Thermal transport properties of monolayer MoSe$_2$ with defects

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Two-dimensional (2D) molybdenum diselenide (MoSe$_2$) as one of the ultrathin transition metal dichalcogenides (TMDs) has attracted considerable attention because of its potential applications in thermoelectric and nano-electronic devices. Here, the thermal conductivity of monolayer MoSe$_2$ and its responses to simulated size and defects are studied by nonequilibrium molecular dynamics simulations. With the increase of sample length, the thermal conductivity of monolayer MoSe$_2$ nanoribbons exhibits an enhancement whereas it is insensitive to the width. At room temperature, the thermal conductivities of monolayer MoSe$_2$ along armchair and zigzag directions are 17.758 and 18.932 W (m K)$^{-1}$, respectively, which are consistent with previous results. The impact of defects on thermal conductivity has also been studied by varying the concentration of the vacancy from 0.1% to 0.5%. The results show that an increase of the defect concentration will greatly suppress the thermal conductivity. The 0.5% defect concentration with a Mo vacancy can result in a thermal conductivity reduction of $\sim$43%. Such a study would provide a good insight into the tunable thermal transport for potential applications of not only monolayer MoSe$_2$, but also many other TMDs.

1 Introduction

The thermal transport behavior is one of the major fundamental properties in the application of various devices. For instance, high thermal conductivity is needed to solve the heat dissipation issues, but low thermal conductivity is desirable for thermoelectric applications.$^{1-4}$ Obviously, material properties have a major impact on the performance of devices. Single-layer transition metal dichalcogenides (TMDs) with quasi-two-dimensional (2D) honeycomb structures have attracted great interest due to their potential advantages, such as an intrinsic bandgap, efficiently photovoltaic response and a tunable Seebeck coefficient.$^{5-10}$ Monolayer MoSe$_2$, as one typical member of the ultrathin 2D-TMDs, is regarded as an alternative to graphene for nanoelectronic and thermoelectric devices.$^{11}$

To date, several methods, including chemical vapor deposition (CVD), molecular-beam epitaxy (MBE) and atomic layer deposition (ALD) growth techniques,$^{6,12,13}$ have been successfully applied to the production of monolayer MoSe$_2$. However, structural defects including vacancies, dislocations and grain boundaries are inevitable in using all of these preparation methods. In addition, defect-induced phonon scattering in monolayer MoSe$_2$ provides a means to modify the lattice thermal conductivity. To expedite the applications of monolayer MoSe$_2$ as a device, it is necessary to investigate its thermal conductivity and study the influence of defects.

The thermal properties of MoSe$_2$ have been investigated by using experimental and theoretical methods. Jiang et al.$^{14}$ measured the in-plane thermal conductivity of MoSe$_2$ as 35 W (m K)$^{-1}$ using the variable-spot-size time-domain thermoreflectance approach. Using the novel nanosecond energy transport state resolved Raman technique, Wang et al.$^{15}$ found that the thermal conductivities of four suspended MoSe$_2$ (45–140 nm thick) increase from $11.1 \pm 0.4$ to $20.3 \pm 0.9$ W (m K)$^{-1}$ with the increase of the sample thickness. Based on molecular dynamics (MD) simulations, Hong et al.$^{16}$ predicted the $\kappa$ values of monolayer MoSe$_2$ to be $43.88 \pm 1.33$ and $41.63 \pm 0.66$ W (m K)$^{-1}$ in armchair and zigzag directions, respectively. However, Peng et al.$^{17}$ obtained a much lower $\kappa$ value of $17.6$ W (m K)$^{-1}$ for monolayer MoSe$_2$ using first-principles calculations. Although these reported results have covered the thermal properties of monolayer MoSe$_2$ structures, it is still unclear how the defects will affect the thermal conductivity of monolayer MoSe$_2$. 

