Thermal transport in MoS$_2$/Graphene hybrid nanosheets

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Abstract

Heat dissipation is a very critical problem for designing nano-functional devices, including MoS$_2$/graphene heterojunctions. In this paper we investigate thermal transport in MoS$_2$/graphene hybrid nanosheets under various heating conditions, by using molecular dynamics simulation. Diverse transport processes and characteristics, depending on the conducting layers, are found in these structures. The thermal conductivities can be tuned by interlayer coupling, environment temperature, and interlayer overlap. The highest thermal conductivity at room temperature is achieved as more than 5 times of that of single-layer MoS$_2$ when both layers are heated and 100% overlapped. Different transport mechanisms in the hybrid nanosheets are explained by phonon density of states, temperature distribution, and interlayer thermal resistance. Our results could not only provide clues to master the heat transport in functional devices based on MoS$_2$/graphene heterojunctions, but are also useful for analyzing thermal transport in other van der Waals hybrid nanosheets.

Keywords: MoS$_2$, graphene, thermal transport, hybrid nanosheet

(Some figures may appear in colour only in the online journal)

1. Introduction

The intrinsic zero band gap of graphene limits its extensive applications in electronics and optoelectronics [1, 2], although the first single-layer nanosheet exhibits many outstanding properties such as super-high carrier mobility and super-high thermal conductivity [3–6], in addition to its superior stiffness [7]. After graphene, many other nanosheets were proposed and synthesized successfully in recent years [8–11]. In all of the new nanosheets, single-layer molybdenum disulfide (MoS$_2$) has attracted much attention because of its direct band gap and high carrier mobility [12–14]. Many theoretical studies have been carried out to explore the electronic and optoelectronic properties of MoS$_2$ nanosheets [14–17] as well as their mechanical properties [18]. Experimentally, single-layer MoS$_2$ transistors have been reported, which show high performance, such as a mobility of at least 200 cm$^2$ V$^{-1}$ s$^{-1}$ and room-temperature current on/off ratios of $1 \times 10^8$ [14, 15]. These studies indicate that the single-layer MoS$_2$ may be an ideal electronic and optoelectronic material. However, the thermal conductivity of MoS$_2$ is much lower, which may induce problems in its thermal stability and restrict development of devices based on the new nanosheet [19–21].

In order to combine the advantages of single-layer MoS$_2$ and graphene nanosheets, various functional devices based on MoS$_2$/graphene hybrid nanosheets (MGHN) have been a new focus recently [22–27]. For example, Chang et al studied a MGHN with external electrodes applied on both layers, as shown in figure 1(a) [23]. High electrochemical performances for lithium ion batteries are exhibited in these layered composites. Zhang et al reported that another hybrid nanosheet in figure 1(b), where the MoS$_2$ layer is a transport layer while graphene is a substrate, is a potential photodetector with high photoresponsivity [24]. A field-effect transistor based on a MoS$_2$/graphene heterojunction is reported by Kwak et al and Myoung et al, which has a large current modulation, spin-dependent tunneling, and lower barrier height [25, 26]. The heterojunction is illustrated in figure 1(c). Although these functional devices based on MGHN show excellent electronic
or optoelectronic properties, to the best of our knowledge, thermal transports in these hybrid nanosheets have never been reported. It is natural to ask about the ability of these devices to conduct heat and what new transport phenomena these structures have.

In this paper, thermal transports in three types of MGHNs, as shown in figure 1, are studied by using molecular dynamics methods. Although all of the three structures consist of the same MoS$_2$ and graphene layers, thermal transport processes within them are completely different, as well as their abilities to conduct heat. The first MGHN (MGHN-1) in figure 1(a) has the highest thermal conductivity, followed by MGHN-2 in figure 1(b), while the thermal conductivity of MGHN-3 in figure 1(c) is the lowest. We analyze the transport mechanisms in these hybrid nanosheets by using the phonon density of states (PDOS), temperature distribution, and interlayer thermal resistance (ITR). It is interesting to find that ITR has a positive relation to thermal transport in MGHN-1, while the transport in MGHN-2 and MGHN-3 are negative. In addition, the relation between interlayer coupling strength, environment temperature, number of graphene layers, and thermal conductivities of these structures is discussed.

