



Numerical analysis on vacancy induced vibrational properties of graphene nanoribbons



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ARTICLE INFO

Article history:

Received 9 May 2013

Received in revised form 23 June 2013

Accepted 24 June 2013

Available online 17 July 2013

Keywords:

Lattice vibrations

Graphene nanoribbons

Vacancy-type defects

Forced vibrational method

Armchair-edge

ABSTRACT

The effect of vacancy-type defects on the vibrational properties of graphene nanoribbons has been discussed numerically. We have computed the phonon density of states and mode pattern over a broad range of vacancies using the forced vibrational method which is based on the mechanical response to extract the pure vibrational eigenmodes by numerical simulation. We find that the armchair-edge and the vacancy-type defects break down the phonon degeneracy at the Γ point of the LO and TO mode, distort and shift down the phonon density of states significantly. The phonon density of states in the armchair graphene nanoribbons with vacancy-type defects show the remarkable increase in the low frequency region induced by their defect formations. The mode patterns obtained by our numerical experiments reveal that the in-plane optical phonon modes in the K point are localized near the armchair-edges which are in good agreement with the high intensity D peak in the Raman spectra originate from the armchair-edge. The simulation results also demonstrate that the lattice vibrations in the defective graphene nanoribbons show the remarkably different properties such as spatial localizations of lattice vibrations due to their random structures from those in the perfect graphene nanoribbons. These differences manifest themselves in the predicted temperature behavior of the constant-volume specific heat capacity of both structures.

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1. Introduction

Since a few years, a tremendous amount of attention has been focused on the graphene and graphene-related materials because of fundamental physics interests and promising applications [1–7]. A terminated strip of graphene, so-called graphene nanoribbons (GNRs), which shows finite energy band gap due to quantum confinement of electrons has aroused special interest recently. The quasi one dimensional (1D) GNRs have edge structures specified either armchair or zigzag. Narrowing the width of armchair GNRs (AGNRs) results in a transforming from semi-metallic to semiconducting, especially below 10 nm [8,9]. If the width of the armchair GNRs is reduced to 1–2 nm, a discrete quantum levels between the conduction and valence band (energy gap) similar to the band gap of Si, InP, or GaAs can be produced [10]. Recently, GNRs with controlled edge orientation have been fabricated by scanning tunneling microscope (STM) lithography, and opening of energy gaps up to 0.5 eV in a 2.5 nm wide AGNR is reported [11]. The quasi relativistic behavior of electrons and the finite energy gap by varying the ribbon widths make GNRs an attractive candidate for the future electronic devices.

The transport of valence electrons in graphene-related materials have been significantly affected by the lattice vibrations due to a strong electron–phonon coupling [12]. Previous theoretical studies [13,14] predict that the phonon modes are thermally excited at room temperature and that the transport properties of GNRs depend on the nature of edge-phonon modes in addition to the roughness of the ribbon edge [15]. The investigation of the vibrational properties of graphene nanoribbons is thus of fundamental importance for the electron transport in electronic devices and of great general interest for the physical understanding of those structures.

From a practical point of view, when nanoribbons are fabricated experimentally, they will have some structural defects. Vacancy and adatom-vacancy defects are among the most probable ones [16]. Even small concentrations of vacancy-type defects in graphene-based 1D and 2D nanostructures may alter the vibrational properties significantly and thus change their optical absorption, low temperature specific heat and transport properties. So far, several works have been done on the vibrational properties of GNRs using various theoretical approaches including force constant fittings [17,18], the continuum model [19], density functional theory [20,21], and the first-principles calculations [22,23], the most of which focus on the pristine GNRs only. When defects present in a system, they may induce the symmetry breakdown

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of elemental topological arrangement, which generate more complex lattice structures. Therefore, first-principles method requires huge computational resources. These long computational times and convergence problems in the first-principles calculations limit the systems of interest to benchmark molecules. However, a significantly larger scale model is essential for an in-depth understanding of vibrational properties of defective atomic structures. Therefore, the estimation of the vibrational properties in natural GNR nanodevices under the free boundary conditions (FBCs) is an extremely important challenge, especially with complication due to chemical modifications or dangling bonds at GNR edges. It is thus crucial to build a reliable model to measure such physical properties of the defective GNRs or to observe the vibrational mode directly.

In this work, we present a systematic analysis of defect-induced vibrational properties of AGNRs under the free boundary conditions. We have employed forced vibrational (FV) method suitable to treat physical systems proposed by Williams and Maris [24], which is based on the mechanical resonance to extract the vibrational eigenmodes for very complex and large systems by numerical calculations to describe the change in the phonon density of states in the presence of vacancy-type defects. The vacancy concentration, which is the most important parameter in this study has been varied over a broad range. In defective cases there may appear vibrational modes [25,26] lying outside of the allowed frequency range of the perfect crystal. These are called localized vibrational modes, or local modes, because the mode energy is spatially concentrated near the defect site. To show the localized phonon properties we have calculated the mode pattern of AGNRs with and without the presence of vacancy-type defects. Moreover, for the AGNRs, the temperature dependence of the specific heat capacity is obtained from the phonon density of states including the vacancy-type defects and the ribbon width effects. In the next section, we briefly elucidate the FV method relevant to treat physical structures, in which we obtain expressions that will be useful for the calculation phonon density of states and mode pattern.

