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In-plane thermal conductivity of graphene nanomesh: A molecular dynamics study

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ABSTRACT

We have computed the thermal conductivity of the so-called graphene nanomeshes (GNMs) via the Green–Kubo method, employing molecular dynamics (MD) simulation method within a constant-(NVE) ensemble. Our results indicate that the thermal conductivity of GNMs is significantly reduced compared with that of pristine graphene so that GNMs may be promising materials in thermoelectric applications. Our simulations exhibit a decreasing behavior and the final convergence of the thermal conductivity as a function of periodicity for a given neck width. Furthermore, our results also show that the thermal conductivity of GNM decreases (increases) as a function of porosity (periodicity) for fixed periodicity (porosity). The effect of the neck width on the thermal conductivity is more pronounced than that of other parameters. It seems that phonon trapping occurs and that the group velocity of heat-carrying phonons decreases. The influence of the geometry of nanoholes on the GNM was also investigated and it was found that GNMs with triangle and square nanoholes, having the same area, offer the lowest and highest thermal conductivities, respectively.

1. Introduction

Understanding the physical properties of graphene has been the subject of intense interest and has led to many advances in the fields of nanoelectronics and thermal management ever since the pioneering works of Novoselov et al. [1]. Many potential engineering applications are foreseen for graphene in the realm of thermal management because of its excellent thermal conductivity properties [2–4]. Different forms of graphene have been studied for their novel and diverse applications in transistors [5], sensors [6,7], solar cells [8], antibacterial materials [9] and for energy storage [10]. Both ultra-high thermal conductivity for heat sinking applications [11–13] and ultra-low thermal conductivity for thermoelectric applications [14–16] are associated with this material. Due to strong in-plane sp^2 bonding and the low mass of carbon atoms, graphene has a high thermal conductivity along the in-plane directions [17]. Thus, graphene can be one of the best candidates for solving heat dissipation problems in micro/nano electronic devices [2,3]. In principle, the thermal conductivity and the electrical conductivity may be independent in semiconducting nanostructures since different length scales are involved with phonon and electric charges.

Electrical conductivity is less sensitive to a decrease in the nanostructure size [16]. Therefore, controlling materials independently of their electrical conductivity is a goal for researchers working on thermoelectric materials for use in energy applications [14]. Defects in the lattice, such as vacancies or Stone–Wales defects [18–20], chemical functionalization [21], strain [22], isotopic impurities (^{13}C) [23], substitutional defects [24] and edge roughness [13,25] can all lead to a reduction in the thermal conductivity of graphene by an order of magnitude below its intrinsic value. Also, grain boundaries in graphene cause the appearance of Kapitza resistance and thermal rectification [26,27].

Therefore, it is plausible that, purposeful engineering of defects can be utilized to accurately tune the thermal properties of graphene. Very recently, following the seminal work of Bai and co-workers on a new graphene nanostructure, referred to as *graphene nanomeshes* (GNMs) [28], it has been shown that this material has enormous potentials for various applications. Basically, a graphene nanomesh is a piece of graphene sheet containing a periodic array of nanoscale holes. The centre-to-centre distance between two neighbouring nanoholes is called the *periodicity*, and the smallest edge-to-edge distance between them

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is called the *neck width*, and these form the control parameters for the overall electronic properties of the GNM. Graphene nanomeshes have attracted a great deal of attention, owing to their wide ranging applications in the field of electronics and photonic devices, energy storage, sensors and anti-bacterial materials [10,29–31]. Akhavan and Ghaderi [32] have reported that the graphene nanomesh promises an extremely efficient material for in vivo photothermal therapy in treating cancerous tumours. GNM can be designed with different pore sizes and shapes to filter different gas molecules [33,34] and can also be used for hydrogen storage [35].

Hu [36] has reported that the thermal conductivity of GNMs is an exponential function of the neck width and is independent of the pore lattice arrangement and the pore edge passivation with H atoms for a given density and pore morphology. It is shown that the elastic modulus of GNMs with circular pores scales with the square of density [37]. Also, the thermal expansion of holes in GNMs contradicts the classical prediction [38]. GNM containing a specific hole can tune between metallic and semiconducting states, as well as a semimetal state [39]. Notwithstanding the illuminating insight obtained so far into the electronic properties of GNMs, their thermal properties, namely their thermal conductivities are, however, poorly understood [36].

Since at room temperature the contribution of electrons to the thermal conductivity of graphene is less than that of phonons, classical Molecular Dynamics (MD) simulation [40,41] has been applied to compute the thermal conductivity of graphene as phonons are associated with the displacement of atoms [20,42]. The goal of the present paper is to compute the thermal conductivity of GNMs and its dependence on the periodicity, porosity, neck width and the geometry of the holes.

The paper is organized as follows. In Section 2, the computational methodology and the simulation details for calculating the thermal conductivity of GNM are provided. Section 3 reports the simulation results. Finally, concluding remarks of our study are summarized in Section 4.