2. Model and simulation method

Three types of MGHNs were considered, as shown in figure 1. In all structures, MoS$_2$ and graphene layers have the same width and length, labeled by $W$ and $L$, respectively. Figure 1(a) shows the side view of MGHN-1, where MoS$_2$ and graphene layers are entirely coupled together, and heat...
source and heat sink are applied on both the MoS\(_2\) and graphene layers. The hybrid nanosheets in figure 1(b) are MGHN-2, whereas the heat source and heat sink are applied only to the MoS\(_2\) layer. Therefore, the graphene layer in this structure is somewhat like a substrate. The top views of MGHN-1 and MGHN-2 are shown in figure 1(d). Due to different lattice constants, there exists lattice mismatch between graphene and MoS\(_2\) layers. Here, the unit cell of the hybrid structure is constructed by matching a 4 \times 4 supercell of MoS\(_2\) and a 5 \times 5 supercell of graphene with a tensile strain of \(\sim 1.5\%\) (see the diamond box). The lattice constant of the unit cell is \(a = 12.48\) Å, while the lateral width of the unit cell is \(b = (\sqrt{3}/2)a\). Then, the width \(W\) and length \(L\) of the hybrid structure can be defined in units of \(a\) and \(b\), respectively, and we set \(W = 6b\) and \(L = 12a\). Figure 1(c) shows the side view of MGHN-3, which is a MoS\(_2\)/graphene heterojunction by the overlap of partial MoS\(_2\) and graphene layers. The length of the overlap region is labeled by \(L'\), and the stacking form of the overlap region is the same as in the former two structures. The heat source and heat sink are separately applied on one side of the MoS\(_2\) and graphene layers. Besides these three bilayer structures, we also consider trilayer structures in which another graphene layer is covered by MoS\(_2\) and a 5 \times 5 supercell of graphene with a tensile strain of \(\sim 1.1\%\) in graphene. The width and length of all graphene and MoS\(_2\) layers are \(W = 6.46\) nm and \(L = 14.93\) nm, respectively. The interlayer distance between MoS\(_2\) and graphene is calculated as 3.35 Å, which coincided well with the reported parameter of 3.32 Å [35].

In our simulations, the hybrid structures are initially relaxed in canonical ensemble (NVT) conditions for 50 picoseconds (ps), with a time step of 0.46 femtoseconds. Their left/right boundaries are fixed while the other two are periodic boundaries. Next to the fixed boundaries the adjacent two cells are coupled to Nosé–Hoover thermostats, to achieve temperature gradients, with temperatures \(T_0 + \Delta T\) and \(T_0 - \Delta T\), respectively. Herein, \(T_0\) is the environment temperature and the temperature drop is \(\Delta T = 10\% T_0\). From Fourier’s law, the thermal conductivity \(K\) is defined as [36]:

\[
K = \frac{J}{\nabla T \cdot S}
\]

where \(\nabla T\) is the temperature gradient and \(J\) is the heat flux from the heat source to heat sink, which can be obtained via calculating the heat bath’s power. \(S = W \times H\) is the cross-sectional area, \(W\) is the width, and \(H\) is the thickness of the hybrid structure, which we have chosen for MoS\(_2\) to be 3.66 Å [27] and 1.42 Å for graphene [37, 38]. To reach the non-equilibrium steady state, the system was relaxed for 60 ps under NVE ensemble. After 50 ps, the temperature difference has reached the steady state. During this procedure, the total energy and average temperature both were fluctuating around targeted values. After that, 100 ps was used to calculate the thermal conductivity. In all of our simulations, the hybrid structures show good stability even at high temperature, which was confirmed by checking their atomic configurations and radial distribution functions (not shown). It indicates that the potential we selected is effective and reliable.

To understand the underlying mechanisms of phonon transport, the phonon density of states (PDOS) has been studied. The PDOS is calculated from the Fourier transform of the velocity autocorrelation function [39]:

\[
PDOS(\omega) = \frac{1}{\sqrt{2\pi}} \int e^{-i\omega t} \left( \sum_{j=1}^{N} v_j(t) v_j(0) \right)
\]

where \(v_j(0)\) is the average velocity vector of a particle \(j\) at initial time, \(v_j(t)\) is its velocity at time \(t\), and \(\omega\) is the vibration wave number.

