Computational Materials Science 151 (2018) 153–159

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

On the diversity in the thermal transport properties of graphene: A first-principles-benchmark study testing different exchange-correlation functionals

Guangzhao Qin[a], Zhenzhen Qin[b], Huimin Wang[a], Ming Hu[a,b,*]

[a] Institute of Mineral Engineering, Division of Materials Science and Engineering, Faculty of Georesources and Materials Engineering, RWTH Aachen University, Aachen 52064, Germany

[b] Aachen Institute for Advanced Study in Computational Engineering Science (AICES), RWTH Aachen University, Aachen 52062, Germany

ARTICLE INFO

Keywords:
Thermal conductivity
Graphene
Exchange-correlation (XC) functionals
First-principles

ABSTRACT

Due to the extraordinary mechanical, electronic, optical, and thermal transport properties, graphene had been one of the most fascinating and extensively studied two-dimensional materials in recent years. Benefiting from the extremely high thermal conductivity, the thermal transport in graphene has received exceptional attention in both experimental and theoretical studies. In this paper, based on first-principles calculations, we performed systematic study on the thermal transport properties of graphene using 10 different exchange-correlation (XC) functionals combined with ultrasoft or projector augmented wave (PAW) pseudopotentials. The thermal transport properties of graphene show distinct diversity for different XC functionals despite their overall good agreement with experimental measurements. It is found that the thermal conductivity of graphene could range from 1936 to 4376 $W m^{-1} K^{-1}$ with different XC functionals employed. The reason for the diversity in the thermal transport properties of graphene is analyzed based on the insight into the mode level phonon behaviors. Our study executed a comprehensive investigation of the thermal transport properties of graphene with different XC functionals employed, which would shed light on future researches related to graphene and other novel materials.

1. Introduction

Graphene, the first two-dimensional (2D) atomic crystal available to us, possesses honeycomb lattice structure and exhibits numerous striking properties [1]. Ever since the discovery in 2004, graphene had been one of the most fascinating and extensively studied materials in recent years and the field of graphene research took off rapidly due to its extraordinary mechanical, electronic and optical properties [2]. Graphene can also, in principle, be considered as an elementary building block for all carbon allotropes. These developments in the science of graphene prompted an unprecedented surge of activity and demonstration of new physical phenomena. In addition, the thermal and thermoelectric properties of graphene are also very fascinating, especially the thermal transport properties [3]. Experiments have shown that the lattice thermal conductivity (κ) of graphene reaches as high as more than 5000 $W m^{-1} K^{-1}$, which makes graphene very promising for high-performance thermal management applications such as heat dissipation in electronics [4]. Benefiting from its extremely high κ, thermal transport in graphene receives exceptional attention in both experimental and theoretical studies [3]. In addition, graphene also plays a benchmark role in the studies of thermal transport in broad 2D materials [5].

Despite the intensive studies on the thermal transport in graphene, it has been a long time debate on how large the thermal conductivity of graphene exactly is, since the reported κ values from both experimental and theoretical studies could range from several hundreds to several thousands [3]. There are lots of possible reasons for the diversity in the thermal transport properties of graphene. For instance, it might be due to the divergence of the κ of graphene with respect to system length. In the presence of extrinsic scattering mechanisms such as scattering from defects or boundary, or coupling to the substrate, the κ of graphene indeed converges as reported in lots of literature [5,6]. However, for samples with infinite size the intrinsic κ of graphene is reported to logarithmically diverge with length [3,7,8]. Thus, with different system length the κ of graphene may run in a wide range. Another possible reason for the diversity in the thermal transport properties of graphene may lie in the phonon hydrodynamics. The common calculations based on the relaxation time approximation (RTA) treat both the U and N-

* Corresponding author. Present address: Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA.
E-mail address: minghu@cec.sc.edu (M. Hu).

https://doi.org/10.1016/j.commatsci.2018.05.007
Received 29 January 2018; Received in revised form 4 May 2018; Accepted 4 May 2018

processes as resistive, which will lead to a large underestimation of the thermal conductivity [9]. The full solution of the phonon Boltzmann transport equation (BTE) based on the iterative method provides mode-dependent nonequilibrium populations to calculate phonon-phonon scattering rates, which can give a precise description of the phonon hydrodynamics in graphene [10–12]. Due to the large proportion of N-process and strong phonon hydrodynamics in graphene, the difference in the results obtained using the RTA and iterative methods is significant. Therefore, the accuracy for the description of the phonon hydrodynamics could lead to the diversity in the thermal transport properties. In addition, the different empirical potential functions or force fields for describing interatomic interactions in classical molecular dynamics (MD) simulations and different pseudopotentials and exchange-correlation (XC) functionals in the local-density approximation (LDA) and generalized gradient approximation (GGA) from first-principles could also have remarkable effect on the thermal conductivity of graphene. Previous theoretical studies report different values for the κ of graphene using different methods for describing interatomic interactions [3,13]. However, a systematic study on the dependence of the thermal transport properties of graphene on different pseudopotentials and XC functionals based on first-principles calculations is lacking, which could be helpful for understanding the diversity in the obtained thermal transport properties of graphene.

In this paper, based on first-principles calculations, we performed systematic study on the thermal transport properties of graphene using different XC functionals combined with ultrasoft or projector augmented wave (PAW) pseudopotentials. The thermal transport properties of graphene show distinct diversity for different XC functionals despite their overall good agreement with experimental measurements. It is found that the thermal conductivity of graphene could range from 1936 to 4376 $W\,m^{-1}\,K^{-1}$ with different XC functionals employed. The reason for the diversity in the thermal transport properties of graphene is analyzed based on the insight into the mode level phonon behaviors. Our study make a comprehensive investigation of the thermal transport properties of graphene with different XC functionals employed, which would shed light on future researches related to graphene and other novel materials.

