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Layer and size dependence of thermal conductivity in multilayer graphene nanoribbons

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ABSTRACT

Using nonequilibrium molecular dynamics method (NEMD), we have found that the thermal conductivity of multilayer graphene nanoribbons monotonously decreases with the increase of the number of layers which can be attributed to the phonon resonance effect of out-of-plane phonon modes. The reduction of thermal conductivity is proportional to the layer size, which is caused by the increase of phonon resonance. The results clearly show the dimensional evolution of thermal conductivity from quasi-one dimension to higher dimensions in graphene nanoribbons.

1. Introduction

The fresh comings of carbon family, the two-dimensional (2D) graphene and quasi-one-dimensional (1D) graphene nanoribbon (GNR), have attracted strong interest due to their fundamental physical properties and potential applications in nanoelectronic devices [1–4]. Experimental developments have enabled the growth of the high quality multilayer graphene [5] and the control of GNR edge geometries [6]. As we know, the thermal property is a crucial aspect that determines the application of a material in nanoelectronics [7]. In recent years, the thermal properties of monolayer graphene and GNRs has aroused much attention [8–17]. Very recently, the thermal conductivity of few layer graphene has also been studied experimentally and theoretically [5]. However, the thermal conductivity of multilayer GNRs has not been well investigated so far. Its clarification is becoming desirable due to the forthcoming application of multilayer GNRs in nanoelectronics [18–20].

On the other hand, the mechanism of thermal conduction on the nanoscale is currently a controversial issue [7,21]. Investigating the dimensional evolution of thermal conductivity could provide a new insight to clarify the fundamental mechanism on nanoscale. The thermal conductivity evolution from 2D to 3D has been investigated experimentally [5], while the number and size of layer evolution in multilayer GNRs are not well understood. The multilayer GNR is an ideal system for investigation on dimensional evolution of thermal conductivity from quasi-1D [22,23] to higher dimensions, which can be easily realized through the number and size variation of GNR layers.

In this work, we employ the nonequilibrium molecular dynamics (NEMD) method [15–17,24,25] to investigate layer and size effect on thermal conductivity of multilayer GNRs with different edge shapes, such as the armchair multilayer GNRs and the zigzag multilayer GNRs. The number of layers varies from 1 to 5 and the width of layers varies from 1 to 10 nm. We find that both the size and number of layers have strong influence on thermal conductivity of multilayer GNRs. The intrinsic mechanism of thermal conductivity variation is further illustrated by a phonon resonance model.

2. Simulation method

The structure of multilayer GNRs is constructed based on the theoretical prediction of bilayer GNRs which has a small deviation from Bernal stacking [26].

In the NEMD simulation, Tersoff potential [27] is utilized to describe the in-plane C–C bonding interactions. Lennard-Jones potential [28] is used to describe the inter-layer interaction. It can well describe the phonon spectrum of graphite [29] and the interfacial thermal conductivity of multilayer graphene, both of which agree well with the previous experimental results above room temperature [30,31].

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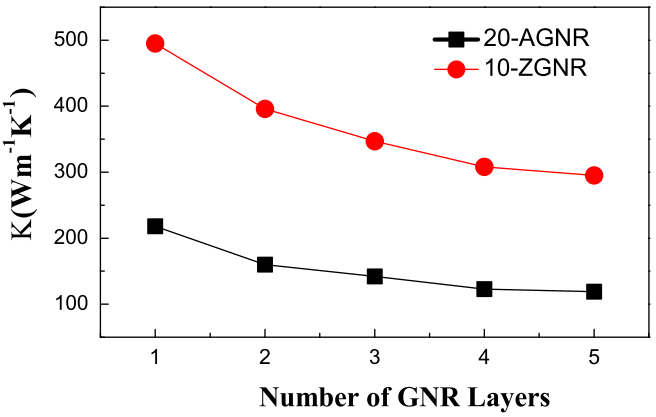

Fig. 1. Thermal conductivity κ as a function of the number of layers with length and width around 10 nm and 2 nm. κ decreases monotonously with number of GNR layers increasing, indicating the enhancement of inter-layer phonon coupling.