3. Results and discussion

We first study the homogeneous temperature gradient in both layers in the MGHN-1 structure. The thermal conductivity of MGHN-1 as a function of environment temperature \(T_0\) is calculated as shown in figure 2. To calculate the thermal conductivity of MGHN-1, the total system cross-section is included. For comparison, thermal conductivities of single-layer MoS\(_2\) and graphene are also presented. One can find that the thermal conductivity of graphene increases while that of MoS\(_2\) decreases as \(T_0\) ascends; moreover, the former is much larger than the latter, especially at high temperature. The
The thermal conductivity of MGHN-1 is between them, which is about five and one-third times that of MoS2 and graphene, respectively, at room temperature (300 K). The coupling between layers might play an important role in the thermal transport in the hybrid structures. To examine this interlayer-coupling effect, we compute the thermal conductivity of MGHN-1 without interlayer coupling, as shown in figure 2.

The comparison between the conductivities of MGHN-1 with and without interlayer coupling indicates that the interlayer coupling reduces the thermal conductivity (see the red solid and blue dotted lines). The higher the temperature, the more significant the reduction of the conductivity. This implies that the interlayer coupling is enhanced with respect to an increment of temperature. As a further study, we investigate the sandwiched GMGN-1 nanosheets. We find that the thermal conductivity of the sandwiched GMGN-1 nanosheets is higher than the thermal conductivity of MGHN-1, but lower than that of MGHN-1 without interlayer coupling after $T_0$ is higher than room temperature (see the green line in figure 2). This further indicates that the coupling between the MoS2 and graphene layers has a large effect on the thermal transport in MGHN-1.

The mechanism of thermal transport in MGHN-1 is schematically displayed in figure 3(a). As the heat source and heat sink are applied on both the MoS2 and graphene layers, the temperature gradients are homogeneous when out-of-plane. In other words, there is no temperature drop in the vertical direction, and thus no net heat flux exists between two layers. The heat fluxes only flow in the MoS2 or graphene layer, as shown by the red arrows. However, the interlayer coupling will lift the interlayer exchange of phonons and strengthen interface scattering [34, 40]. We compare the out-of-plane PDOS for isolated graphene and graphene after it is coupled with MoS2 in figure 3(b). It is seen that the PDOS is reduced by the interlayer coupling, especially for the phonons whose frequencies are less than 15 THz. The phonon frequency range of single-layer MoS2 is only from 0 to 15 THz [41, 42]. This demonstrates that all phonon modes in the MoS2 layer have interactions with those in the graphene. The interaction of phonon modes enhances the phonon scattering; as a result the thermal conductivity of the hybrid nanosheets decreases. The interactions of phonon modes are also tightly associated with the environment temperature $T_0$. With an increase in $T_0$, high-frequency phonons gradually participate in the transport process, and thus the phonon interactions between the two layers become more dramatic. This is the reason why at higher temperatures the differences in thermal conductivities between MGHN-1 with and without coupling are larger.

The interlayer interactions of phonons can also be reflected by ITR between two layers, which is usually expressed as $R = \Delta T/J$, i.e., temperature change $\Delta T$ divided by heat flux $J$. To calculate the ITR between MoS2 and graphene layers, we set the graphene and MoS2 layers as heat source and sink, respectively, and the temperature drop is $\Delta T = 10\% T_0$. Figure 3(c) shows the ITR between MoS2 and graphene as a function of temperature. It is seen that the ITR decreases with an increase in temperature, indicating that the phonons are more easily transmitted from one layer to another. The phonon communication between the two layers enhances the interlayer scattering and reduces the thermal conductivity. Therefore, in MGHN-1, the thermal conductivity is in direct proportion to ITR.

The thermal conductivity of MGHN-2 as a function of environment temperature $T_0$ is shown in figure 4(a), where the blue and red lines represent the cases for MGHN-2 and GMGN-2, respectively. The geometry of MGHN-2 is similar to that of MGHN-1. However, the thermal function of the graphene layer in MGHN-2 is something like a substrate because the heat baths are applied only on the MoS2 sheet in MGHN-2. Therefore, when we calculate the thermal conductivity of the structure by using equation (2), the cross-sectional area S includes only the cross-section of MoS2. One can find from figure 4(a) that the thermal transport of the MoS2 sheet is improved by the help of the graphene substrate(s), compared with the thermal conductivity of isolated MoS2 in figure 2. The thermal conductivities of MGHN-2 and GMGN-2 are about 2.0 and 2.6 times that of the isolated MoS2 at $T_0 = 300$ K, respectively. The dotted lines in figure 4(a) present increased thermal conductivities as a function of temperature under the help of graphene sheet(s). The trend indicates that the contributions of the graphene layers increase with $T_0$.

