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Impacts of potential models on calculating the thermal conductivity of graphene using non-equilibrium molecular dynamics simulations

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ABSTRACT

This work employs non-equilibrium molecular dynamics (NEMD) simulations to examine the applicability of four kinds of interatomic potential models: the Tersoff, the REBO, the opt-Tersoff and the AIREBO, which are widely used to model the thermal transport in single- and multi-layer graphene, as well as graphite crystallites. Thermal conductivities of $\sim 17 \times 5$ nm^2 and $\sim 50 \times 5$ nm^2 graphene are calculated in the temperature range of 200∼500 K with the four potentials and quantum correction is applied due to an extremely high Debye temperature of about 2100 K for graphene. The predicted thermal conductivities are compared with experimental data and phonon spectrum functions are calculated to quantify the degree of phonon scattering. The results show that two original potentials, the Tersoff and the REBO, as well as the AIREBO significantly underestimate thermal conductivities of single-layer graphene but they can qualitatively describe the trend of thermal conductivities with temperature. The opt-Tersoff is found to be the most suitable potential for modeling the thermal conductivity of both single- and multi-layer graphene because it predicts a larger frequency range and a larger frequency value for the high frequency peak, while appropriately capturing phonon scattering in thicker multi-layer graphene when Lennard-Jones term is added into the opt-Tersoff to describe interlayer atomic interactions.

1. Introduction

Carbon/carbon composites, or carbon fiber reinforced carbon composites, have been extensively utilized in aerospace and military applications [1], such as fins of ballistic missiles [2], nose cones and wing edges on aerospace vehicles [3], and rocket components [4]. The range of its civilian applications is also expanded recently, such as heat sinks, turbine rotors, and high-temperature engine [5], where the extremely high thermal conductivity, low coefficient of thermal expansion, and good mechanical strength are advantageous factors. For instance, a thermal conductivity of ~ 800 W m^{-1} K^{-1} at ~ 300 K [6] can be offered, which can also maintain the magnitude in high temperature environment (∼2000 K). The excellent thermophysical properties are highly related to microstructural features of materials, especially orientations and arrangements of graphite crystallites in carbon/carbon composites [7].

Graphite crystallites are typical nano-structures in carbon/carbon composites. As shown in Fig. 1(a), carbon layers are characterized by parallel lines and several parallel carbon layers form a graphene-like micro-crystallite (Fig. 1(b)). Every carbon layer can be regarded to be a single-layer graphene which is composed of periodical lattices of hexagonally arranged carbon atoms [1]. Yuan et al. [6] have verified that the sheet size and the number of layers significantly affect the thermal conductivities of graphite crystallites, and hence the thermal conductivity of carbon/carbon composites increases from ∼40 to ∼860 W m^{-1} K^{-1} since the average crystal coherence length L_a increases from 8 nm to 78 nm.

The measurement of thermal conductivity for the single-layer and the multi-layer graphene is very challenging due to their atom-scale thickness. Several experimental studies [8–12] have been carried out to measure the thermal conductivity of graphene, but the measured values strongly depend on sample quality, sample size, and experimental strategy. Especially, for Raman techniques, improper laser absorption rate will affect the accuracy of

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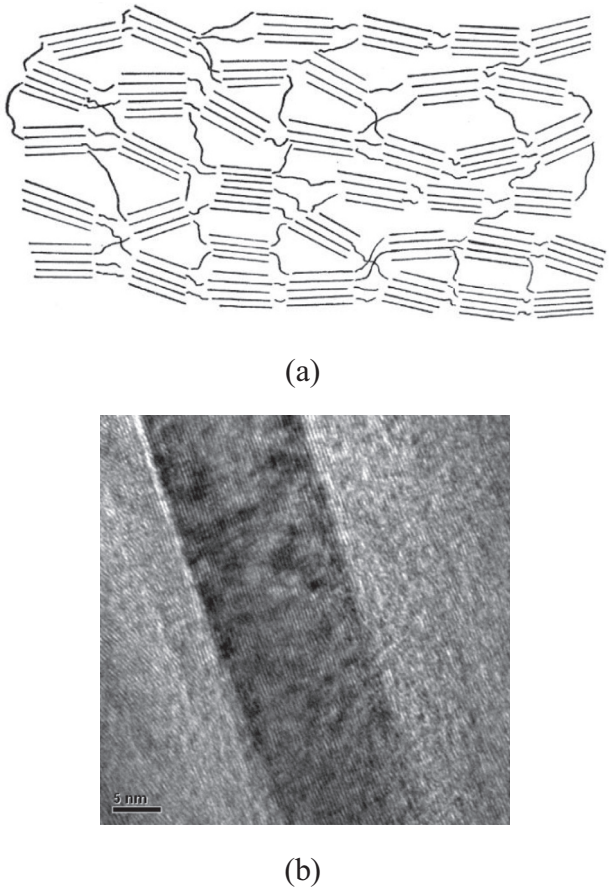

