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Continuum model for low-frequency phonons of boron nitride nanotubes

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HIGHLIGHTS

- We report calculations of acoustic oscillation modes of BN NT in a framework of a continuum model.
- A simple formula for the RBM frequency is provided in terms of the sound velocities.
- The general behavior of acoustic modes is correctly described.

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ABSTRACT

A continuum model is employed to calculate the low-frequency phonons of boron nitride nanotubes. We find an excellent agreement of the optically active modes calculated within this approach and those from more elaborate calculations within an energy and wavelength window that can be established beforehand, from the choice of the bulk input parameters. We verify that this model describes correctly the dependence of radial breathing mode with the radius, the existence of parabolic modes at small wavevectors, and other general characteristics of the dispersion relations of these systems.

1. Introduction

The geometry of boron nitride nanotubes (BNNTs) is very similar to that of carbon nanotubes (CNTs): while for the latter the two triangular sublattices are obviously occupied by carbon atoms, in BNNTs one of the sublattices is composed of B atoms and the other of N. The labeling of BN tubes is identical to that of CNTs: like their carbon analogs, they can be viewed as rolled-up hexagonal boron nitride (h-BN) strips, identified by their circumference vector in the two-dimensional (2D) BN hexagonal sheet. However, unlike CNTs, their electronic properties barely depend on their geometry: they are all wide bandgap materials, with significant luminescence and absorption in the UV. In fact, this gap can be tuned by applying an electric field due to the absence of screening; a giant Stark effect has been measured in BNNTs [1], increasing the prospective electronic and optoelectronic uses of these nanotubes.

Indeed, two-dimensional BN is much more stable from the thermal and chemical viewpoint than graphene; this also applies to the tubular forms [2]. They are excellent thermal conductors, an important property with key applications in nanodevices as heat dissipators. Notwithstanding, BN nanotubes have been much less studied than their carbon counterparts. This is due to the fact that the synthesis of BNNTs is much harder than that of CNTs [3]. Recent advances in BNNT growth techniques may result in an increase of experimental research that has already provided rich evidence of their potential applications [4,5]. For example, BNNTs are exceptionally stiff and lightweight materials, like CNTs, which could be used for protecting devices and reinforcement of composites. Due to their boron content, they can be employed for neutron absorption, which can be enhanced by hydrogen doping.

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The combination of mechanical resistance and UV plus neutron absorption points toward their foreseeable application as protective materials in adverse environments, as the outer space.

BNNTs are polar materials. Because of their ionic bonds, they can have piezoelectric properties; they are also expected to be of interest for desalination and filtration at the nanoscale. It has been recently measured the production of electric currents through a BNNT piercing an ultrathin membrane due to salinity gradients, constituting a nanofluidic device [6]. In addition, measurements in multiwalled BNNTs evidence an ultrahigh friction force which has been related to their ionic character [7]. This characteristic is relevant for the design of shock absorber materials.

In order to identify BNNTs, the study of low-frequency phonons is crucial, for Raman and infrared (IR) spectroscopy. While in CNTs Raman spectra are the main optical technique for determination of the nanotube radii, in BNNTs Raman intensity is lower, so IR experiments are also used for their characterization. Besides, acoustic phonons are relevant for transport properties; in these grounds, continuum models are helpful for the understanding of the physical mechanisms of electron-phonon interaction.

From the theoretical viewpoint, phonon modes in BNNTs have been studied by means of various models, such as valence shell [8], tight-binding plus electrostatic interaction [9], and *ab initio* [10–12]. In this work, we employ a continuum approach to model the low-frequency phonons of these nanotubes, which has been successfully applied to CNTs [13], without the restrictions of more sophisticated method with respect to the size of the systems studied.

This work is organized as follows: Section 2 presents the details of the phenomenological model. In Section 3 we present our results. Finally, we draw our conclusions in Section 4.

2. Phenomenological continuum model in cylindrical geometry

We model the nanotubes as infinite cylindrical shells with radius R and thickness h, so that the inner and outer radii are $R \pm h/2$. We choose the axis of the wire along the z direction of the cylindrical coordinates (r, θ, z). Although the continuum approach employed in this work has been reported elsewhere [14–16,13,17], for the sake of completeness we summarize here the main features of the model, particularizing for the tubular geometry.