2. Computational methodology and simulation details

There are two MD-based approaches for the computation of thermal conductance, namely the equilibrium MD (EMD) and the non-equilibrium MD (NEMD) [43] methods. Thermal conductivities computed via NEMD are commonly smaller than the experimental results, but follow the same trend. EMD simulations have much smaller size-effect in contrast to NEMD, in which heat sources and sinks are employed that scatter phonons. Therefore, EMD is employed in this work. All simulations were carried out using the LAMMPS software package [44,45]. A previous study based on the Boltzmann transport equation has shown that the use of original Tersoff and Brenner potentials underestimate the thermal conductivity of graphene due to the inaccurate handling of phonon dispersion [42]. Therefore, the optimized Tersoff potential is employed in this paper to model the energetics and dynamics of graphene atoms. Equations of motion were integrated via the velocity Verlet algorithm [40] and the time-step of the simulation was set at 0.5 fs. Periodic boundary conditions were applied in-plane, in both the x and y directions to avoid the influence of the fixed walls, and the out-of-plane dimension of graphene was kept sufficiently large. Nose–Hoover thermostat [46,47] was applied to maintain the system at a constant temperature.

Before calculating the heat flux and its autocorrelation function, we first equilibrated each structure for 0.2 ns (400,000 time steps) within the constant-(NVT) ensemble, with the temperature kept at $T = 300$ K. Following equilibration, we turned off the thermostat and the simulation was carried out in the constant-(NVE) ensemble for another 1million time steps (0.5 ns). Ultimately, our simulations were continued in the NVE ensemble to calculate the in-plane heat flux vector $\vec{J}$ and the heat flux autocorrelation function $\langle \vec{J}(t) \cdot \vec{J}(0) \rangle$ for 3–10 ns, depending on the system size to obtain a converged thermal conductivity value. The heat flux vector was computed as [43]

$$\vec{J}(t) = \frac{1}{\Omega}\left\{ \sum_i \varepsilon_i \vec{v}_i + \frac{1}{2}\sum_{i,j,i\neq j} \vec{r}_{ij}(\vec{F}_{ij}\cdot\vec{v}_i) + \sum_{i,j,k} \vec{r}_{ij}(\vec{F}_j(ijk)\cdot\vec{v}_j) \right\} \quad (1)$$

where Ω is the system's volume calculated as the product of graphene's area and its thickness that is typically assumed to be equal to the graphite interlayer spacing, i.e., 3.35 Å [48], $\vec{v}$ and ε denote the velocity and energy of atom i, and $\vec{r}$ and $\vec{F}$ are the distance and the two/three-body interactions between the carbon atoms. The heat flux was recorded every 5 time steps (2.5 fs) to obtain the heat flux autocorrelation function.

The thermal conductivity was obtained via the Green–Kubo theory,

$$\kappa_{xx} = \frac{\Omega}{k_B T^2}\int_0^{T_m} \langle Jx(t)Jx(0)\rangle dt \quad (2)$$

where k_B is the Boltzmann constant and T is the temperature of the system. The bracket term denotes the heat flux autocorrelation function in the x-direction and the average is taken over the time origins. The integration is from zero to a cut-off time (T_m) which is determined by "first avalanche method" to discard the effect of noise [49]. The final result is the mean value of twenty realizations with different initial conditions. Analogously, we can obtain the thermal conductivity in the y-direction.

All of GNMs that we simulated were composed of regular periodic arrays of nanoholes, and the porosity was defined as the ratio of the volume of a nanohole to the volume of the supercell. The geometry of a typical GNM is shown in Fig. 1.

We investigated the influence of the nanoholes with different geometries, having the same area, as shown schematically in Fig. 2.

3. Simulation results

At first, we calculated the thermal conductivity (TC) of an approximately square graphene sheet without nanomesh. TCs were computed by averaging the integral of heat flux autocorrelation function (HFACF) curves from twenty uncorrelated NVE ensembles with different initial conditions. Our result for the thermal conductivity, i.e., 2710 ± 140 W/mK, is consistent with that

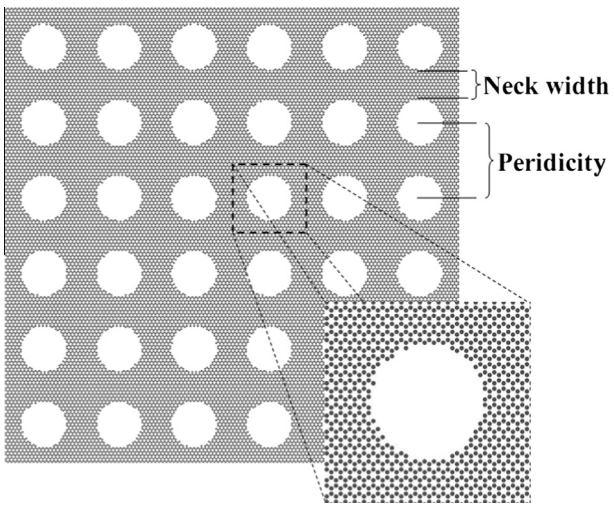

Fig. 1. Schematic representation of the atomic structure of a graphene nanomesh and its supercell.