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2 Computational methods

All MD simulations in this work are performed by utilizing the LAMMPS package. The in-plane thermal conductivities are computed by using the NEMD method. The Stillinger–Weber (SW) potential is used to describe the interatomic interactions in monolayer MoSe$_2$, which has already been used in the theoretical study of low dimensional nanomaterials, and can be expressed as

$$\Phi(1, \ldots, N) = \sum_{i<j} V_2(r_{ij}) + \sum_{i<j<k} V_3(r_{ij}, r_{ik}, \theta_{ijk})$$  \hspace{1cm} (1)

where $V_2$ and $V_3$ represent two-body bond-stretching and three-body bond-bending interactions, respectively. In order to ensure the accurate description of the three-body bond-bending term, the Se atoms in the top layer and bottom layer are treated as different types (see Fig. 1b). The interactions of $V_2$ and $V_3$ can be written as

$$V_2(r_{ij}) = A_{ij} \left( \frac{B_{ij}}{r_{ij}} - 1 \right) \exp \left( \frac{\gamma_{ij}}{r_{ij} - r_{cut}} \right)$$  \hspace{1cm} (2)

$$V_3(r_{ij}, r_{ik}, \theta_{ijk}) = K_{ijk} \exp \left( \frac{\gamma_{ij}}{r_{ij} - r_{cut}} + \frac{\gamma_{ik}}{r_{ik} - r_{cut}} \right) \times \left( \cos \theta_{ijk} - \cos \theta_{0,ijk} \right)^2$$  \hspace{1cm} (3)

where $r_{ij}$ and $r_{ik}$ are the pair separations between atoms $i, j$ and atoms $i, k$, $\theta_{ijk}$ is the angle between the separation vectors centering on atom $i$ and $\theta_{0,ijk}$ stands for the equilibrium angle. The terms $\rho_{cut}$, $r_{cut}^i$ and $r_{cut}^k$ indicate the cutoff radii from the surrounding atoms to the central atom $i$, which are determined by the material's structure. $A_{ij}, B_{ij}, K_{ijk}$ and $\gamma_{ij}$ are geometrical parameters to identify the rationality of $V_2$ and $V_3$. These parameters are generated by fitting lattice constants, bond angles, bond lengths, elastic constants and phonon frequencies of monolayer MoSe$_2$ utilizing the particle swarm optimization method.

Atomic configuration schematic of monolayer MoSe$_2$ is shown in Fig. 1. The Mo atom layer is sandwiched between two Se atom layers and connected by covalent bonds. The thermal conductivities along armchair and zigzag directions are computed using the NEMD method. The periodic boundary condition is used in the $x$ and $y$ directions to eliminate the edge effects while the free boundary condition is applied in the out-of-plane ($z$) direction. The initial system of monolayer MoSe$_2$ is placed in the canonical ensemble ($NVT$) for 500 ps to reach thermal equilibrium at designated temperature, and then switched to a microcanonical ensemble ($NVE$) for another 500 ps. After the thermal equilibrium simulation, the NEMD simulations are performed to calculate the thermal conductivity for an additional 8 ns, during which the system will build a steady-state temperature gradient.

As shown in the inset of Fig. 2, one-quarter site of the simulation system is chosen as a heat source while the three-quarter site is chosen as a heat sink. Kinetic energy is constantly added to the heat source region at each time step of 0.5 fs, while the same amount of energy is subtracted from the heat sink region in the NEMD simulation process. During this process, the total energy of the system remains constant. The addition and subtraction of energy can be performed by multiplying or dividing the velocity of atoms. In order to calculate the temperature and evaluate the temperature gradient, the heat flux region is divided into $n$ slabs, and the temperature $T$ in each slab is generated by the average temperature of all atoms in the slab, which can be written as

$$T = \frac{1}{3Nk_B} \sum_{i=1}^{n} m_i v_i^2$$  \hspace{1cm} (4)
where \( N \) is the total number of atoms in each slab, \( k_B \) is the Boltzmann constant, and \( v_i \) and \( m_i \) are the velocity and weight of each atom \( i \), respectively. Once the heat current becomes time independent, a stable temperature gradient along the heat flux direction is well established.

The thermal conductivities of monolayer MoSe\(_2\) are obtained by Fourier’s law of heat conduction:

\[
K_x = \frac{-Q}{A \cdot |\nabla T|} \tag{5}
\]

where \( Q \) and \( |\nabla T| \) are the heat flux and slope of temperature gradient along the \( x \) direction, respectively, and \( A \) is the cross-sectional area of heat flux. When calculating the in-plane thermal conductivity of the 2D monolayer structure, conventionally, the distance between adjacent layers in the bulk structure is selected as the layer thickness.\(^{30-32}\) In this work, the thickness of monolayer MoSe\(_2\) is set as 6.469 Å, as reported in previous literature,\(^{32-34}\) the heat flux of \( J_{in} = 3.204 \times 10^{-7} \) W is added to the heat source and the same amount \( J_{out} \) is subtracted from the heat sink.