Assuming a harmonic time-dependence for the oscillations, the equations of motion for the acoustical modes are given by [18]

$$\omega^2 \vec{u} = v_L^2 \nabla(\nabla \cdot \vec{u}) + v_T^2 \nabla \times \nabla \times \vec{u}, \tag{1}$$

where $\vec{u}$ is the relative mechanical displacement of the ions, ω is the frequency of the vibrational modes, and v_L, v_T are the longitudinal and transverse sound velocities of the bulk material, i.e., hexagonal boron nitride. This model assumes that the corresponding bulk material, h-BN, is isotropic. This assumption is valid if the two sound velocities are approximately the same. i.e., when the elastic constants verify $C_{11} - C_{12} \approx 2C_{44}$ [19,20].

The procedure for obtaining a general basis for the solutions of Eq. (1) in cylindrical coordinates, Helmholtz's method, has been previously reported [21,16]. For the sake of completeness, we give here the explicit expression for the basis, which is useful to elucidate the couplings of the different modes

$$\vec{u}_{T1} = \begin{pmatrix} \frac{ik_z}{q_T} f_n'(q_T r) \\ -\frac{nk_z}{q_T}\frac{1}{q_T r} f_n(q_T r) \\ f_n(q_T r) \end{pmatrix} e^{i(n\theta + k_z z)}$$

$$\vec{u}_{T2} = \begin{pmatrix} \frac{in}{q_T r} f_n(q_T r) \\ -f_n'(q_T r) \\ 0 \end{pmatrix} e^{i(n\theta + k_z z)}$$

$$\vec{u}_L = \begin{pmatrix} f_n'(q_L r) \\ \frac{in}{q_L r} f_n(q_L r) \\ \frac{ik_z}{q_L} f_n(q_L r) \end{pmatrix} e^{i(n\theta + k_z z)}. \tag{2}$$

The vector components of the basis functions above are given in cylindrical coordinates, (u_r, u_θ, u_z); n is an integer label related to the angular dependence of the modes; k_z the continuum wavevector along the axis of the tube, and the wavevectors $q_{L,T}$ are given by

$$q_{L,T}^2 = \frac{\omega^2}{v_{L,T}^2} - k_z^2. \tag{3}$$

If $q_{L,T} \in \mathbb{R}$ ($q_{L,T} \in \mathbb{C}$) the function f_n is an order-n Bessel function of the first or second kind, i.e., Bessel J_n or Neumann N_n (Infeld I_n or McDonald K_n). The longitudinal or transversal character of the solution is given by $\nabla \times \vec{u}_L = \vec{0}$ and $\nabla \cdot \vec{u}_{T1} = \nabla \cdot \vec{u}_{T2} = 0$ respectively. Besides these solutions, there is another one not given by Helmholtz's method, a transverse $n=0$ twiston mode. It only has a non-zero component, the angular u_θ proportional to the cylindrical radial coordinate r and velocity equal to that of the transverse 2D bulk mode. The twiston mode was already reported in cylindrical shells and rods [22–24], and more recently described for carbon nanotubes [25–27,13]. This solution is not included in the obtained basis because it is not regular at infinity; however, in a bounded region it should also be taken into account.

The general solution to the problem can be written as a linear combination of the basis vectors, whose coefficients are determined by imposing the appropriate boundary conditions. For free-standing nanotubes, these conditions are those of free surfaces, which means that the momentum transmitted outside the cylindrical shell is zero. In terms of the stress tensor, this amounts to setting the radial stress components to zero at the inner and outer nanotube surfaces. More details are given in Ref. [13].

The explicit form of the basis allows us to elucidate the uncoupled modes for special symmetries, such as $n=0$ or $k_z=0$. For $n=0$, $k_z=0$, L, $T1$ and $T2$ modes are uncoupled. If $n \neq 0$, $k_z=0$, the $T1$ mode remains uncoupled, but there is a $L - T2$ coupling. Likewise, if $n=0$, $k_z \neq 0$ it can be seen that it is the $T2$ mode the one that remains uncoupled, and $L - T1$ coupling develops with increasing k_z. Notice that this analysis also holds for other types of boundary conditions, such as continuity of the amplitude at the interfaces or the stress tensor, provided that they only involve linear relations of the basis vectors and its derivatives.