



Research Paper

First-principles investigation on thermal properties and infrared spectra of imperfect graphene



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HIGHLIGHTS

- Imperfect graphene properties were calculated based on first-principles theory.
- Defects in graphene structure results in lower specific heat and higher free energy.
- Specific heat rises quickly with temperature and flattens at high temperature.
- Peaks and splits were observed in Raman and IR spectra of imperfect graphene.

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ABSTRACT

In this study we used first-principles density functional theory to investigate the thermal and optical properties of graphene. Graphene phonon properties were first calculated by the density-functional perturbation theory and then used to acquire thermal properties such as the specific heat, free and total energy, and entropy, as well as the infrared and Raman spectra. Results show that the peaks of phonon density of states at about 40 and 45.5 THz in the perfect graphene (G) were shifted to 40.5 and 46 THz in the imperfect graphene (G-D), respectively. There are peaks at 16.5, 19, 25, and 43.5 THz in the G-D curve, while there is no obvious peak at same frequencies in that of the G. The specific heat and entropy are lower for the G-D than for the G at temperature >280 K, but the tendency is slightly reversed at temperature <200 K. The total energy, change in vibrational internal energy, and change in the vibrational Helmholtz free energy are all lower for the G-D than for the G. The Helmholtz free energy for the G-D is higher at temperature >1300 K, but lower at temperature below 1250 K than for the G. In the infrared (IR) spectrum, no absorption peak exists for perfect graphene, but strong absorption is found at about 233, 830 and 1392 cm^{-1} for the G-D. The character peak of sp^2 carbon atom in-plane vibration in the Raman spectrum is shifted from 1589 cm^{-1} for the G to 1530 cm^{-1} for the G-D. The defects in the G-D caused the peaks and splits in the IR and Raman spectra.

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1. Introduction

Graphene, the two-dimensional carbon film has aroused tremendous research interests for exploring innovative electrical, mechanical, and thermal properties in the past few years [1,2]. Graphene could replace some materials in use for many existing applications. For example, the composite of graphene/ Fe_2O_3 was used as an anode material for Li-ion batteries and it exhibited discharge and charge capacities of 1693 and 1227 mAh/g, respectively [1]. Graphene oxide/ Fe_2O_3 -nanotubes composites exhibited a high

specific capacitance of 133.2 Fg^{-1} and the electrode showed good long-term cycle stability [2]. Thermal conductivity of the graphite composite enhances the heat transfer rate about 3.35 times with Graphite at 5.0 vol.% in phase change materials [3]. Feng et al. [4] reported the measurement of thermal conductivity of a suspended single-layer graphene, and found the thermal conductivity at room temperature was 4840–5300 $\text{W}/(\text{m}\cdot\text{K})$. Zhang et al. [5] calculated the thermal conductivity of graphene by Green-Kubo method. Their results showed $2903 \pm 93 \text{ W}/(\text{m}\cdot\text{K})$ for the pristine graphene, in which the out-of-plane phonon mode contribution was $1202 \pm 32 \text{ W}/(\text{m}\cdot\text{K})$. Wirth et al. [6] investigated how thermal conductance responded to edge defects in narrow graphene. They showed that Hydrogen absences produce reductions in conductance in planar graphene. Cao et al. [7] studied the thermal

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Nomenclature

A_T	Helmholtz free energy
C_v	vibrational specific heat at constant volume
d	the number of degrees of freedom
E_{elec}	the electronic energy of formation
E_0	= E_{elec} + ZPE
E_T	the total energy
$E_{vib(T)}$	the change in vibrational internal energy
h	Planck constant
j	the phonon mode
k_B	the Boltzmann constant
n	the wave vector
S_T	the vibrational entropy
T	temperature
x	the dimensional vector

Greek symbols

k	the discrete wave vector
$\Delta\omega$	frequency interval
ω	frequency

Abbreviations

G	perfect graphene
G-D	imperfect graphene
MD	molecular dynamics
ZPE	the zero point energy

transport behavior in an 18.2-nm-long graphene sheet and found a parallel relationship on ballistic resistances in parallel systems, and a complicated superimposed effect of arrangement mode on ballistic resistances in series systems governed by the phonon localization and corresponding change of phonon transmission angle.

