Heat flow diversion in supported graphene nanomesh

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Redirection of energy carrier propagation by geometric confinement is studied through the analysis of in-plane and cross-plane thermal transport within various graphene nanomesh (GNM) configurations using molecular dynamics (MD) simulations. As the transport channel width decreases with an increase in porosity, the effect of redirection increases; thus, the in-plane thermal conductivity of large-porosity GNM is more dependent on hole arrangement. Since higher porosities weaken the GNM structure due to a larger population of broken bonds, carbon atoms within the graphene structures are more easily influenced by interactions with the substrate silicon (Si) block. Subsequently, increase in porosity leads to the decrease of interfacial thermal resistance. At higher porosities, lower interfacial resistance and in-plane thermal conductivity cause diversions (and redirections) in heat flow from the GNM to the underlying Si substrate. Our study suggests that this method of heat flow redirection can be applied as an effective means to control and manage heat transfer within numerous applications; extension to the improved conductivity calculation accuracy can also be achieved through the inclusion of this diversion analysis.

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1. Introduction

Since graphene’s first successful isolation [1], and the identification of its high electrical [2] and thermal [3,4] conductivity properties, these characteristics have made this novel material very promising for advancement and innovation within electronic applications [5–8]. Many research efforts have explored extensions of graphenes highly desirable attributes to more diverse and broader applications by manipulating its properties (e.g., boosting desirable and suppressing undesirable properties). Controlling thermal transport (i.e., direction and magnitude) is of great interest for energy conversion and electronic system design, with thermoelectric (TE) energy conversion being one such example of manipulation [9–12]. For optimal performance within TE devices, the reduction of thermal conductivity (k), while maintaining or enhancing the TE power factor (σsS2, σs: electrical conductivity and S: Seebeck coefficient), is critical. Moreover, the direction of heat transfer can be controlled by altering thermal transport properties; utilization of such methods can be employed to enhance heat dissipation [13].

Previous efforts to manipulate the thermal conductivity of graphene have emphasized the use of chemical approaches to introduce defects and/or functional groups as an avenue to control resultant thermal properties [14–18]. Defects increase phonon scattering to thereby suppress thermal transport; however, defects are difficult to control and their effect on thermal transport is reported to be minor when defect concentration is large [19,20]. Moreover, defects parasitically degrade other desirable properties (e.g., electrical conductivity in TE applications) [14]. Edge passivation [21], isotope engineering [22], strain [23], and grain boundary [17,24] have also been considered for thermal transport control; among the various methods, the technique of geometrically modifying or constraining a graphene sheet is suggested as one of the most feasible and affordable methods [25] to effectively control thermal transport [26]. The use of graphene nanomesh (GNM), which contains nano-sized periodic holes on a graphene sheet, is one such example representative of the application of geometric constraints towards effective thermal transport control [27,28]. Due to their tunable bandgap through adjustment of pore size and periodicity, GNM presents itself as an excellent candidate for thermoelectric energy conversion [29] and field-effect transistors [6,7,27,30], energy storage [31], as well as gas detection [32,33].
Recent studies utilizing molecular dynamics (MD) have primarily investigated free-standing GNM, whereas experimental studies and applications mainly employ GNM within supported/sandwiched form [27,32–34]. As the presence of a substrate is known to greatly influence thermal behaviors of single-layer graphene (SLG) and graphene nanoribbon in a dramatic way [12,35–39] studying GNM in a supported form provides more accurate insight to thermal transport behaviors within applications. In the study of supported GNM, Si is selected as a substrate material to achieve maximized heat diversion effect (due to its high thermal conductivity), and because of our continuing interest in Si-supported graphene [40] and wide engineering applications (e.g., detectors in aqueous environments [41], Schottky junction solar cells [42], and photonics [43]). Hole arrangement and porosity are controlled in suspended and Si-supported GNM; their effects on thermal transport, and the underlying physics of said effects, are examined.

