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Co-existing heat currents in opposite directions in graphene nanoribbons

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ABSTRACT

Using molecular dynamics simulations, we create an unprecedented scenario in graphene nanoribbons: co-existence of two heat currents in opposite directions at the same location. One heat current is carried by flexural mode phonons, and the other one by transverse/longitudinal modes phonons in the opposite direction. The local apparent thermal conductivity (κ_{app}) varies in a very large range: −468 to 1434 W/m K. The negative κ_{app} does not violate the second law of thermodynamics. It is a combined effect of the much higher thermal conductivity of flexural mode phonons and the weak coupling between them and transverse/longitudinal modes phonons.

1. Introduction

Graphene is a two-dimensional (2D) material that exhibits exceptional electric and optical properties [1,2]. The high electron mobility and thermal conductivity of graphene are of great interest for interconnects, electronic devices and radio frequency devices [3,4]. Similar to carbon allotropes like graphite and carbon nanotubes, graphene possesses high basal plane thermal conductivity due to its strong covalent bonding, light atomic weight and large crystalline domains [5]. Balandin et al. [6,7] reported extremely high thermal conductivity (κ) values in the range of 4840 ± 440 to 5300 ± 480 W/m K for mechanically exfoliated single layer graphene at room temperature (RT). Several groups have since measured the thermal conductivity of suspended graphene using different methods [4,8–10]. Their measured κ values range from 1800 W/m K to 5150 W/m K near RT. While for supported monolayer graphene, much lower κ values have been measured at ~600 W/m K at RT due to the flexural phonon coupling with the substrate [9,11]. The experimental work on the thermal conductivity of graphene stimulated extensive numerical work on this subject. Using classical molecular dynamics (MD) simulation, Hu et al. [12] calculated the thermal conductivity of symmetric graphene nanoribbons (GNRs) with dimension of 1.5×5.7 nm^2 to be around 2100 W/m K at 400 K. Evans et al. [13] reported a thermal conductivity at ~6000 W/m K for graphene sheet with dimensions of 10×10 nm^2 at 300 K. Other groups using equilibrium molecular dynamics (EMD) [14] and non-equilibrium molecular dynamics (NEMD) [15] came up with much lower thermal conductivities at 630 W/m K and 218 W/m K respectively for isolated graphene and armchair GNR at 300 K.

For a long time it has been tacitly accepted that the in-plane acoustic phonons are dominant in the thermal transport of graphene [16–19], recent studies have shown that the fact is quite different. Saito et al. [20] calculated the ballistic thermal conductance of graphene by investigating the dispersion relation of phonons and electrons. They demonstrated that the ballistic phonon conductance of graphene below about 20 K is mainly determined by the out-of-plane acoustic mode (ZA branch) and the in-plane acoustic modes (LA and TA branches) cannot be ignored above 20 K. By measuring the thermal transport of single layer graphene (SLG) supported on amorphous SiO_2, Seol et al. [11,21] performed a revised calculation and they showed that the ZA branch can contribute as much as 77% at 300 K and 86% at 100 K of the calculated thermal conductivity for suspended graphene due to the high specific heat and long mean scattering time of ZA phonons. Based on the exact numerical solution of the linear Boltzmann transport equation, Lindsay et al. [22,23] calculated the lattice thermal conductivity (κ_L) of graphene at 300 K and it turned out that the dominant contribution to κ_L comes from the ZA branch, which is greater than the combined TA and LA contributions. A symmetry-based selection rule and the anomalously large density of states of flexural phonons are used to explain their results. This unique feature in graphene's thermal conductivity gives rise to many peculiar properties of its thermal transport.

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Our previous study revealed the fact that in a GNR system, the ZA branch has much higher thermal conductivity than the LA and TA branches [24,25]. Also, ZA ↔ ZA energy transfer is much faster than the ZA ↔ LA/TA phonon energy transfer. Using MD simulations, we have shown that under the influence of a moving or static localized heat source, the flexural mode (FM) phonons dissipate heat much faster than the longitudinal mode (LM) and transverse mode (TM) phonons, which gives rise to an energy inversion phenomenon at the system level [26]. Besides, due to the high thermal conductivity of flexural mode (ZM) phonons in GNRs, energy separation is observed between the in-plane and out-of-plane phonon modes after a steady state heat flux (q'') is imposed on the system. Such energy separation can hold for about 50 nm from the heating region.

The differential form of Fourier's law of heat conduction is expressed as $q'' = -\kappa \cdot \nabla T$, where q'' is the local heat flux, κ the material's thermal conductivity and ∇T the temperature gradient. The minus sign indicates the heat current flows from higher temperature regions to lower ones. For bulk materials, κ is size independent and only determined by the material's composition and structure. While for micro/nanoscale materials, κ is also affected by parameters like dimension and boundary condition. Non-Fourier thermal transport in micro/nanoscale materials has been studied extensively by previous research [27,28]. Generally, in order to define the local temperature, mode-wide thermal equilibrium among different phonon modes should be reached. However, since the thermal conductivities of different phonon modes in graphene have huge differences, it is possible that there is mode-wide energy difference during steady state heat conduction in graphene. In such scenario, the definition of temperature is no longer accurate to describe graphene's local energy level. And strictly speaking, thermal conductivity is also not well defined. Therefore, a nominal temperature (E_T) with unit K and apparent thermal conductivity (κ_{app}) with unit W/m K are brought up to give a better description.