Fig. 2 shows an example of the stable temperature gradient for MoSe\(_2\) nanoribbons along the armchair direction. The black squares represent temperature at the corresponding position of the system within the MD method and the red line stands for the linear fitting of the temperature gradient based on eqn (5). Near the heat source and heat sink regions, the kinetic energy and potential energy are at nonequilibrium due to the extremely fast energy exchange. Hence, these regions are removed in linear fittings.

3 Results and discussion

3.1 Size-dependent thermal conductivity

In the NEMD method, the size effect is significant when the sample size is shorter than the phonon mean-free path (MFP).\(^{35-38}\) To describe the size effect, we perform MD simulations to study the length dependence along the heat flux direction and the width dependence perpendicular to the heat flux direction. To analyze the width dependence on the thermal conductivity of monolayer MoSe\(_2\), a set of nanoribbons with different widths are investigated, whereas the length is fixed at 500 nm and the temperature is set at 300 K. The in-plane thermal conductivities are calculated using eqn (5), as shown in Fig. 3a. The thermal conductivity is converged with the system width, and the result clearly shows that the width of the system has no effect on the in-plane thermal conductivity. This is primarily due to the fact that the periodic boundary condition is applied to the monolayer MoSe\(_2\) system, which approximates an infinite system in perpendicular to the heat flux direction. Considering the utilization of computing resources, we employ the periodic boundary condition and 10 nm width for all systems in the calculation of the thermal conductivity of monolayer MoSe\(_2\).

To analyze the length dependence on the thermal conductivity of monolayer MoSe\(_2\), we present a comparative analysis for a set of nanoribbons with different lengths varying from 30 to 500 nm. The calculated in-plane thermal conductivity results are shown in Fig. 3b. One can find that the thermal conductivity shows a linearly increasing trend with the length varying from 30 to 90 nm. In these cases, the lengths of monolayer MoSe\(_2\) with 30, 50, 70 and 90 nm correspond to their own effective phonon MFP \( \lambda \) of 59, 61, 63 and 68 nm, respectively. The computed \( \kappa \) values rise from 5.92 to 10.33 W (m K\(^{-1}\)). The size effect is obvious when the length is not sufficiently large enough than MFP. As pointed out by An et al.,\(^{39}\) the thermal conductivity becomes dependent on the characteristic length of the system when the length is comparable to MFP in low-dimensional nanostructures. To reduce the size effect of length on the thermal conductivity, the investigated lengths of MoSe\(_2\) nanoribbons are enlarged to 100, 200, 300, 400 and 500 nm. Overall, the thermal

![Fig. 2](image-url)  
**Fig. 2** Temperature distributions along the armchair direction for MoSe\(_2\) nanoribbons in the steady state, the red line stands for the linear fitting of the temperature gradient result. The inset schematic is plotted to illustrate the NEMD simulation setup, the arrow represents the direction of the heat flux, and red and blue atoms indicate heat source and heat sink regions, respectively.

![Fig. 3](image-url)  
**Fig. 3** (a) Width dependence and (b) length dependence of in-plane thermal conductivity of monolayer MoSe\(_2\) along the armchair direction.
conductivity remarkably increases with the system length and the increase rate goes down gradually. Since low frequency acoustic phonons play a dominant role in the thermal transfer process of 2D materials, the number of excited low frequency waves increases as the length of the nanoribbons increases and more acoustic phonons facilitate the heat transfer process and increase the thermal conductivity. These facts are also applicable in our present system of monolayer MoSe$_2$.

To address the length dependence of the in-plane thermal conductivity, an inverse fitting procedure is employed to extrapolate the values of the infinite systems from our obtained value for the finite cases. The formula is proposed by Schelling et al.:

$$\frac{1}{\kappa(L)} = \frac{1}{k_\infty} \left( 1 + \frac{\lambda}{L} \right)$$  \hspace{1cm} (6)

where $\kappa_\infty$ is the intrinsic thermal conductivity of an infinite length system ($L \rightarrow \infty$) and $\lambda$ is the effective phonon MFP. The computing results of monolayer MoSe$_2$ nanoribbons along armchair and zigzag directions are shown in Fig. 4a. The results show that the thermal conductivity of monolayer MoSe$_2$ nanoribbons is very sensitive to temperature and length. As expected, the thermal conductivity increases with length at different constants of temperatures. Under the condition of constant length of nanoribbons, the thermal conductivity of monolayer MoSe$_2$ decreases upon heating from 300 to 700 K. The inverse of the thermal conductivity of finite MoSe$_2$ nanoribbons in both armchair and zigzag directions is plotted in Fig. 4b versus the inverse of the length at different temperatures.