2. Simulation methods

Periodic boundary conditions are applied in the y-axis direction, while fixed and free boundary conditions are used for the x- and z-axis directions (to avoid interactions between periodic cells), respectively. Here, x and y are in-plane directions, and heat flows in the x direction (Fig. 1a–c). A sample length (l in x direction) of 47.2 nm and a width (w in y direction) of 23.4 nm are selected to minimize lattice mismatch in Si/SLG heterostructures. The Si block length and width are of the same dimensions as the graphene sheet; the height of the Si block is 3.80 nm in the z-axis direction. Adaptive intermolecular reactive empirical bond order (AIREBO) [44] potential is used to model C–C bonded interactions, and the three-body Stillinger-Weber [45] potential is employed for modeling Si–Si interactions. Short-range van der Waals (vdW) interactions [46,47] between C and Si atoms are modeled by the 12–6 Lennard-Jones (LJ) potential, $\phi_{ij} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where $\epsilon$ is the minimum energy, $\sigma$ is the distance at which the intermolecular potential between the two particles is zero, and $r$ is the distance of separation between particles. The potential parameters used in our simulations are based on the vdW interactions in the universal force field (UFF) model by Rappe et al. [48]. All simulations were performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [49]; the total simulation time and time step size for all simulations are chosen to be 2.5 ns and 0.5 fs, respectively. In this work, reported results are the average of five independent simulations.

Two different arrangements of holes [square (SA) and zigzag (ZA)] are employed within this research (Fig. 1a and b). In each simulation, hole sizes are uniform and the radius ranges from 0 to 28.5 Å, while the hole center positions are fixed; thus, the porosity (of the simulation cell central region) is controlled up to 75%. With the maximum possible porosity being 78.5%, to avoid potential tearing and distortion of the graphene sheet structure, we select a porosity of 75% as the maximum investigated porosity size. With various hole arrangements and porosities, we investigate in-plane thermal transport in both stand-alone and Si-supported GNMs, as well as cross-plane transport in Si/GNM systems.

Thermal transport, characterized by conductivity and
conductance (or resistance), is evaluated by determining resultant heat flow and temperature distributions under non-equilibrium temperature settings [18,50,51]. Initial equilibration is performed for 0.5 ns in the NVT ensemble (constant number of particles, volume, and temperature) to rescale velocities to a prescribed temperature. After equilibration is complete, four layers of atoms are fixed at both ends of the structure (x- and y-axis directions); hot and cold Langevin thermostats are then applied next to these fixed regions so to generate a heat flux in the direction marked by arrows in Fig. 1a–c [21,25,51]. Thermal conductivity, $k$ (W/m-K), is calculated by using Fourier’s law, $q = -k \nabla T$, the heat flux from the hot to the cold region, $q$ (W/m$^2$), and the resulting temperature gradient, $\nabla T (=dT/dx$ in 1D transport). $q$ is the average heat addition/removal by the thermostats per unit cross-sectional area over a time span of 2.0 ns. For the cross-sectional area, the thickness of single-layer graphene is selected as the inter-layer spacing of graphite (0.335 nm [52]). In the determination of $\nabla T$, local temperature is calculated from the ensemble average of local atomic energy over a sufficient period of time (1.0 ns) so to minimize noise within temperature distributions. Considering stimulating effects and temperature dependences on thermal transport, the linear portion near the prescribed $T$-value of the temperature profile is selected for our analyses.

In order to calculate the thermal conductivity of graphene with a Si substrate, hot and cold thermostats are separately placed on both graphene and Si as in Fig. 1c. In addition to using thermostat heat flow ($q_{\text{fl}}$), heat flow along the graphene sheet and Si block is obtained from the ensemble average of the x component of heat flux ($q_{\text{fl},x}$), which is given by Ref. [52].

$$q_{l,x} = \frac{1}{V} \left[ \sum_{i} 2 m_i (u_i \cdot \partial u_i) | u_{ix} | + \sum_{i} q_i | u_{ix} | + \frac{1}{2} \sum_{i} \sum_{j} x_{ij} | (u_i \cdot F_{ij}) | \right],$$

(1)

where $V$ is the volume, $m_i$ is the mass of particle $i$, $u_i$ is the velocity vector, $u_{ix}$ is the x component of $u_i$, $q_i$ is the potential energy, $x_{ij}$ is the x component of the interatomic separation ($r$), and $F_{ij}$ is the interaction force between $i$ and $j$ particles. To estimate the separate contributions of phonon modes to thermal transport, either the x and y components of vectors (for the in-plane contribution) or only the z components (for the out-of-plane contribution) are included in heat flux calculations (Eq. (1)). To illustrate local heat flow direction and magnitude (Fig. 6a–d), we divide the simulated GNM into small groups of atoms creating a 50×50 mesh grid (Fig. 2a) to capture all geometrical and heat flow details, as well as to ensure sufficient number of atoms for the statistically meaningful heat flux calculations. To find an appropriate mesh size, we tested different grid dimensions and calculated temperatures of hole edge cells with the smallest number of atoms ($T_{\text{cell}}$), which has potential for the largest deviations from a prescribed, overall temperature ($T_0$). The difference between selected cell and overall equilibrium temperature of a sample ($T_{\text{cell}} - T_0$) decreases as the mesh size and number of atoms in the cell increases; ultimately, this difference reaches almost zero when the cells contain a sufficient number of atoms for thermal analysis (Fig. 2b). The local heat flux vector is determined by applying Eq. (1) every time step and is averaged for 2.5 ns.

