Significant reduction of graphene thermal conductivity by phononic crystal structure

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ABSTRACT

We studied the thermal conductivity of graphene phononic crystal (GPnC), also named as graphene nanomesh, by molecular dynamics simulations. The dependence of thermal conductivity of GPnCs (κ_{GPnC}) on both length and temperature are investigated. It is found that the thermal conductivity of GPnCs is significantly lower than that of graphene (κ_G) and can be efficiently tuned by changing the porosity and period length. For example, the ratio κ_{GPnC}/κ_G can be changed from 0.1 to 0.01 when the porosity is changed from about 21% to 65%. It is also shown quantitatively that there are more states available for Umklapp three-phonon scatterings in GPnCs. The phonon participation ratio spectra reveal that more phonon modes are localized in GPnCs with larger porosity. Our results suggest that creating GPnCs is a valuable method to efficiently manipulate the thermal conductivity of graphene.

1. Introduction

As collective lattice vibrations, phonons are responsible for the heat conduction in semiconductors and dielectric materials. Management of phonons provide advances in thermal devices, such as thermal diodes which could control heat flow in a preferred direction [1–3], thermal cloaking which could hide objects from heat [4–7], thermocrystals which could manipulate heat by phonons [8], and thermoelectrics which could convert heat into electricity directly or be used as Peltier refrigerator [9–11].

The graphene has been widely studied because of its fascinating properties. It has extremely high thermal conductivity [12,13], which is very useful in heat dissipation of electronic devices. Moreover, because the contribution to thermal conductivity mainly comes from phonons [12–14], the thermal conductivity of graphene can be manipulated by phonon engineering, such as the size confinement [15,16], defect scatterings [17,18], boundary

and junctions [19,20], inter-layer couplings [21–23], foldings [24,25], mass loading [26], and phononic crystals [27–29]. Therefore, graphene is a promising candidate for phononic engineering devices.

When the period length decreases to nanometers, the transport of phonons in phononic crystals (PnCs) will be affected [30–36]. Due to the periodic change of the density and elastic constant, PnCs could exhibit phononic band gaps at high frequencies [37]. PnCs could also have boundary scatterings [30] and phonon localizations [31] which could block high-frequency phonons. This remarkable property is very different from those of traditional materials, and allows PnCs to achieve new functionalities. In recent years, much work has been done to utilize the unique properties of PnCs for thermal applications. It is reported that silicon nanomesh [38], silicon by PnCs patterning [39], nanoporous silicon [40] and isotopic silicon PnCs [37] have very low thermal conductivity but maintain sufficient electrical properties [38] which is favorable for thermoelectric applications.

Recently, a graphene PnC (GPnC) also named as nanomesh, a single layer graphene with periodic holes, has been fabricated [27–29]. The process of fabricating graphene nanomesh is improved a lot recently. The combination of holography lithography and O_2 plasma etching method has been developed to create

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large area graphene nanomesh in recent work [41]. Other methods such as CVD growth of graphene nanomesh on nanostructured substrate [42] and fabrication of graphene nanomesh by block copolymer lithography [27,42] are also reported. It is reported that GPnCs could open up a conduction bandgap in graphene and the on–off ratio of the GPnC as a field-effect transistor can be tuned by varying the neck width [27]. Graphene phononic crystal can be modified as metallic or semimetallic depending on the geometry of the surface of porous [43]. Theoretical study has shown that Bragg scatterings can lead to a dramatic change in the thermal conductivity of GPnCs, κ_{GPnC}, with a very small feature size (7.5 nm in period length) [44]. However, the experimental fabrication of graphene with such small period is still challenging. The neck width observed in the previous experimental study of nanomesh graphene [27] is 5–15 nm, corresponding to the period length about 25–75 nm with porosity of 50%.

In this work, we studied the thermal conductivity of GPnCs using nonequilibrium molecular dynamics (NEMD) method. The period length of GPnCs is varied from 10.4 nm to 62.5 nm which could be fabricated in experiment [27]. The dependences of thermal conductivity on both length (L) and temperature (T) are studied. Moreover, the porosity is tuned from 0.0041% to 66% by varying the diameter (D) of holes, and its impact on the thermal conductivity of GPnCs is investigated. Vibrational eigen-modes analysis reveals that the phonon modes localization in GPnCs is enhanced at large porosity.

2. Structure and method

The structure of GPnC is a single layer graphene embedded with periodic circular holes, which is characterized by period length L_0 and diameter D. Neck width corresponds to L_0–D. The same L_0 is used in the longitudinal and transverse direction. Fig. 1(a) shows a simulation cell with 5 periods in longitudinal direction and 1 period in transverse direction, where $L_0 = 25$ nm and $D = 15$ nm.

The periodic boundary condition is used in transverse direction and the fixed boundary condition is used in longitudinal direction. Optimized Tersoff potential is applied to describe the C-C interactions, which can better describe the lattice properties of graphene [45]. A temperature gradient is established along the longitudinal direction by applying Langevin heat bath [46] at the two ends (boxes in Fig. 1(a)).

