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Molecular dynamics predictions of the influence of graphite stacking arrangement on the thermal conductivity tensor

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ABSTRACT

The effect of stacking configuration on the phonon-based thermal conductivity of graphite is investigated using equilibrium molecular dynamics. Hexagonal (AAA), Bernal (ABA), and Rhombohedral (ABC) stacking forms are considered in a 5×5 nm domain. The intralayer thermal conductivity values are predicted to be 450–800 W/m K for both zigzag and armchair directions for different configurations, which are in agreement with previous results for graphite and few-layer graphene. The interlayer thermal conductivity values are calculated in the range of 9–55 W/m K. The intralayer thermal conductivity in the armchair direction appears to increase with increasing vertical alignment of carbon atoms in adjacent layers.

1. Introduction

Graphite, known since 1789 due to its use in pencils, has increased in interest over the past decade due to the growth in research in graphite nanofibers (GNFs) [1,2]. Graphite is comprised of hexagonally-structured layers of carbon atoms with a bond length of 0.142 nm, stacked with a nominal distance of 0.335 nm. The layered structure of graphite determines its anisotropic thermal and electrical properties. Since phonons propagate quickly through the carbon bonds in each layer and are slow to travel between layers, graphite is expected to have high intralayer and low interlayer thermal conductivity values. On the other hand, graphite is a good electrical conductor due to its large electron delocalization between the carbon layers, which allows the valance electrons to move and conduct electricity. Therefore, the use of graphite in refractory and battery technologies has recently increased. Furthermore, graphene – a single sheet of graphite – is the best known heat conductor [3]. The thermal conductivity of graphene has been recently studied both theoretically [4,5] and experimentally [3,6], and a range of 100–5000 W/m K was reported depending on the size, temperature, and the method of the calculations [7]. Also, recent predictions on the thermal conductivity of few-layer graphene [8,9] show a reduction in the intralayer thermal conductivity values (350–850 W/m K) as a result of the transition of 2D graphene to the 3D graphite.

It has been known since 1924 that different stable atomic configurations of graphite layer stacking exist [10]. Past studies show that the composition of natural graphite is approximately 85% ABA and 15% ABC, and AAA stacking has only been observed in graphite intercalation compounds [11]. The ABA and ABC graphite stacking arrangements are shown in Figure 1. Although some studies have been previously performed on the electrical, thermal, and physical properties of graphite with different stacking arrangements [12–14], to the best of our knowledge, there has been no discussion on the effect of stacking arrangement on thermal conductivity predictions.

Molecular dynamics (MD) simulations are widely used to predict the thermal properties of nano-scale materials [15–17]. Equilibrium and non-equilibrium MD (EMD and NEMD) simulations are the two common approaches for the thermal conductivity calculations. Schelling et al. [18] studied and compared the features of each method, and they realized that NEMD might contain nonlinear effects due to the high temperature gradient applied to the system. Also, the effect of real interfaces results in size effects, which is more severe for systems with longer atomic mean free paths. Furthermore, the use of EMD with Green–Kubo (GK) relations [19] is beneficial for thermal conductivity calculations of symmetric nano-systems in that (1) no boundary scattering exists, and (2) predictions of the entire thermal conductivity tensor may be achieved with a single MD simulation. Therefore, in this study, the GK relation for thermal conductivity is used to predict the thermal conductivity of graphite with all three types of stacking arrangements. The domain size used in this study is limited to 5×5 nm due to computational restrictions, and therefore it must be noted that size effects on MD-based thermal conductivity predictions of carbon-based materials are unavoidable due to their large phonon mean free paths (e.g. ~700–800 nm for graphite) and complex phonon scattering processes [20–22]. It has been shown that even with domain sizes larger than the phonon mean free path the diffusive thermal conductivity of graphene might not be saturated [21].

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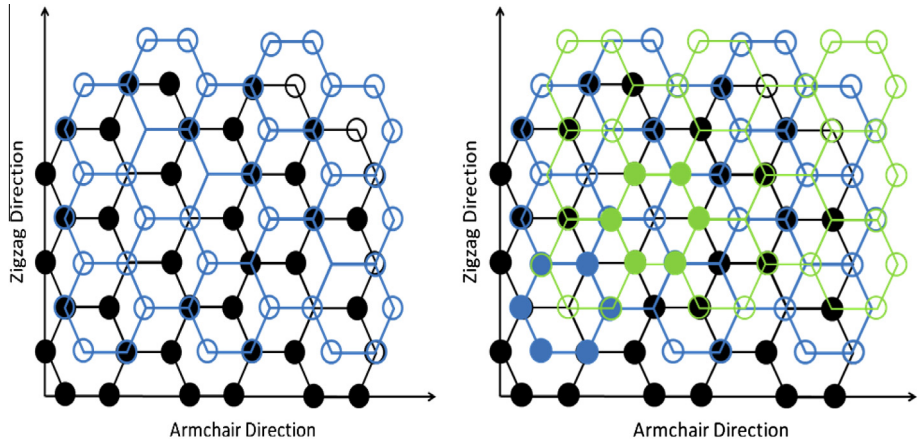

Figure 1. The atomic structure of two-layer ABA (left panel) and three-layer ABC (right panel) graphite. Black atoms belong to the first layer, blue atoms to the second layer, and green atoms to the third layer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this book.)