Cross-plane thermal transport across the GNM/Si interface is investigated by means of the temperature relaxation method [53,54]. The GNM/Si system is first equilibrated at 300 K; hot and cold thermostats at 350 K and 250 K are then respectively placed on the GNM and Si block in the NVE ensemble. After reaching steady-state, the thermostats are then removed to allow for thermal relaxation of the simulated structure. During this thermal relaxation period, temperature and energy changes of GNM and Si block are recorded; the interfacial thermal resistance, $R$ (K/W) can be obtained by Refs. [53,55,56].

$$R = \frac{\int_0^t (T_{\text{GNM}} - T_{\text{Si}}) dt}{E_t - E_0},$$

(2)

where $E_t$ is the total energy of the supported graphene, $E_0$ is the initial energy of GNM at the beginning of relaxation period, $A$ is the thermal transport interface area, and $T_{\text{GNM}}$ and $T_{\text{Si}}$ are the GNM and Si temperatures.

In order to identify phonon behaviors within thermal transport of the GNM/Si system, phonon density of states ($D_p$) is calculated through the Fourier transform of the velocity autocorrelation function [57]. In addition, atomic density distribution ($\rho$) is determined as a representative parameter for the average distance between GNM and Si layers; this is performed by averaging the number of particles per unit volume during the temperature relaxation stage of simulations.

3. Results and discussion

3.1. Suspended GNM

In MD, with a non-equilibrium temperature setting for in-plane thermal conductivity, the heat transfer path is comparable to the mean free path (MFP, 240–750 nm in graphene [45,58]) of thermal energy carriers, i.e., phonons. Thus, the resulting thermal conductivity depends on the size of the simulation domain [59]; the thermal conductivity size dependence of pristine graphene has been extensively studied in our previous research [40]. The size dependence of GNM is also examined by comparing thermal conductivities from MD with two different porosities ($\zeta$ = 20% and 56%), and three different dimensions of simulation domain (1/2, 1, and 2l). As Fig. 3 demonstrates, although MD thermal conductivity of GNM increases with simulation domain size, it is much less sensitive to sample length (i.e., the length dependency is reduced) as porosity increases, which is attributed to an increasing dominance of boundary/edge scattering.

The in-plane thermal conductivity ($k_{\text{GNM}}$) significantly decreases with increasing porosity in both hole arrangements, as shown in Fig. 4a. This reduction of thermal conductivity, by increasing porosity, is more significant for larger samples due to a smaller size dependence at higher porosities (Fig. 3). This resulting porosity dependency is much greater than predictions made by a classical (Eucken) model, where the ratio of thermal conductivity of a material with porosity ($\zeta$), $k_{\text{GNM}}$, to its non-porous counterpart (same size GNM without pore, $k_{\text{GNM,mp}}$), is given by $k_{\text{GNM}}/k_{\text{GNM,mp}} = (1 – \zeta)/(1 + \zeta/2)$ [60]. This classical model is developed based on the premise that a subject system is within the continuum (diffusive) regime, where system dimensions are much larger than the MFP, to allow for the Fourier’s law-based assumption of constant thermal conductivity within a system. However, as transport channels (or neck sizes) in GNM are smaller than that of graphene MFP, ballistic size-dependent thermal transport (i.e., conductivity decreases as size decreases) induces excessive reduction of overall thermal conductivity [61]. Thermal conductivities of both hole arrangements are very similar to each other when their porosities are small (< 20%); however, their difference is seen to increase with increasing porosity as in Fig. 4b. With a porosity of 75%, the thermal conductivity of the zigzag arrangement is found to be roughly half of that determined within the square arrangement. In consistency with another study [28], this implies that phonons within a narrowed channel due to a higher porosity are more influenced by hole
arrangements. As hole edges appear on the path of phonon propagation, whose direction is limited by channel width, scattering is more frequent within the zigzag arrangement.