The equations of motions are integrated by velocity Verlet method with a time step of 0.5 fs. In the beginning, simulation runs 0.6 ns to reach a steady state by applying heat baths with high temperature at left end and low temperature at right end. Then the simulation runs 7 ns to get an averaged heat current and temperature profile. The thermal conductivity is calculated from Fourier's law

$$\kappa = -\frac{J \cdot L}{A \cdot \Delta T} \tag{1}$$

where J is the heat current, L is the length of the simulation cell, ΔT is the temperature difference and A is the cross section area. $A = W \times 3.4$ Å, where W is the width and 3.4 Å is the graphene inter-layer distance [17,47,48]. Another method is used to calculate the thermal conductivity in Ref. [38]. Instead of using the cross section area A, they use the reduced cross section area $A_{reduced}$, $A_{reduced}$ = neck width × 3.4 Å, by assuming that the heat flows equivalently in the necks along longitudinal direction. The values calculated by the method in Ref. [38] will give the upper bound value of thermal conductivity in phononic crystal. We also calculated the thermal conductivity with reduced cross section area (κ_{GPnC}^{up}) which is shown in Fig. 3. The final result is the mean value of twelve realizations with different initial conditions. The error bar is the standard deviations of the results of 12 simulations. As the
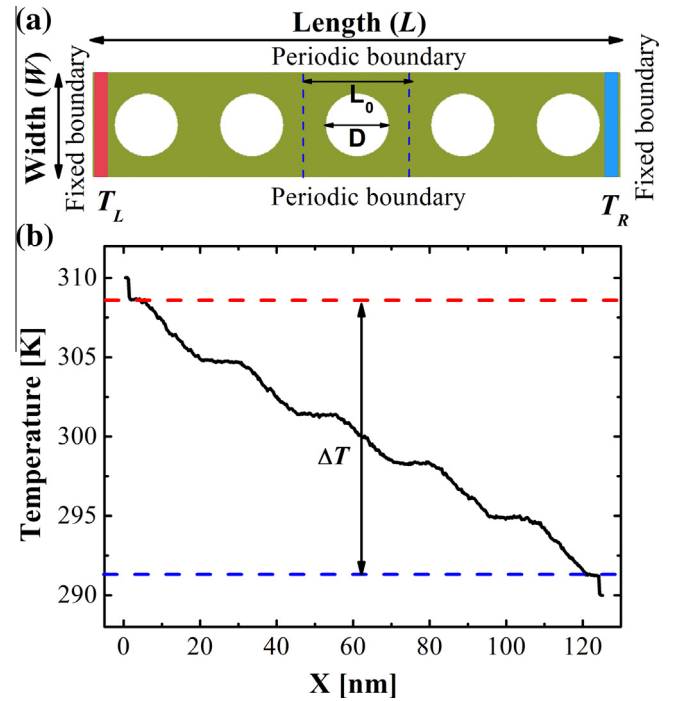

Fig. 1. (a) Simulation setup and structure of GPnC with periodic circular holes. L_0 is the period length, L is the length of simulation cell, and D is the diameter of the hole. The same L_0 is used in the longitudinal and transverse direction. $L_0 = 25$ nm, $D = 15$ nm and $L = 125$ nm in (a). Periodic boundary condition is used along transverse direction and fixed boundary condition is used in longitudinal direction. Heat bath with higher temperature (red box) T_L and lower temperature (blue box) T_R are applied at two ends. (b) Temperature profile of simulation of GPnC in (a). Temperature of two heat baths is set as $T_L = 310$ K and $T_R = 290$ K. There are boundary jumps at the two ends. Temperature difference ΔT is between the two dash lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in-plane heat transport in graphene is isotropic, the thermal conductivity is the same in zigzag and armchair direction [21,49,50]. Only zigzag graphene and zigzag GPnCs are studied in this work.

In Fig. 1(b), we show the temperature profile of a simulation cell. The temperatures at two ends are set as $T_L = 310$ K and $T_R = 290$ K. Heat bath region is the region where the heat bath is applied; buffer region is the region which is used to exclude the nonlinear effect from the heat bath. The heat bath region is set as 0.74 nm. Based on the temperature profile in Fig. 1(b), the buffer region is around 4.2 nm in width. Both the heat bath region and buffer region are excluded in the calculation of temperature difference. There are temperature jumps at the two boundaries due to the couplings with heat baths. The ΔT is defined as the temperature difference between the two dash lines, which excludes the temperature jumps next to heat bath.

3. Simulation results

The size effect could arise if the simulation cell is not sufficiently large in the transverse direction [51]. Based on the period length $L_0 = 25$ nm and length $L = 125$ nm, we examined the thermal conductivity dependence on the width of simulation cell. The thermal conductivities of GPnC with the width one period and two periods are 143.05 ± 2.84 and 143.09 ± 1.33 W/m-K at room temperature, respectively. That is, one period in transverse direction is enough to get a saturated thermal conductivity. In the following simulations, we choose one period in transverse direction in all simulation cells of GPnCs.

Along the heat transfer direction (longitudinal), the thermal conductivity depends on the length of material in nanoscale.