Thermal transport engineering in amorphous graphene: Non-equilibrium molecular dynamics study

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A B S T R A C T

Thermal conductivity of amorphous graphene was investigated using non-equilibrium molecular dynamics (NEMD) method for structures with different defect concentrations (up to 54%) and under various tensile strains (up to 0.12). Although the sensitivity of amorphous graphene to the imposed strain was found to be lower than that for single crystalline graphene, it was observed that the thermal conductivity decreases for both structures by increasing the strain. By considering hybrid pristine/amorphous graphene coplanar structure, the influence of defects distribution on thermal transport was investigated and it was shown that there exists no clear sign of Kapitza thermal resistance at their interface. The effect of temperature (300–700 K) on the thermal conductivity of amorphous and single crystalline graphene was also studied. It was observed that the variation of thermal conductivity with temperature for single crystalline graphene is more considerable than that of amorphous graphene. We finally discussed the underlying mechanism for thermal conductivity suppression in amorphous graphene by calculating the atomic bond length and phonon power spectra.

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1. Introduction

Graphene [1] is known as one of the most important carbon allotropes with extremely high thermal conductivity about 4000 W/m K [2,3]. Due to its outstanding mechanical [4], thermal [5] and electrical [6] properties, it has attracted attentions due its potential applications from nano/micro-electronics to the aerospace. Strong C—C bonds and low atomic mass of carbon are considered as reasons for high thermal conductivity of graphene, diamond and nanotubes [7]. In experiment, graphene sheets are not generally pristine and have various defects which can dramatically influence their thermal, mechanical and chemical properties [8–10]. Defect types are generally mono vacancy, double vacancy, Stone-Wales, imperfection, grain boundary and dislocation [9,11]. Although defects have negative effect on thermal transport, but engineering them can tune the thermal conductivity of nanostructures which is important in thermoelectric applications [12,13]. Chen et al. [14] controlled thermal properties of graphene by doping specific percentages of carbon isotopes into the graphene sheet and Mortazavi et al. [15] did the same by doping nitrogen atoms.

Amorphous or disordered structure graphene is a type of defective graphene. Recently it has been shown that, amorphous graphene can be synthesized by focused ion beam converting ordered hexagonal arrangement of graphene cells to stochastic and disordered polygonal ones [16]. This new structure has opened a new window in potential applications of graphene in nano-electronics and chemical sensors [13]. Recently, Mortazavi et al. [17] have studied thermal properties of amorphous graphene with various defect percentages employing equilibrium molecular dynamics (EMD). They showed that, the thermal conductivity of amorphous graphene could be two orders of magnitude lower than that of its single crystalline structure. However, they considered periodic boundary conditions in their simulation and one has to be cautious when impose artificial length to an amorphous material that does not have translational symmetry unlike crystals [18].

Strain is one of the external parameters that could be used in tuning the thermal [19,20] and mechanical [17,21,22] properties of graphene as well as other nanostructures [23–27]. Bonini et al. found that the strain is a key factor in engineering the thermal transport of free-standing graphene by using first-principles methods [28]. Pereira and Donadio employed equilibrium molecular dynamics and Kuang et al. utilized the first-principles calculation accompanying solving Boltzmann–Peierls transport equation to show that applying strain could eliminate the out-of-plane modes

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in graphene and makes it an ideal 2D structure with divergent thermal conductivity with respect to system size [29–31].

Guo et al. studied the thermal conductivity of graphene with NEMD method and showed its remarkable dependency to the applied uniaxial strain [32]. Wei et al. [33] investigated the effect of strain in both armchair and zigzag directions of graphene. They showed that, due to phonon softening, the thermal conductivity of graphene under tensile strain decreases. Wu et al. [34] investigated the effect of strain on polycrystalline graphene with 2.5–12 nm grains sizes using NEMD simulation. They observed that the thermal conductivity of a pristine sheet decreases with increasing the strain whilst the polycrystalline graphene was less sensitive to the imposed strain and this sensitivity decreases with decreasing the size of the grains. They used AIREBO potential function to describe atomic interactions.

In this investigation, we explore the engineering of the thermal transport along amorphous graphene structures through employing the mechanical strains. To do so, we carried out extensive NEMD simulations using the optimized Tersoff potential function for introducing the atomic interactions. In our modeling, we applied non-periodic boundary condition in the direction of established heat flux. This boundary condition prevents artificial length effect and such that it is more consistent with amorphous graphene's heat carriers studied in an earlier work [17]. Defect concentration of the amorphous graphene structures was considered to be considerably high, up to 54% and we also applied strain levels till 0.12 in both planar directions. We additionally examined the structures with homogenous and composite defect configurations. In the composite structures, the defects are considered only in a specific section of the system, resulting in the construction of the heterostructures consisting of the both pristine (defect-free) and amorphous graphene. The effect of temperature on the thermal conductivity of pristine and amorphous graphene with various defect concentrations are also investigated. Finally, we calculate the phonon spectrum of the constructed samples in order to discuss the underlying mechanism of the heat transfer in amorphous graphene structures. The insight provided by this study can be useful to guide the experimental fabrication of amorphous graphene heterostructures with tunable thermal conduction properties.