According to previous research [62], the high thermal conductivity of suspended SLG is attributed to a larger density of states at lower energies and lower phonon scattering rates of out-of-plane phonon modes, which produces the dominant contribution (more than 77%) made to the in-plane thermal conductivity of suspended graphene. Our relative thermal conductivity calculations of in-plane and out-of-plane phonon modes (Fig. 4c and d) also confirms the importance of out-of-plane phonon contributions to the in-plane thermal transport of defect-free SLG. However, the relative influence of out-of-plane phonons ($k_c/k_{GNM}$) is found to decrease as porosity increases; due to a longer phonon-phonon scattering MFP [63], pore induced phonon scattering more significantly obstructs the out-of-plane modes, and thus, reduces the total thermal conductivity.

For both hole arrangements, as relative contribution of temperature dependent phonon-phonon interactions to overall phonon scattering decreases with porosity, the temperature dependence of thermal conductivity is less significant at larger porosities. Without pores (defect-free, upper line in Fig. 5a), $k$ decreases with temperature. However, this negative temperature dependence is alleviated as porosity increases; eventually, positive temperature dependence begins to emerge at a porosity of 50% (Fig. 5b) as the thermal conductivity peak (Umklapp peak) moves towards higher temperatures at larger porosities.

Fig. 6a and c demonstrate the in-plane projection of local heat flux vectors in the two different hole arrangements under identical simulation conditions (hole radius of 25 Å and porosity of 56%). Although both cases share similar temperature distributions due to identical temperature settings, the square arrangement (Fig. 6a) shows a larger number of high-magnitude heat flux vectors than the zigzag arrangement (Fig. 6c); the average heat flux of the zigzag arrangement is roughly 76% of that determined for the square arrangement. Analysis of local heat flux vectors in polar coordinates illustrates that higher magnitude heat flux vectors are primarily concentrated within an approximately 30° difference from the heat flow direction (0°) in the square arrangement (Fig. 6b). Contrarily, GNM with zigzag hole arrangement (Fig. 6d) has a wider angular distribution of heat flux vectors and a lower centralized density of higher magnitude vectors; this confirms the lower net heat flux in the x-axis direction than of that found in the square arrangement. Geometric constraints in the zigzag hole arrangement impose more frequent scatterings to phonons possessing wave vectors that align with the heat transfer direction (−30° ~ 30°); thus, contributions from these phonons will be suppressed, reducing the net heat flux as well as thermal conductivity.

3.2. Supported GNM

Due to additional scattering and loss of reflection symmetry (which significantly restricts the phase space for phonon-phonon scattering of z-axis direction phonons [64]) caused by the presence of a substrate, thermal conductivity of the supported graphene sheet is reduced to approximately 10% of that determined for suspended graphene ($k_{sus}$). This conductivity reduction caused by the presence of a substrate decreases as porosity increases. In other words, the ratio of supported GNM conductivity to suspended at the same porosity, $k_{sup}/k_{sus}$ linearly increases for GNM of both hole arrangements as shown in Fig. 7a ($k_{sup}/k_{sus} \sim 0.6$ at $\zeta = 76\%$). This
indicates that the effect of substrate-induced scattering becomes less dominant in supported GNM with a higher porosity due to larger scattering rates caused by geometric constraints. In addition, Fig. 7b, where porous GNM thermal conductivity is compared with
non-porous graphene under the same conditions (substrate and porosity), conveys that the porosity dependence of thermal conductivity (i.e., decreasing $k$ with increasing $\zeta$) is less significant in supported GNM systems than in suspended cases. As the influence is shared by both geometric constraints (holes) and substrate effects, each of these influences becomes weakened. We note that as in suspended systems, SA is still found to possess a higher conductivity than ZA in supported configurations.

Porosity also influences thermal transport across the interface of Si/GNM systems. As porosity increases, the GNM/Si system reaches thermal equilibrium at a lower equilibrium temperature and at a quicker rate than systems with lower porosities (Fig. 8a). Despite area ($A$) reduction by increased porosity, interfacial thermal transport ($R, K/W$), calculated from the temperature relaxation method with Eq. (2), is shown to decrease (Fig. 8b); i.e., areal resistance ($R', m^2\cdot K/W$) decreases more quickly than the decrease in area. Here, hole arrangement does not affect cross-plane thermal transport.