To investigate the mechanisms of thermal transport in MGHN-2, the spatial temperature distributions are calculated, as shown in figure 5(a). The black and blue lines present variations of temperature along the transport direction in the MoS2 and graphene layers, respectively. For comparison, variation of temperature in an isolated MoS2 is also shown. One can see that the temperature of the isolated MoS2 drops linearly along the transport direction because the heat energy is conservative in the MoS2 sheet. As the MoS2 layer is coupled to a graphene substrate, its temperature drop is no longer linear, implying that the heat energy in the MoS2 layer is no longer a constant because some heat flows to the substrate. In figure 5(a), the temperature of the graphene layer
seems to be a constant, but a close look at the inset shows that it also drops nonlinearly even if the temperature drop is very small. The temperature difference between the two contacted layers indicates that heat exchange takes place between them.

We use figure 5(b) to illustrate the process of thermal transport and exchange in MGHN-2. At the left high-temperature side, heat fluxes flow vertically from MoS₂ to graphene because the temperature of the MoS₂ layer is higher than that of graphene. The quantity of the vertical flux decreases along the horizontal direction due to the decrease of the temperature difference. The heat energy obtained from the MoS₂ layer flows from the left to the right side in the graphene layer, and then flows back to the MoS₂ layer, because at the right side the temperate of graphene is higher than that of MoS₂. In the horizontal direction, there are two thermal transport channels: one is in the MoS₂ layer and the other is in the graphene. Because the graphene is a high-conductivity material, a lot of heat will transport across it as its two sides

Figure 3. (a) Schematic view of the thermal transport process in MGHN-1. Red arrows show the heat fluxes in the two layers while black arrows illustrate exchange and scattering of phonons. The color bar labels the temperature scale in the structure. (b) The out-of-plane PDOS for isolated graphene and coupled graphene in the MGHN-1. (c) ITR between MoS₂ and graphene layers as a function of temperature T₀.

Figure 4. (a) Thermal conductivities of MGHN-2 and GMGN-2 as functions of temperature T₀ (solid line), and the increased thermal conductivity, compared to isolated ones, as functions of temperature T₀ (dotted line). (b) Thermal conductivity of MGHN-2 (blue line) and ITR between MoS₂ and graphene (black line) as functions of coupling strength η, at T₀ = 300 K.
Figure 5. (a) Horizontal temperature distribution of isolated MoS2 (red line), coupled MoS2 (black line), and graphene layers (blue line) in MGHN-2, at \( T_0 = 300 \text{ K} \). Inset: a closer look at temperature distribution of the coupled graphene layer. (b) Schematic view of thermal transport process in MGHN-2. The horizontal and vertical arrows show heat fluxes in horizontal and vertical directions, respectively. The color bar labels the temperature scale in the structure.

have a small temperature drop. Therefore, although the phonon scattering induced by vertical coupling will decrease the intrinsic thermal conductivity of MoS2, the opening of the additional channel in the graphene substrate improves the ability of the whole device to conduct heat.

As discussed above, the ITR between the MoS2 and graphene layers decreases with the increase of environment temperature \( T_0 \) (see figure 3(b)). Therefore, at high \( T_0 \), thermal exchange between the two layers increases, i.e., the heat energy carried by the graphene layer increases. This explains why the thermal conductivity in figure 4(a) increases with \( T_0 \). In this case, the thermal conductivity is inversely proportional to the ITR.

To fine-tune the interlayer coupling, we introduce the variable \( \eta \) as coupling strength to scale the interfacial couplings between layers, as expressed in equation (1). We find that the thermal transport in the MGHN-2 structure is dependent not only on the environment temperature but also on the interfacial coupling strength \( \eta \). As shown in figure 4(b), the thermal conductivities increase with the coupling strength, which can also be attributed to the decrease of ITR (see the black line in figure 4(b)). When \( \eta = 2.0 \), the thermal conductivity is about 1.4 times that of \( \eta = 1.0 \). So, one can improve the thermal transport in MGHN-2 by applying a vertical compressive strain.