We use the velocity Verlet method to integrate equations of motion with a fixed time step of 1 fs [17,24,25]. On each layer of multilayer GNR, fixed boundary condition is implemented with the atoms at the left and right ends fixed at their equilibrium positions [16,17]. Next to the boundaries, the adjacent two cells of atoms are coupled to *Nosé–Hoover* thermostats with temperatures 310 K and 290 K, respectively. The thermal conductivity for layer i can be calculated directly from the well known Fourier law $\kappa_i = J_i d/(\Delta T wh)$, where $\Delta T = 20$ K is the temperature difference between two thermostats, J_i is the heat flux from the heat bath to the system, which can be obtained via calculating the power of heat baths [32], d is the length, w is the width and h (0.144 nm) [17] is the thickness of a monolayer GNR. All the calculated thermal conductivities are obtained by averaging about 3 ns after 2 ns to establish a stable temperature gradient along the length direction. Thus the thermal conductivity of multilayer GNR can be defined as $\kappa = \sum \kappa_i/n$ with n being the number of layers. In addition, all the GNR structures have been optimized before NEMD simulation. Following previous convention, the width of GNRs with armchair shaped edges on both sides is defined by the number of dimer lines across the ribbon, while ribbons with zigzag shaped edges on both sides are defined by the number of the zigzag chains across the ribbon width. We refer to a GNR with Na dimer lines as a Na-AGNR and to a GNR with Nz zigzag chains as a Nz-ZGNR [17,22,33].

3. Results and discussions

We first investigate the number of layers dependence of thermal conductivity of 20-armchair multilayer GNR and 10-zigzag multilayer GNR. Similar to that of monolayer GNRs, the 20-armchair multilayer GNRs have much lower thermal conductivity than 10-zigzag multilayer GNRs (see Fig. 1), implying a universal edge-shape dependence of thermal conductivity in the GNR family. Moreover, with the number of layers increasing, thermal conductivities of both the armchair multilayer GNR and zigzag multilayer GNR monotonously decrease. When the number of layers gets to 5, the thermal conductivity is reduced to 119 $\mathrm{W\,m^{-1}\,K^{-1}}$ for 20-armchair and 295 $\mathrm{W\,m^{-1}\,K^{-1}}$ for 10-zigzag GNR. Comparing to thermal conductivity of monolayer 20-armchair GNR (195 $\mathrm{W\,m^{-1}\,K^{-1}}$) and 10-zigzag GNR (495 $\mathrm{W\,m^{-1}\,K^{-1}}$) respectively, a significant reduction of thermal conductivity appears and the results show an obvious dependence of reduction on number of layers (see Fig. 1). Moreover, from monolayer GNR to bilayer GNR, the reduction is about 20% much larger than that from four-layer GNR to five-layer GNR which is less than 5%. The trend of our calculation results shows that the thermal conductivity of GNRs has similar layer dependence to that of multilayer graphene [5]. This indicates that the crossplane coupling is enhanced with number of layers increasing, and it plays an important role in the evolution of thermal conductivity from monolayer GNR to multilayer GNR. This is in agreement with recent experiment in few-layer graphene, where a 67% reduction of thermal conductivity is observed as the number of atomic plane increasing from 1 to 4 [5].

Table 1
Thermal conductivity κ of bilayer zigzag GNRs with different constraints. The length and width of the monolayer and bilayer zigzag GNR are around 10 nm and 2 nm.

Type of GNR	Constraint	Thermal conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$)	
		Top	Bottom
Bilayer zigzag GNR	Free	323	335
Bilayer zigzag GNR	Constraint 1	467	330
Bilayer zigzag GNR	Constraint 2	469	480
Monolayer zigzag GNR	Free	490	–

Constraint 1: Out-of-plane modes of top layer are frozen.
Constraint 2: Out-of-plane modes of both layers are frozen.

These results can be further understood by the coupling mechanism [34], there exists a competitive mechanism on thermal conductivity in a coupling system: the phonon resonance effect that decreases thermal conductivity and phonon-band-up-shift effect that increases thermal conductivity [34]. The strength of phonon resonance can be described by the resonance angle Ψ, which is determined by atomic mass and spring constant of two coupled systems. When Ψ is small ($\Psi < \frac{\pi}{24}$), the variation of thermal conductivity is dominated by the phonon-band-up-shift effect; when Ψ comes to be large ($\Psi > \frac{\pi}{12}$), the thermal conductivity is dominated by the phonon resonance effect. The thermal conductivity reduction of multilayer GNRs with the increase of number of layers can be accounted for this mechanism. For the multilayer GNRs, the atomic mass and spring constant of the coupling layers are totally equivalent, thus $\Psi = \frac{\pi}{4}$ and the phonon resonance effect plays a dominant role on thermal conductivity variation. Therefore, the thermal conductivity of multilayer GNRs monotonously decreases with the number of layers increasing which induces more and more intensive phonon resonance.