2. EMD method

The Green–Kubo formula for thermal conductivity takes the following form:

$$k_x = \frac{1}{\Omega k_B T^2}\int_0^{\tau}\langle j_x(t)\cdot j_x(0)\rangle dt \tag{1}$$

where k_x is the x component of the thermal conductivity tensor **K**, j_x(t) is a the x component of the heat current vector, $\vec{j}(t)$, k_b is the Boltzmann constant, Ω is the system volume selected as the area of graphene sheets times the inter-plane distance of graphite (0.335 nm) times the number of graphite layers, and T is temperature. The bracketed term is the heat autocorrelation function (HACF) and its decay to zero is required for thermal conductivity convergence when integrating to a final time τ Eq. (1) is written in the following discrete form:

$$k_x = \frac{\Delta t}{\Omega k_B T^2}\sum_{m=1}^{M}\frac{1}{N-m}\sum_{n=1}^{N-m} j_x(m+n)j_x(n) \tag{2}$$

where Δt is the simulation time step, N represents the total number of time steps of the simulation (after equilibrium), and M is the number of time steps for the correlation of heat flux vectors ($M\Delta t = \tau$).

3. Simulation details

In all the simulations of this study the optimized Tersoff potential is used to account for intralayer carbon–carbon interactions with the parameters proposed by Lindsay and Broido [23]. The general form of the Tersoff potential is as follows [24]:

$$\phi(r_{ij}) = f_c(r_{ij})[\phi^R(r_{ij}) - b_{ij}\phi^A(r_{ij})] \tag{3}$$

where $f_c(r_{ij})$ is the cut-off function, $\phi^R(r_{ij})$ and $\phi^A(r_{ij})$ are the repulsive and attractive parts of the potential, respectively, and b_{ij} is the three-body term. For the interlayer carbon–carbon interactions the Lennard–Jones (LJ) potential with the following form is considered to model the Van der Waals forces between graphite layers:

$$\phi(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{4}$$

where ε is the depth of the potential well, σ is the finite distance at which the pairwise potential is zero, and r_{ij} is the distance between atoms i and j. The parameters of the LJ potential (ε and σ) for graphite have been recently studied by various investigators [25–27] and all three sets of LJ parameters are examined in this study.

A three-body form of the optimized Tersoff potential poses a challenge in heat current vector determination because of the influence of the third atom in the potential energy calculations. However, Khadem and Wemhoff [28] have shown that the most accurate heat current formulation for graphene is the one proposed by Li et al. [29] containing the following form:

$$\vec{j} = \frac{1}{\Omega}\left(\sum_{i=1}^{n}\vec{v}_i\epsilon i + \frac{1}{2}\vec{r}_{ji}(\Delta\vec{F}_j\cdot\vec{v}_j - \Delta\vec{F}_i\cdot\vec{v}_i) - \frac{1}{2}(\vec{r}_{jk} - \vec{r}_{jk} - \vec{r}_{ki})(\Delta\vec{F}_k\cdot\vec{v}_k)\right) \tag{5}$$

where i, j and k are indices for the three particles interacting through the optimized Tersoff potential, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the interatomic separation, ε_i is total energy of particle, i, $\vec{v}_i$ is the velocity of particle, i, $\Delta\vec{F}_\alpha$, $\alpha = i,j,k$, are the force contributions to atom α from the ijk riplet, and $\vec{F}_{ij}$ is the force on atom i due to the interaction with atom j.

The velocity Verlet algorithm [30] was used to integrate the equations of motion. The simulations were performed at 300 K with a time step of 0.5 fs. Periodic boundary conditions were applied in all directions to mimic large dimensions of the graphite. The temperature was set by equilibrating under a constant temperature (NVT) using a Berendsen thermostat [31] for 5×10^5 time steps. After the system reached the desired temperature, the thermostat was turned off and the system relaxed at a constant energy (NVE) for another 5×10^5 time steps to mitigate the effects of velocity scaling via the thermostat. The NVE simulations continued after equilibrium for an additional 2×10^6 time steps (N in Eq. (2)) in the microcanonical ensemble to sample the heat current vectors. The HACFs are also calculated during this time and integrated for 10^5 (M in Eq. (2)) time steps (50 ps) to obtain the thermal conductivity values.

All graphite models in this study are 5×5 nm in size. Periodic boundary conditions are imposed in both zigzag and armchair directions of the layers to mimic an infinitely long domain size. Size effects for the models used in this study are negligible as reported by Schelling et al. [18]. Since it has been previously shown that the values of thermal conductivity saturate for more than four layers [8,32], six layers are considered to sufficiently resolve the effect of the number of layers in this study. It is also worthwhile to note that quantum corrections are not included in this study, since their effect was recently proved to be insignificant on the thermal conductivity of graphene when the system temperature is higher than 280 K [4].