Fig. 1. (a) Schematic of graphite crystallites in C/C composites [7]; and (b) SEM image of graphite crystallite.

thermal conductivity. Consequently, modeling and simulation have been become an important tool for the understanding of their thermal properties, including Molecular dynamics (MD) simulations [13–28], non-equilibrium Green's functions (NEGF) simulations [29–32], and Boltzmann transport equation (BTE) simulations [33–36]. MD simulation is a classical technique which overestimates the specific heat below the Debye temperature (~2100 K for graphene [37]) since quantum effects are neglected in MD studies, and has some discrepancy with BTE studies in prediction of thermal conductivity [38]. BTE method has the advantage of studying large system, but the phonon-dispersion curve is needed in advance, which limits its applications. There are many situations where the phonon-dispersion curve is hardly to obtain, especially the graphene in these studies are not ideal or suspended. Moreover, the *n*-phonon process for $n>3$ has to be ignored in BTE method, which may cause system errors when predicting thermal conductivities of graphene. NEGF can be another way to study the same effects on the thermal properties. However, NEGF approach is difficult to implement when the anharmonic interactions is involved [39]. Unfortunately, the effects of anharmonic interactions are important to thermal properties of a nanomaterial. Thus, MD simulations have been extensively used to analyze the effects of atomistic changes on the thermal properties of a nanomaterial, since the *n*-phonon process and anharmonic interaction can be involved.

Technically, MD simulations employ atomic interactions as a force field and atomic motions can be followed by solving classic Newtonian equations, which have been widely used to reveal properties of molecular materials. Recently, MD simulations were used to investigate the thermal transport in graphene and graphene nano-ribbon [16–28]. As listed in Table 1, non-equilibrium molecular dynamics (NEMD) is commonly used, since the thermal conductivity of materials can be directly calculated by Fourier's law. It is worth noting that NEMD simulations have provided atomistic insights into graphene heat flow, as well as novel routes for tailoring the thermal properties of nanostructured graphene materials [38].

MD simulations require interatomic potentials that properly account for interactions between atoms. For the graphene-related materials such as multi-layer graphene and graphite crystallite, intralayer and interlayer interactions both play decisive roles in predicting their thermal conductivity. For single-layer graphene, several different potential models were employed in the previous works [16–26], as shown in Table 1. Among these models, The Tersoff [40–42] is a traditional potential developed for modeling the energetics of covalent systems with classical inter-atomic potentials. Reactive empirical bond order (REBO) potential [43] is the Tersoff type potential developed for simulating the chemical vapor deposition of diamond. The Tersoff and the REBO potentials have been used to predict the thermal conductivity of single-layer [16,23] and multi-layer [27,28] graphene materials. The two models are both empirical interatomic potentials; however, their potential parameters were not fitted from graphene-related materials. Later, an optimized model referred to as the opt-Tersoff was developed by Lindsay and Broido [44] based on the Tersoff potential, which was aimed at modeling thermal transport in graphene and carbon nano-tube. Stuart et al. [45] extended the REBO potential to the adaptive intermolecular form (AIREBO) for modeling intermolecular interactions and chemical reactions in condensed-phase hydrocarbon systems such as graphite, hydrocarbons, and polymers. It is surprising that, although the improved potentials have been developed, the two original forms are still used to model the thermal conductivity of graphene-related materials [23,27]. This indicates that the choice of potentials is somewhat arbitrary up to now; therefore, a comprehensive comparative study of the four potentials is necessary to clarify the potential applicability in prediction of thermal conductivity for the single-layer graphene.

For multi-layer graphene, the interlayer bonding force is defined by van der Waals interaction. The Tersoff, the REBO, and the opt-Tersoff potentials can only describe intralayer atomic force; thus an extra potential, often Lennard-Jones (L-J) potential, needs to be introduced to describe interlayer interactions when calculating thermal conductivity of multi-layer graphene by the three potentials. On the other hand, for the AIREBO potential, non-bonded interactions term and dihedral-angle interactions term have been added to the REBO potential. Therefore, the AIREBO potential can describe both interlayer van der Waals interaction and intralayer atomic force. A very recent experimental measurement [46] demonstrated that thermal conductivity of the multi-layer graphene shows significantly decreasing trends with an increase in the number of layers. Thus, for the calculation of thermal conductivity of multi-layer graphene, it is still needed to assess which potential can capture this observation.

In this work, the commonly used Tersoff and REBO potentials and their optimized forms (the opt-Tersoff and the AIREBO) are tested in the NEMD simulations. The predicted thermal conductivities are compared with the experimental data. The focus of this work is to provide a guideline for choosing appropriate interatomic potential when the thermal properties of single- and/or multi-layer graphene are evaluated by molecular dynamics simulations, and MD simulations is an appropriate method to study the applicabilities as the phonon scattering dominates the thermal transport of graphene and the effects of layer numbers can be effectively incorporated in MD simulations.