2. Computational details

All the first-principles calculations are performed based on the density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [14]. For the structure optimization and following DFT calculations of graphene, different poeudopotentials [ultrasoft [15] and PAW [16]] and XC functionals in the LDA and GGA are employed: LDA [17], Perdew-Burke-Ernzerhof (PBE) [18], revised PBE (rPBE) [19], PBE revised for solids (PBEsol) [20], Perdew-Wang 91 (PW91) [21], ultrasoft pseudopotential GGA (USPP_GGA), ultrasoft pseudopotential LDA (USPP_LDA) [15,22], the "opt" functionals (optB88, optB86b, optPBE) where the exchange functionals are optimised for the correlation part [23,24] to include *van der Waals* (vdW) interaction, and the vdW-DF2 of Langreth and Lundqvist groups [25]. Based on careful convergence tests, the kinetic energy cutoff of wave functions are set as 1000 and 700 eV for PAW and ultrasoft poeudopotentials, respectively. A Monkhorst-Pack [26] *k*-mesh of $15 \times 15 \times 1$ is used to sample the Brillouin Zone (BZ) for the structure optimizations, with the energy convergence threshold set as 10^{-8} eV. These parameters ensure the stability of the calculations with well convergence and limited numerical noise. A large vacuum spacing of 20 Å along the *out-of-plane* direction is used to hinder the interactions arising from the employed periodic boundary conditions. Both the cell shape and volume are fully optimized and all atoms are allowed to relax until the maximal Hellmann-Feynman force acting on each atom is no larger than 10^{-8} eV/Å.

In the calculations for obtaining harmonic (second order) interatomic force constants (IFCs) and anharmonic (third order) IFCs, a sufficiently large supercell is necessary for the accurate prediction of lattice dynamics properties. After performing calculations with different supercell sizes, the supercell size is chosen as $5 \times 5 \times 1$ for graphene based on the convergence of the phonon dispersions. Moreover, the electronic wave vector grid density (*k*-mesh) is found to have significant effect on the calculated phonon vibrational frequency, especially for the frequency of longitudinal optical (LO) phonon branch at the Brillouin zone (BZ) center (Γ point). Based on the full convergence test, we choose a *k*-mesh of $5 \times 5 \times 1$ for the supercell force calculations. For all the calculation of IFCs in graphene, the space group symmetry properties are employed for reducing the computational cost and the numerical noise of the IFCs [27]. The cutoff distance (r^{cutoff}) introduced during the calculations of the anharmonic IFCs is also fully tested, which is used to discard the interactions between atoms with distance larger than a certain value for practical purposes. The r^{cutoff} of 10th nearest neighbors (~0.7 nm) is found to be large enough to obtain converged and reliable κ of graphene [28]. Detailed discussions on the convergence are presented later based on Fig. 2. The translational and rotational invariance of IFCs are enforced using the Lagrange multiplier method [29,30]. The dielectric constant (ϵ) is obtained based on the density functional perturbation theory (DFPT). The thickness for calculating κ is chosen as the vdW diameter (3.4 Å). The κ is obtained by solving the linearized phonon BTE using an iterative procedure as implemented in the ShengBTE package based on IFCs [30,31]. Isotopes are included for simulating the natural cases.

3. Results and discussions

The optimized lattice constants of graphene using different XC functionals are listed in Table 1. It shows that the LDA functionals based on both the ultrasoft and PAW pseudopotentials significantly underestimate the lattice constant (2.441 and 2.446 Å, respectively) compared to other GGA functionals (>~2.46 Å) and the experimental measurements [35]. Such underestimation of LDA has been well acknowledged in literature [36]. The difference may lie in the fact that LDA functionals only depend on the local density while GGA functionals also depend on the spatial variation of the density (density gradients). It is well known that the geometry structure is the basic of all the other properties and one of the most typical characteristics of geometry structure is the lattice constant. The geometry parameters are anticipated to have an effect (sometimes important, sometimes not) on the lattice dynamics and thermal transport properties in most cases [37]. In the following we will show that, the prediction of thermal related properties is much more complex than just concerning the lattice constants. In fact, the diversity in the lattice constants predicted using different XC functionals reflects the different specific implementations, which is responsible for the diversity in the thermal transport properties.

Based on the optimized geometry structure with high precision, the phonon dispersions of graphene are obtained. The calculated phonon dispersions using different XC functionals are plotted together in Fig. 1(a) for comparison. The absence of imaginary frequency in the phonon dispersion imply the thermodynamical stability, except the USPP_GGA functional. The failure of USPP_GGA to correctly capture the lattice vibrations may lie in the incompatible combination of the USPP and GGA features. In the following we only consider and discuss the XC functionals with no imaginary frequency. We also plotted in Fig. 1(a) the experimentally measured phonon frequency of graphene and graphite for further verification [32–34]. It shows almost no difference for the acoustic phonon modes among different XC functionals and experiments. However, there exist some differences in the optical phonon modes, which can be quantified by the frequency of LO phonon branch at the BZ center (Γ point) as listed in Table 1. The frequency of LO at Γ point is 1580 cm^{-1} as reported from experimental measurement [38]. If we consider the uncertainty as 2%, all the calculated frequencies of LO at Γ using different XC functionals agree very well with experiment,