In this work, phonon thermal transport in GNRs is investigated by using MD simulation. A peculiar heating and cooling technique is developed to induce mode-wide energy difference during steady state heat conduction. The unique thermal properties of GNR enable it to support a bi-directional heat transfer in the system. And when the bi-directional heat conduction reaches steady state, a single thermal conductivity cannot be used to reflect the relation between the heat flux and the temperature gradient. The calculated thermal conductivities are dependent on the net heat fluxes and the κ_{app} of graphene are calculated at positive, negative, zero and infinite values, depending on the proportions of each phonon mode energy added/subtracted to/from the heating/cooling areas.

2. Basis of physical problem and modeling

The second generation of Brenner potential [29]: reactive empirical bond-order (REBO), based on the Tersoff potential [30,31] with interactions between C–C bonds is applied in our MD simulation. In this work, the GNR systems have zigzag boundaries in the width direction and armchair boundaries in the length direction. Definitions of the zigzag and armchair boundaries can be literally understood and are depicted in Fig. 1(c). The edge carbon atoms are not hydrogen-passivated. Atomic configuration of the GNR system is shown in Fig. 1. The outermost layer of carbon atoms at each end (denoted in black) are fixed to avoid the spurious global rotation of the GNRs in the simulation [32]. Free boundary conditions are applied to the x and z directions. To compare the energy evolution of different phonon modes and the whole system, a nominal temperature E_i defined as $E_{k,i}/(1/2)k_B$ with unit K is used to represent the energy values in each phonon mode and a value E_T defined as $E_{k,T}/(3/2)k_B$ with unit K stands for the system's total energy. Here $E_{k,i}$ is the kinetic energy of carbon atoms for phonon mode i ($i = TM$, LM, or FM); $E_{k,T}$ is the total kinetic energy of carbon atoms and k_B is the Boltzmann constant.

Within the linear response regime, one would expect from Fourier's law of heat conduction that q'' changes proportionally with ∇T. However, in many low dimensional systems [33–37], it is found that q'' decreases with an increasing temperature bias (ΔT), which is known as negative differential thermal conductance (NDTC). Recent study by Hu et al. [33] revealed a tunable NDTC in rectangular and triangular GNRs, which results from the competition between decreasing κ and increasing ΔT beyond linear response regime. They demonstrated that the NDTC in GNR is caused by its temperature dependent thermal conductivity. However, it is worth noting that the thermal conductivity of GNR is not only temperature dependent, but also deviates much among in-plane and out-of-plane directions [11,20,22,24]. Therefore, it is of great interest to explore the peculiar thermal properties brought up by the thermal conductivity deviations among different phonon modes. Inspired by the strong mode-wide difference in sustaining thermal transport in GNR, bi-directional heat transfer in a rectangular GNR is explored in this work (as shown in Fig. 1). Four layers of carbon atoms at each end of the GNR system is grouped to add/subtract kinetic energy to/from the out-of-plane phonon mode (E_{FM}) and in-plane phonon modes (E_{LM} and E_{TM}) respectively. In traditional non-equilibrium molecular dynamic methods for thermal conductivity calculation, the hot and cold regions are created in the simulation domain by adding kinetic energy ΔE_k in the hot region and removing the same amount from the cold one while preserving linear momentum at each time step. The velocity of each atom is rescaled by the same factor χ. In this work, we use a modified velocity rescaling method to control the energy variation for each phonon mode, i.e., instead of adding/subtracting kinetic energy to all phonon modes, we manage to add kinetic energy only to the specified phonon mode and subtract kinetic energy from the others in the same region. Specifically, by adding kinetic energy to E_{FM} while subtracting kinetic energy from E_{LM} and E_{TM} at the left end of GNR and doing the opposite at the right end, a bi-directional heat conduction phenomenon is observed. This physical process is demonstrated in Figs. 1(a), (b) and (c). The local nominal temperature along the GNR is calculated from the kinetic energy of the three phonon modes averaged for 50 ps.

In this work, the phonon–phonon couplings among different phonon modes are considered in the graphene system naturally since the MD simulation tracks the full movement of each atom and the inter-atomic interaction. In our previous study [26], it has been demonstrated that the energy coupling between TM and LM phonons is much faster than that between TM/LM and FM phonons. At temperature ~80 K, it is calculated that the phonon relaxation time between FM and TM/LM is 4.7 times larger than that between TM and LM, meaning the energy transfer between TM/LM and FM is much slower than that between TM and LM. Also, it is concluded that the energy coupling between FM and TM/LM phonons is not constant against their energy level: the coupling becomes stronger when the phonon energy is higher.

3. Results and discussion

3.1. Negative apparent thermal conductivity in GNR

A GNR with dimensions of 2.0×50.1 nm^2 ($x \times y$) is built. After 400 ps canonical ensemble (NVT) and 150 ps microcanonical ensemble (NVE) calculations, the system reaches thermal equilibrium at temperature 50 K. In our previous studies on GNR's thermal conductivity, we showed that quantum correction is of great importance to graphene's temperature and thermal conductivity calculations [24]. The MD temperature 50 K we used in this work corresponds to ~300 K after quantum correction, which is