2. Forced vibrational method

The FV method is based on the fact that if a periodic external force with frequency Ω is applied to a system consisting of N atoms which are coupled together by linear springs, the response of the system will be dominated by the eigenmodes with the eigen frequency near to the Ω . At time $t = 0$, we prepare the lattice system with each atom at rest and with zero displacement. In general, the equation of motion of the systems with the scalar displacement of the l th mass, $u_l(t)$, is:

$$M_l \ddot{u}_l(t) + \sum_r \phi_{lr} u_r(t) = 0 \quad (1)$$

where M_l is the mass of l th atom and ϕ_{lr} is the strength of the spring between the l th and l' th atoms. The displacement can be composed into a set of normal modes according to following equation:

$$u_l(t) = \sum_{\lambda} Q_{\lambda}(t) \frac{e_l(\lambda)}{\sqrt{M_l}} \quad (2)$$

where $Q_{\lambda}(t)$ and $e_l(\lambda)$ are the amplitude and the eigenvector of the normal modes (λ), respectively. For $t > 0$ an external periodic force $F_0 \sqrt{M_l} \cos(\phi_l) \cos(\Omega t)$ is applied to the each atom l , where F_0 is a constant independent of time and ϕ_l is a random quantity. Thus, for large times the periodic external force excites only those modes whose frequency is close to Ω . When we average all possible values of ϕ_l and use the orthonormality of the eigenvectors $\{e_l(\lambda)\}$, the average value of energy $\langle E \rangle$ becomes as follows:

$$\langle E(\Omega) \rangle \approx \frac{\pi t F_0^2}{8} \sum_{\lambda} \delta(\omega_{\lambda} - \Omega) = \frac{\pi t F_0^2 N g(\Omega)}{8} \quad (3)$$

where $g(\Omega)$ is the phonon density of states. Therefore:

$$g(\Omega) = \frac{8 \langle E(\Omega) \rangle}{\pi t F_0^2 N} \quad (4)$$

Thus, we can obtain the phonon density of states to carry out the time development in the presence of the periodic force. Moreover, if the system is driven for a long time, the response will mainly come from the modes of frequency close to Ω . If the modes of frequency around Ω are localized, the energy distribution of the system will be inhomogeneous. Since the numbers of excited modes are small, they will have a very small probability of overlapping. Therefore, any region of high energy density can be assumed to be caused by single mode. As a result, the displacement u_l of the atoms within a particular localized region should be:

$$u_l = C e_l(\lambda_0) / \sqrt{M_l} \quad (5)$$

where C is a constant factor independent of l and $e_l(\lambda_0)$ is the displacement pattern or polarization vector of the mode λ_0 . Thus, we can obtain the mode pattern of the eigenmodes in the system.

3. Computational details

The FV method has been applied to a numerical investigation of vibrational properties of the pristine AGNR and the defective AGNR lattice structures. Following previous convention [27–38], the GNRs with armchair shaped edges on both sides are classified by the number of dimer lines (N) across the ribbon width, W as shown in Fig. 1a. We refer to the AGNR with N dimer lines as a N -AGNR. The relationships between W and N are given by following equation:

$$W_{\text{AGNR}} = \frac{1}{2} (N - 1) a \quad (6)$$

where a is the lattice constant of graphene. Barnard and Snook [39] has shown that the average bond length in a GNR rapidly converges to the average bond length of a relaxed sheet of graphene when increasing the number of atoms. In our calculation, the GNR relaxation is thus neglected and the lattice constant of a relaxed graphene sheet, i.e., $a = 0.246$ nm is used throughout this work. The Brillouin zone of graphene with high-symmetry points such as Γ , K , and M points are shown in Fig. 1b. The simulations are performed on the graphene nanoribbons under the free boundary conditions (FBCs), for which the width of the sheet is confined to be a finite size of up to 4 nm (33-AGNR) while the length is considered about 0.12 μm long in the total of 17,474 atoms. The elemental lattice structure of the model is considered without the strains, torsions and the surface reconstructions for the simplicity. Vacancies are introduced randomly into the graphene nanoribbon honeycomb lattices using bond percolation procedures. It is well known that the bond probability of a percolation network of honey comb lattice is 65%. Therefore, vacancy concentrations (i.e., defect density) up to 35% are used in the present simulation. Fig. 1c shows the lattice structure of the elementary percolation network used in the works. Only interactions up to the fourth nearest neighbor atoms are used and the force constant tensor between two carbon atoms is taken from Jishi et al. [40]. For atoms near an edge, only the force constant of actual atoms is included in the calculation under the FBC. This is different from periodic boundary conditions (PBCs). For example, the leftmost atom in the dashed frame in Fig. 1a is only restored by its right atoms when it leaves its equilibrium position. In this case, the force constants are only comprised of its right atoms. For

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