The structure of graphene and its chemically derived forms were studied for realizing special properties [8]. The research of in-plane thermal conductivity of graphene showed that thermal conductivity increases with length. Surface oxidation and phonon-defect scattering at the surface oxidized groups suppress the density of state of the phonon mode due to C–C bonds [9]. Research showed that the graphene nano-ribbons (GNR)s exhibit a rapid drop in thermal conductivity with increasing degree of functionalization of methyl and phenyl groups at random positions. The thermal conductivity of nanoribbons with zigzag edges is more sensitive in the degree of functionalization than nanoribbons with armchair edges [10].

In addition to experimental works to explore new applications of graphene and new properties of the derivatives [11,12], theoretical studies have been carried out to simulate the structure and unique properties of the carbon nanotube [13,14] and graphene [15,16]. The simulation was done for the effect of optical and acoustic phonon-scattering in the presence of line-edge-roughness on the electronic properties of ultra-scaled armchair graphene nano-ribbons. It was shown that the edge roughness slightly reduces the onset of optical phonon emission, acoustic phonons reduce off-state conductance and optical phonons reduce on-state conductance [17]. The first-principles density functional calculations were performed for the hydrogen transfer reaction between graphene surface and a mixture of hydrogen carrier and electron donor to investigate the microscopic mechanism for the wet-chemical hydrogenation of graphene. The electronic structure and energetics of the hydrogen transfer from hydrogen carriers, such as CH_3OH or CH_3NH_2^+ , are considered with an alkali atom as an electron donor, or with externally added electrons. Researchers deduced from the results that the hydrogen carrier system with CH_3NH_2^+ does not require the presence of an alkali atom [18]. The thermal transport properties of graphene and graphene nano-ribbons were simulated by non-equilibrium molecular dynamics simulation; results revealed abnormal thermal transport in graphene, and a low thermal conductivity at room temperature compared to graphene [19]. The atomistic Green's function study was adopted to simulate the phonon transport through a heterogeneous interface between bulk TiC substrates and graphene nanoribbons [20].

The substitution of atom in graphene is important for production of soluble materials or adding the functional group onto the

graphene wall to make novel composite materials [21,22]. However, it is very difficult for imaging techniques to visualize the substitution on the graphene wall and to reveal how the substitutions affect the properties of the graphene. The current work aims at investigating the sensitivity of infrared (IR) and Raman parameters and the phonon properties upon the absent C atom in graphene (see Fig. 1) using first-principles theoretical approach.

2. Theoretical method

The present calculations were carried out by VASP code [23,24], which is a complex package for performing ab-initio quantum-mechanical molecular dynamics (MD) simulations based on the first-principles density functional theory (DFT). For calculation of a system, the approach implemented in VASP is based on the (finite-temperature) local-density approximation with the free energy as variable quantity and an exact evaluation of the instantaneous electronic ground state at each MD time step. VASP uses efficient matrix diagonalization schemes and an efficient Pulay/Broyden charge density mixing. These techniques avoid all problems possibly occurring in the original Car-Parrinello method [25], which is based on the simultaneous integration of charged particles, both electronic and ionic, equations of motion. The interaction between them is described by ultra-soft Vanderbilt pseudopotentials (US-PP) [26] or by the projector-augmented wave (PAW) method. US-PP (and the PAW method) allows for a considerable reduction of the number of plane-waves per atom for transition metals and first row elements.

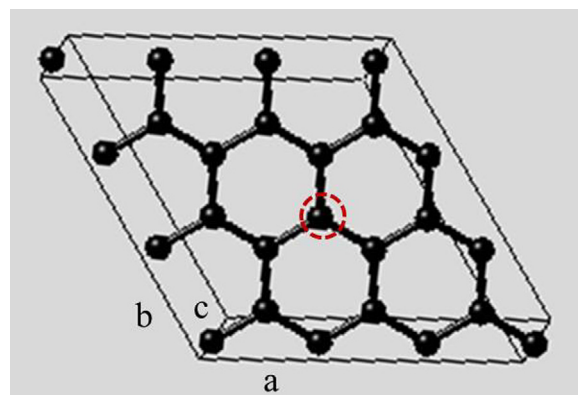


Fig. 1. The structure of a unit cell of graphene with an absent C atom in the circled position for the G-D.

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