By comparing the equation of the fitted lines with eqn (6), the thermal conductivity of infinite monolayer MoSe$_2$ is obtained. The fitted thermal conductivities of monolayer MoSe$_2$ are plotted in Fig. 5. The results clearly indicate that the zigzag nanoribbons have higher thermal conductivities than the armchair ones. This trend is in good agreement with what has been reported for other graphene-like 2D materials. The reported value of Debye temperature for MoSe$_2$ is 177.6 K.\(^{17}\) In Fig. 5, one can find that our calculated thermal conductivity with temperature can be well fitted with $T^{-1}$ function. This relationship is characteristic of phonon-mediated thermal transport limited by Umklapp scattering. A similar result is also found in a previous study on MoS$_2$ nanotubes.\(^{27}\)

At room temperature, the values of the thermal conductivities for armchair and zigzag nanoribbons are 17.758 and 18.932 W (m K)$^{-1}$, respectively. For comparison, some related theoretical and experimental results are also presented in Fig. 5. The realistic experiments report the $\kappa$ values of monolayer MoSe$_2$ varying from 11 to 35 W (m K)$^{-1}$,\(^{14,15}\) while previous theoretical predictions give the $\kappa$ values within the range of 15.9–44 W (m K)$^{-1}$.\(^{16,17,47,48}\) Our estimated $\kappa$ values at room temperature are close to the lower limit of the theoretical data, and well in the range of reported experimental values. The difference of the thermal conductivities between armchair and zigzag nanoribbons is 6% at room temperature, and this difference exhibits a decreasing trend with increasing temperature. Besides, we can clearly see that the lattice thermal conductivity of monolayer MoSe$_2$ reduces almost monotonically when the...
temperature increases from 300 to 700 K. Upon heating, most of the phonons with high frequency are excited and the Umklapp phonon scattering process is enhanced. As a result, the enhancement of phonon scattering can prominently limit the thermal conductivity of monolayer MoSe$_2$. The values of thermal conductivities at 700 K are lower by 41.94% and 44.74% than those at room temperature for armchair and zigzag nanoribbons, separately.

3.2 Vacancy-dependent thermal conductivity

So far, we have discussed the thermal conductivities of the pristine monolayer MoSe$_2$ nanoribbons along armchair and zigzag directions. However, in the experiments of preparing 2D materials, the localized defects such as vacancies inevitably appear in the crystal due to the imperfection of growth processing. Many works$^{49-52}$ have indicated that the defect engineering in the monolayer TMDs can further suppress the thermal transport and provide promising opportunities for tailoring their thermal conductivities. In this part, we explore the vacancy dependence of the thermal conductivities of monolayer MoSe$_2$ along the armchair direction. Three common types of vacancies are focused, (1) mono-Se vacancy (MSeV), (2) mono-Mo vacancy (MMoV), and (3) double-Se vacancy (DSeV), as shown in Fig. 6. For DSeV, three kinds of relative positions of two Se vacancies are also included with ortho (DSeV-$_o$), meta (DSeV-$_m$) and para (DSeV-$_p$) in Fig. 6(d)–(f), respectively.

The vacancy defects are generated by removing atoms from the pristine monolayer MoSe$_2$ nanoribbons and distributed in the samples randomly. The defect concentration $f$ is introduced by the ratio of removed atoms to the total number of available atoms in the pristine sample. In Fig. 7, the thermal conductivities of different defect types over the defect-concentration range of 0.1–0.55% are plotted on various sample lengths. We find that the thermal conductivities increase with increasing length but decrease with increasing defect-concentration. Similar scenarios have been seen in the cases of other 2D materials.$^{29,53}$ When the defect concentration is set at 0.3%, the $\kappa$ values changed from 7.87 to 13.08 W (m K)$^{-1}$ for the SSeV defect, from 7.09 to 11.84 W (m K)$^{-1}$ for the MMoV defect, and from 8.76 to 13.95 W (m K)$^{-1}$ for the DSeV-$_o$ defect, respectively, with different lengths varying from 100 to 500 nm. By fitting the $\kappa$ values versus the length with eqn (6), the corresponding $\kappa$ value of one defect at one defect density is obtained simultaneously.