In order to identify the phonon resonance effect in multilayer GNRs, we freeze the out-of-plane atomic vibration of multilayer GNRs and re-calculate their thermal conductivity. For simplicity, here we only present the calculated thermal conductivity values for the zigzag bilayer GNR, the results for armchair bilayer GNR are qualitatively similar. Two cases are considered: out-of-plane vibration of the top layer is frozen (constraint 1) and out-of-plane vibration of both layers is frozen (constraint 2).

As shown in Table 1, freezing out-of-plane atomic vibration would considerably change the layer's thermal conductivity. If only top layer's out-of-plane vibration is frozen, thermal conductivity of top layer would increase by 40% (from 334 $\mathrm{W\,m^{-1}\,K^{-1}}$ to 467 $\mathrm{W\,m^{-1}\,K^{-1}}$) while thermal conductivity of bottom layer is nearly unaffected by the artificial constraint. If the out-of-plane vibration is frozen in both layers, thermal conductivity of bilayer zigzag GNR almost equals to that of monolayer zigzag GNR. This indicates that, in the multilayer GNRs, the phonon resonance of stacking layers is mainly from the coupling between the crossplane out-of-plane ZO' phonon modes [35] and the out-of-plane phonon modes that propagate in the basal plane.

For the purpose of investigating finite size effect, we calculate thermal conductivity of both monolayer and bilayer GNRs with various width of GNRs. Fig. 2 shows the obtained thermal conductivity of monolayer and bilayer GNRs, whose width ranges from 1 nm to 10 nm. As one can see, the thermal conductivity of zigzag bilayer GNR increases firstly and then turns to decrease with the width increasing, while the armchair bilayer GNR's thermal con-

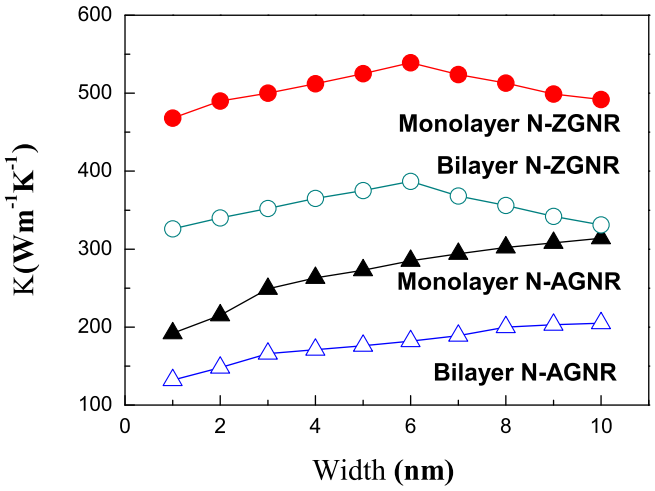

Fig. 2. Thermal conductivity κ as a function of the width of monolayer or bilayer armchair GNR and zigzag GNR with fixed length about 10 nm. The behavior of κ for monolayer and bilayer is similar and the difference of κ between monolayer and bilayer GNRs increases with the width of GNRs increasing.

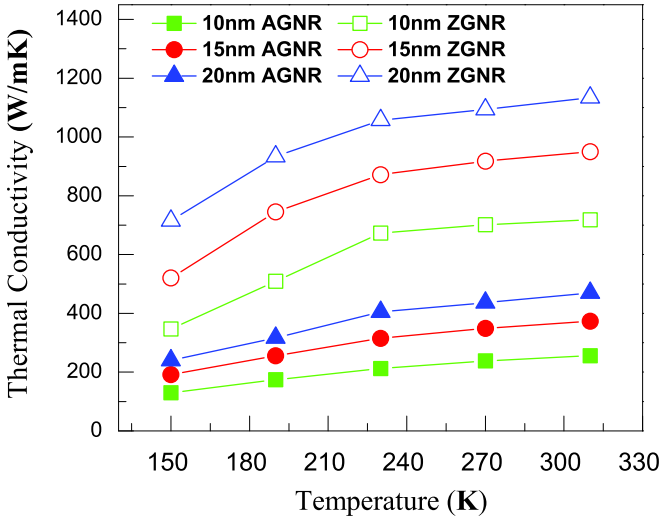

Fig. 3. Thermal conductivity κ of trilayer armchair GNR and zigzag GNR with different length including 10 nm, 15 nm and 20 nm as a function of the temperature. The thermal conductivity of both the armchair GNR and the zigzag GNR increases with the temperature rising from 150 K to 310 K. Besides that, the longer trilayer armchair GNR or zigzag GNR would obtain higher thermal conductivity. Both the size and temperature dependence of trilayer nanoribbons is in good agreement with the previous experiment on supported trilayer graphene.

