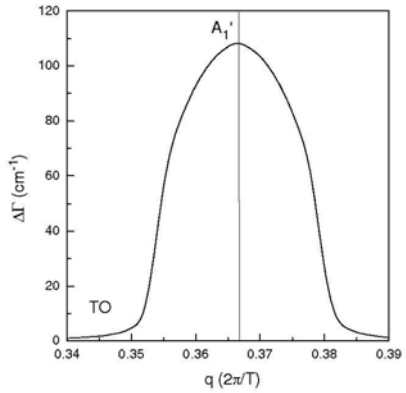

Figure 5 Damping of the TO phonon branch of nanotube (5,5) close to the Kohn anomaly along the Γ*X* direction of the Brillouin zone. For details, see, Fig. 4.

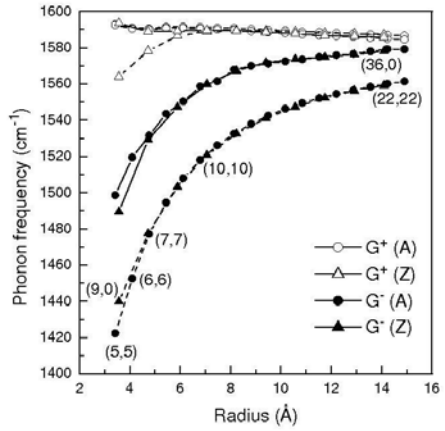

Figure 6 The G^+ and G^- phonon frequency of all armchair and zigzag nanotubes in the radius range between 3 Å and 15 Å vs. nanotube radius. The data obtained in the adiabatic approximation is drawn with dashed lines and those with dynamic corrections is drawn with solid lines.

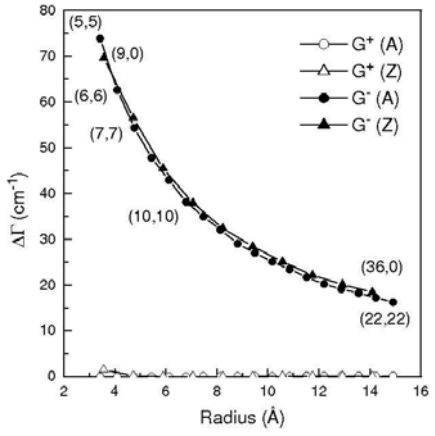

Figure 7 The damping of the G^+ and G^- phonon frequency of all armchair and zigzag nanotubes in the radius range between 3 Å and 15 Å vs. nanotube radius.

For practical use, we fitted our G^- data (in cm^{-1}) vs. radius R (in Å) with the expression

$$\omega(G^-) = \omega_\infty - A / R^2 \qquad (1)$$

The parameters of this power law are $\omega_\infty = 1582$ cm^{-1} and A = 1119 $cm^{-1}Å^2$. Similar power law has been derived from Raman data on nanotubes on a substrate [3].

4 Conclusions We calculated the dynamic corrections to the phonon dispersion of armchair and metallic zigzag SWNTs. We showed that only the G^- phonons increase their frequencies significantly, when dynamic effects are accounted for. The obtained G^- phonon frequencies are in good agreement with other estimations of the dynamic effects and available experimental data. For future use, we fitted the G^- data with a simple expression, containing an exponential function.

Acknowledgements The author was supported partly by Marie-Curie European Re-integration Grant MERG-CT-2007-201227 within the 7th European Community Framework Programme and partly by NSF under grant DO 02-136/15.12.2008 (IRC-CoSiM).

References

[1] Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, edited by A. Jorio, M. S. Dresselhaus, and G. Dresselhaus, Topics in Applied Physics, Vol. **111** (Springer, Berlin, 2008).
[2] S. Reich, C. Thomsen, and J. Maultzsch, Carbon Nanotubes: Basic Concepts and Physical Properties (Wiley-VCH, New York, 2004).
[3] A. Jorio, A. G. Souza Filho, G. Dresselhaus, M. S. Dresselhaus, A. K. Swan, M. S. Ünlü, B. B. Goldberg, M. A. Pimenta, J. H. Hafner, C. M. Lieber, and R. Saito, Phys. Rev. B **65**, 155412 (2002).
[4] V. N. Popov, L. Henrard, and Ph. Lambin, Phys Rev B **72**, 035436 (2005).
[5] S. Piscanec, M. Lazzeri, J. Robertson, A. C. Ferrari, and F. Mauri, Phys. Rev. B **75**, 035427 (2007).
[6] A. Das, A. K. Sood, A. Govindaraj, A. Marco Saitta, M. Lazzeri, F. Mauri, and C. N. R Rao, Phys. Rev. Lett. **99**, 136803 (2007).
[7] H. Farhat, H. Son, Ge. G Samsonidze, S. Reich, M. S. Dresselhaus, and J. Kong, Phys. Rev. Lett. **99**, 145506 (2007).
[8] J. C. Tsang, M. Freitag, V. Perebeinos, J. Liu, and P. Avouris, Nature Nanotech. **2**, 725 (2007).
[9] K. Sasaki, R. Saito, G. Dresselhaus, M. S. Dresselhaus, H. Farhat, and J. Kong, Phys. Rev. B **77**, 245441 (2008).
[10] A. W. Bushmaker, V. V. Deshpande, S. Hsieh, M. W. Bockrath, and S. B. Cronin, Nano Lett. **9**, 607 (2009).
[11] V. N. Popov and L. Henrard, Phys Rev B **70**, 115407 (2004).
[12] S. Piscanec, M. Lazzeri, F. Mauri, A.C. Ferrari, and J. Robertson, Phys. Rev. Lett. **75**, 185503 (2004).