2. Molecular dynamics simulation

In this research, all molecular dynamics simulations were done by LAMMPS package [35]. The accuracy of the predicted properties is highly dependent to the accuracy of the potential functions. In this study, carbon atoms interactions have been modeled using optimized Tersoff potential function developed by Lindsay and Brodio [36]. The optimized Tersoff potential function can better predict phonon dispersion relation compared to those predicted by an old version of Tersoff [37,38]. Recent simulations show that, among all force-fields which have been used in molecular dynamics simulation of graphene, the optimized Tersoff potential function is the best choice for balancing between precision and computational time at the same time [7,29,39,40].

In order to generate atomistic models of amorphous graphene structures, an algorithm developed in which the density of defects can be variable but more controllable compared to other quenching methods [41,42]. In this algorithm, Stone-Wales defects are only created in which neither an atom is added nor eliminated [9,43–45]. A single Stone-Wales defect can be generated just by rotating a C—C bond 90 degrees in which four carbon hexagons turn into two pentagons and two heptagons. Stone-Wales defects have been spread out randomly over a pristine sheet but the periodicity of the structure still remains unchanged [45]. According to Ref. [16] which was experimentally done and supported with first-

principles calculations, the random arrangement of polygons has sp^2 hybridization and the amorphous graphene is a 2D material with one-atom-thick flat carbon atoms. The utilized model exactly follows the experimental structure and the MD potential function preserves the structure very well. In this study, defect concentration is defined as the ratio of non-hexagons in an amorphous structure to all hexagons in the initial pristine sheet. After generating amorphous structure with various defects, they have been relaxed and equilibrated using molecular dynamics simulations. Fig. 1(a) shows an amorphous graphene sample with 54% of defect concentration. The radial distributing functions (RDF) of both pristine and amorphous graphene have been shown in Fig. 1(b).

It worth mentioning that thermal transport in amorphous materials has differences and complexities compared to crystalline materials and their vibrational modes are categorized into three regimes: propagons with low frequencies, diffusons with intermediate frequencies and locons with high frequencies [46]. It has been shown that the contribution of diffusons in thermal transport and vibrational spectrum of amorphous materials is major [47]. Therefore low frequencies in amorphous materials have lower contributions in the thermal conductivity compared to crystalline materials and using NEMD approach for finite lengths is appropriate for investigating the heat transport in amorphous materials [48].

In this study, samples sizes are 30 nm × 30 nm with average defects varying from 1 to 54%; structure have been relaxed for 100 ps in NPT ensemble using Nose-Hover thermostat at 300 K. Molecular dynamics model evaluating the thermal conductivity has been shown in Fig. 2. Timestep is equal to 0.1 fs and non-periodic frozen boundary condition is applied in X-direction, while periodic boundary condition has been imposed in Y-direction.

In order to calculate the temperature profile of the system, we have divided the simulation box into 30 slabs in X-direction (except fixed atoms at both ends). In the next step, two different temperatures were imposed to the first and the thirtieth slabs. The temperature of the first slab (hot bath) and the thirtieth slab (cold bath) were set on 320 K and 280 K respectively employing NVT ensemble and all other slabs under NVE ensemble. In Fig. 3a which belongs to the amorphous graphene with defect concentration of 30%, the steady state temperature profile of the system
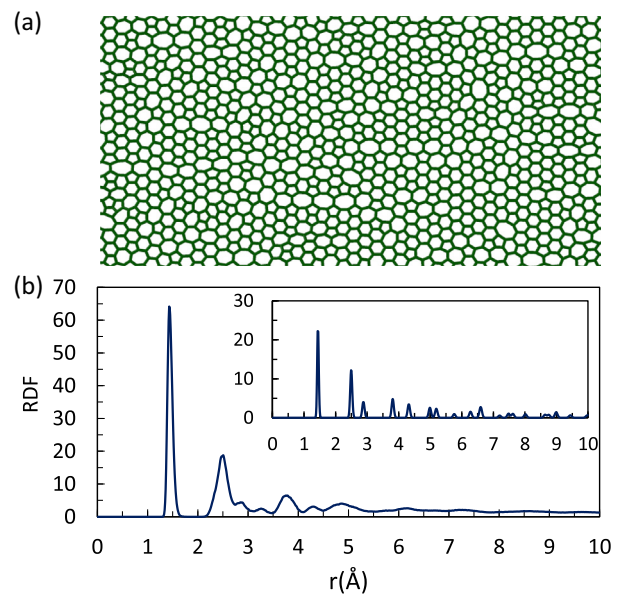

Fig. 1. Atomic positions of amorphous graphene with defect concentration of 54% (a). The radial distribution function for amorphous graphene (b) at room temperature in comparison to crystalline pristine graphene (see the inset).