ductivity monotonously increases with the width increasing. The width dependence of thermal conductivity of bilayer GNRs is very similar to that of monolayer GNRs (Fig. 2). The peak and subsequent decrease in thermal conductivity with increasing width of nanoribbon for monolayer ZGNR has also been discovered in other work [8,17]. This result has been discussed in previous work [17] clearly by taking account of the competition between the edge-localized phonon effect [36] and phonons' Umklapp effect, both of which have negative effects on thermal conductivity [37]. For the ZGNR with small width, the reduction of edge-localized phonon effect is dominating with width increasing, thus the thermal conductivity increases with width. When the width gets large enough, however, the phonons' Umklapp effect becomes dominating and the thermal conductivity begins to decrease with width increasing [17].

In addition, the difference of thermal conductivity between monolayer and bilayer GNRs also exhibits an obvious layer-size dependence. For the armchair GNRs (zigzag GNRs), the reduction of thermal conductivity monotonously increases from 31% (30%) to 35% (32%) with the width increasing from 1 nm to 10 nm. This means the difference of thermal conductivity between monolayer GNR and multilayer GNR is proportional to the layer size, because the phonon resonance strength between different layers is proportional to the number of total phonon modes which is in turn corresponding to the size of ribbon. Our results on thermal conductivity reduction of multilayer GNRs are smaller than that of few layer graphenes [5]. The above results indicate that the difference in dimension evolution of thermal conductivity between multilayer graphene and multilayer GNRs comes from the finite size effect. It is well known that the NEMD simulation can well describe the finite-length dependence of thermal conductivity [38–40]. In our calculation, the 10 nm length of GNR is much smaller than the phonon mean free path (PMFP), one can expect that the calculated results are smaller than the experimental data. According to this well accepted strong size effect in NEMD simulation [41,42], it can be reasonably expected that if the length of calculated sample is comparable to the PMFP, the calculated results would also be comparable to the experimental results.

In order to evaluate the temperature and size dependence of thermal transport in multilayer graphene nanoribbons, the thermal conductivity of trilayer armchair GNR and trilayer zigzag GNR is calculated with different length of sample and simulation temperature. The result is shown in Fig. 3, which reveals that the thermal conductivity of both armchair GNR and zigzag GNR strongly depends on the size and temperature. With the temperature increasing from 150 K to 310 K, the calculated thermal conductivity also increases to a large extent. While the length of trilayer GNR varies from 10 nm, 15 nm to 20 nm, the thermal conductivity of both the armchair and zigzag GNR increases with the length increasing. The thermal conductivity of the 20 nm trilayer armchair GNR and zigzag GNR is about twice as much as that of the 10 nm GNR. In the recent experimental study on thermal transport in supported and suspended few-layer graphene [43], the thermal conductivity of trilayer graphene supported on SiO_2 shows strong temperature and size dependence. It is revealed that the thermal conductivity of trilayer graphene increases with the temperature increasing from 150 K to 300 K. Besides that, while the length of supported trilayer graphene sample changing from 1 μm to 2 μm, the thermal conductivity is almost doubled. Our simulation results are in quite good agreement with the trend of size and temperature dependence displayed in supported trilayer graphene sample. From this point of view, we can predict that the suspended armchair and zigzag multilayer GNR systems follow the similar rule on the temperature and size dependence of thermal conductivity as that in supported multilayer graphene systems.

4. Conclusion

In conclusion, we have investigated the thermal conductivity of multilayer GNRs using the NEMD method. Comparing to monolayer GNR, the thermal conductivity of multilayer GNRs has a significant reduction which is in agreement with available experiments [5]. Based on the phonon resonance model, we propose that the reduction of thermal conductivity is attributed to the resonance of out-of-plane phonon modes. Moreover, the difference between thermal conductivities of GNRs with different number of layers is found to be proportional to the layer size, which is directly determined by the number of the total phonon modes. Besides that, the thermal conductivity of trilayer armchair and zigzag GNR is shown directly depending on the length of layer and the temperature, which follows the same trend in supported few-layer graphene according to recent experiment [43]. The present study suggests that the ther-

mal conductivity of multilayer GNRs can be manipulated by changing the number and size of layers, which provides potential applications of multilayer GNR-based materials in future nanodevices.

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