In figure 6(a), the thermal conductivity of MGHN-3 as a function of \( R_{\text{overlap}} (L' / L \times 100\%) \) is shown at \( T_0 = 300 \text{ K} \). In this structure, the cross-section of MoS2 is included to calculate thermal conductivity. One can find that thermal conductivity increases with the overlap ratio. At 50% overlap ratio, i.e., half contact of two layers, the thermal conductivity is 3.4 W mK\(^{-1}\), which is close to the value of isolated MoS2, while the thermal conductivity of full contact is about 4.5 W mK\(^{-1}\). Figure 6(b) shows the modulation of interfacial coupling strength \( \eta \) on thermal conductivity for the MGHN-3 structure with 50% overlap ratio. The ITR between the two layers decreases with the coupling strength and the environment temperature \( T_0 \). As a result, the thermal conductivities increase with \( \eta \) and \( T_0 \). This is similar to the case of the MGHN-2 structure. However, the thermal conductivities of the MGHN-3 structure are lower than those of MGHN-1 and MGHN-2.

To explore the thermal transport process in MGHN-3, we calculate the temperature distributions of the MoS2 and graphene layers, as shown in figure 7(a). Here, the two layers are in half contact (50% overlap ratio) and the temperatures of the left and right sides are 330 K and 270 K, respectively. It is seen that the temperature drop in the graphene layer is very small, while a temperature drop \( \Delta T \approx 30 \text{ K} \) is observed in the MoS2 layer. According to the temperature distributions, figure 7(b) presents the distribution of heat fluxes in the structure. The heat flux horizontally flows in the graphene layer from left to right; at the overlap region it flows vertically from the graphene to the MoS2 layers because of the temperature difference of the two layers, and then flows horizontally in the MoS2 layer from left to right. In the whole process, the heat energy should be conservative. Because the thermal conductivity of graphene is much larger than that of MoS2, the temperature drop of the graphene layer is very small while the MoS2 layer has a big temperature drop.

In the MGHN-3 structure, the overlap region is the transport bottle-neck, because the ITR (interlayer thermal resistance) is higher than the intralayer thermal resistance. Therefore, the thermal conductivity of the MGHN-3 structure can be enhanced by weakening the ITR, for example by increasing the overlap ratio and increasing the coupling strength.

It should be noted that in real applications most devices are supported on a substrate of insulating layer, such as SiO2. The insulator layer should have some effect on the thermal transport in the devices. The previous studies showed that, when a graphene layer is supported by an insulator, thermal conductivity of the graphene drops slightly because of the phonon scattering between layers [43, 44]. Therefore, when MGHN-1, MGHN-2, and MGHN-3 are placed on a substrate of insulator layer, their thermal conductivities will also decrease slightly.

4. Conclusions

In summary, we have studied thermal transport in three types of hybrid MoS2 and graphene structures with three heating conditions, by using molecular dynamics simulation. These structures show diverse transport processes and abilities of thermal transport. The MGHN-1 structure has the highest thermal conductivity (about 5 times that of MoS2), because the graphene layer can carry most of the heat energy. Although the interlayer scattering induced by interlayer
coupling reduces the out-of-plane PDOS, the super-high conductivity of the graphene layer makes the structure a good thermal transport. In the MGHN-2 structure, the MoS$_2$ layer is the main layer to transport heat while the graphene layer is just a substrate. During a process of heat transfer between MoS$_2$ and graphene layers, graphene can only transport a small part of the heat, and thus its thermal conductivity is lower than that of the MGHN-1 structure (about 2 ~ 3 times of MoS$_2$). The thermal transport ability in the MGHN-3 structure is the lowest, because there is a bottle-neck of transport at the contact region between the two layers. In addition, the conductivities of these structures can be slightly tuned by the interlayer coupling strength, environment temperature, and contact area. These findings could improve our knowledge of MoS$_2$-based hybrid structures that may be useful for the applications of MoS$_2$ in nanoscale devices.

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