The calculated relative thermal conductivities of monolayer MoSe$_2$ nanoribbons with different defect types and concentrations are shown in Fig. 8. It can be clearly seen that the thermal conductivities of monolayer MoSe$_2$, whatever the type of vacancy is, decreases monotonically with increasing defect concentration. A defect concentration of 0.5% for MSeV and DSeV-$_o$ types can result in a reduction of the thermal conductivities of monolayer MoSe$_2$ nanoribbons including (a) perfect, (b) MSeV, (c) MMoV, (d) DSeV-$_o$, (e) DSeV-$_p$ and (f) DSeV-$_m$. [Fig. 6]

![Fig. 6 Schematic representations of the perfect and defected monolayer MoSe$_2$ nanoribbons including (a) perfect, (b) MSeV, (c) MMoV, (d) DSeV-$_o$, (e) DSeV-$_p$ and (f) DSeV-$_m$.](image)

![Fig. 7 Length-dependent thermal conductivity of defective monolayer MoSe$_2$ for three vacancies at different defect concentrations.](image)

![Fig. 8 Variations of the thermal conductivities of monolayer MoSe$_2$ with respect to the concentrations of MSeV, DSeV and MMoV defects. The lines are the fitting curves.](image)
conductivity by ~35%, while the MMoV defect with the same \( f \) can result in a reduction of ~43%. These significant reductions of the thermal conductivities can be mainly attributed to the phonon-defect scattering. Fitting the simulation results in Fig. 7 gives \( \kappa_{\text{MoSe}_2/0} = (1 + 1.013 f)^{-1} \), \( \kappa_{\text{DSeV-o}} = (1 + 1.007 f)^{-1} \) and \( \kappa_{\text{MMoV/0}} = (1 + 1.527 f)^{-1} \) for MSeV, DSeV-o and MMoV types of defects, respectively, where \( \kappa_0 \) is the thermal conductivity of the pristine monolayer MoSe\(_2\) at 300 K. Interestingly, we find that the thermal conductivities of monolayer MoSe\(_2\) with MSeV defects are pretty close to those with DSeV-o defects, which is consistent with the study of monolayer MoS\(_2\).\(^{29}\)

In addition, it is also found that the thermal conductivity of monolayer MoSe\(_2\) drops sharply at a small defect concentration, and then is insensitive to the variation of the defect concentration after the defect ratio reaches ~0.3%.

As for DSeV, the defect concentration-dependent thermal conductivities of three different defect shapes (DSeV-o, DSeV-m and DSeV-p) are presented in the inset of Fig. 8. Our calculations show that when increasing defect concentration, thermal conductivities follow the sequence: \( \kappa(\text{DSeV-o}) > \kappa(\text{DSeV-p}) > \kappa(\text{DSeV-m}) \). At a defect concentration of 0.5%, the thermal conductivity is reduced by ~29% with the DSeV-p defect, while it is reduced by about ~27% with the DSeV-m defect. Obviously, these three kinds of DSeV defects have much less influence on the thermal conductivity than the SmoV defect. Thus, we can conclude that the atomic species of vacancy defects has more influence on the thermal conductivity of monolayer MoSe\(_2\) than the defect shape.

The above research results show that introducing a small number of defects can effectively reduce the thermal conductivity of monolayer MoSe\(_2\), and provide an opportunity for its applications in thermoelectric devices.

4 Conclusions

In summary, we have systematically investigated the role of size and defects in the thermal conductivity of monolayer MoSe\(_2\) by performing molecular dynamics simulations. Our calculations reveal that the thermal conductivity of MoSe\(_2\) nanoribbons is remarkably sensitive to the length, but insensitive to the width of the samples. At room temperature, the thermal conductivities of the monolayer MoSe\(_2\) predicted by NEMD are 17.758 and 18.932 W (m K\(^{-1}\)) in armchair and zigzag directions, respectively, very close to the values from previous computation. The thermal conductivity of monolayer MoSe\(_2\) decreases as the system temperature increases, and can be effectively tuned by changing the defect concentrations, especially at low concentrations. Introduction of 0.5% Se or Mo vacancies can decrease the thermal conductivities of the monolayer MoSe\(_2\) by ~35% and 43%, respectively. Overall, these results will help to understand the thermal transport properties of monolayer MoSe\(_2\) under the influence of size, temperature and defects, and provide a potential way to tune the thermal conductivity for thermoelectric devices.

Conflicts of interest

There are no conflicts to declare.

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