This enhancement to cross-plane transport within high-porosity GNMs is attributed to an increased strength of interactions between the Si and carbon atoms, stemming from a reduction in interfacial distance between Si and GNM. Carbon atoms in non-porous graphene are constrained by three C–C (sp$^2$) bonds, while edge atoms are connected with one or two neighboring atoms. As porosity increases, a larger fraction of these atoms are located at hole edges with dangling bonds; in turn, this causes GNM structures to become less rigid and more susceptible to deformation by van der Waals forces. Thus, the average distance between Si and GNM decreases with increasing porosity, and is described by the atomic density distribution in Fig. 8c. Since vdW interactions become stronger at shorter distances, this reduction in interfacial distance leads to the expectation of stronger interactions across the interface and thus, lower interfacial resistances [65–67]. In addition, the increasing size of the near-zero peaks in $D_p$ (Fig. 8d), which have a longer

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**Fig. 6.** In-plane local heat flux distribution. (a) Heat flux distribution in the square hole arrangement GNM with hole radius of 25 Å. (b) Magnitude/angle distribution of the in-plane heat flux vectors within the square hole arrangement. (c) Heat flux distribution in the zigzag arrangement GNM with hole radius of 25 Å. (d) Magnitude/angle distribution of the in-plane heat flux vectors within the zigzag hole arrangement. (A colour version of this figure can be viewed online.)
wavelength and higher transmission across interface [68,69], enables for lower interfacial thermal resistance, and evidences the emergence of stronger interactions between Si and GNMs [40].

Since the nanomesh (porous) structure is locally included within...
our simulated systems, thermal conductivity is spatially distributed and the variation of thermal resistance ($\tau \sim 1/k$) produces a diversion in heat flux to the substrate. Reduction of interfacial thermal resistance, via increase in porosity, enhances this process. Due to heat redirection to the substrate, the heat flux at both thermostated ends ($q_T$, obtained from recorded thermostat heat exchange data) is larger than that of the central porous region [$q_{f,x}$, calculated from averaged heat flux in the x-axis direction using Eq. (1)]. This heat redirection is shown schematically in Fig. 9, demonstrating two possible paths for heat to flow; the first path is without heat leakage to Si and along the GNM, and the second path is heat leakage and reaching the cold thermostat through the Si block. The resistance of the first path is synonymous with thermal resistance of the GNM and can be calculated from its thermal conductivity ($R = 1/kA$). When heat flow leaks to the substrate, as in the second path, interfacial thermal resistance (Fig. 8b) and thermal resistance of the Si block are included in total resistance of the path. The thermal resistance of the first path displays an increase as porosity increases, while the resistance of the second path is shown to decrease with increasing porosity; thus, a higher porosity leads to a larger mismatch between $q_T$ and $q_{f,x}$ (i.e., larger heat leakage) as Fig. 9 shows.

4. Conclusions

Propagation of thermal energy carriers is redirected by geometrical confinement on graphene (hole arrangement and size); this redirection of heat flow is shown to effectively control thermal transport. The transport channel scale (width) in GNMs is critical to resultant variations of in-plane thermal transport as: 1) nanoscale channel size and hole pitch less than the phonon mean free path induce ballistic transport between holes and promote porosity dependence of conductivity, and 2) smaller channel widths, as found within larger porosities, more significantly confine the direction of thermal carrier propagation (more aligned with channel direction), thus magnifying the effect of hole arrangement (different conductivities of GNMs with ZA and SA). Although additional scatterings caused by the GNM supporting substrate do not change the tendencies of conductivity variation by porosity and arrangement, their influences on in-plane transport are weakened by diversified scattering mechanisms. Contrarily, GNM porosity is shown to greatly affect cross-plane transport as interfacial thermal resistance decreases with increasing porosity. This is in spite of a decreasing area available for thermal transport to take place; as the average atomic distance between the substrate and GNM is reduced due to structure weakening from broken bonds near holes, the strength of vdW interactions increase between the two layers. With increasing porosity of supported GNM, we observe heat leakage to the substrate stemming from decreases of in-plane conductivity and cross-plane thermal resistance; considerations should be given to this diversion of heat flow within conductivity measurements and simulations for improved accuracy. This study presents an effective means to control heat flow direction and magnitude, in addition to accurate prediction of thermal transport results; these findings have possible extension to enhanced thermal system design and evaluation of electronics.

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