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COMPUTATIONAL STUDIES OF THERMAL PROPERTIES AND DESALINATION PERFORMANCE OF LOW-DIMENSIONAL MATERIALS

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COMPUTATIONAL STUDIES OF THERMAL PROPERTIES AND DESALINATION PERFORMANCE OF LOW-DIMENSIONAL MATERIALS

by

Hong Yang

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THEORETICAL STUDIES OF LOW-DIMENSIONAL MATERIALS THERMAL PROPERTIES AND DESALINATION PERFORMANCE

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Advisor: Xiao Cheng Zeng

During the last 30 years, microelectronic devices have been continuously designed and developed with smaller size and yet more functionalities. Today, hundreds of millions of transistors and complementary metal-oxide-semiconductor cells can be designed and integrated on a single microchip through 3D packaging and chip stacking technology. A large amount of heat will be generated in a limited space during the operation of microchips. Moreover, there is a high possibility of hot spots due to non-uniform integrated circuit design patterns as some core parts of a microchip work harder than other memory parts. This issue becomes acute as stacked microchips get thinner. In other applications, laser devices can generate heat fluxes up to 1000 W/cm² in less than 0.5 mm² areas. Light-emitting diodes also entail high heat intensities between 300 and 600 W/cm² due to extremely high power density. Therefore, it is of technological importance that heat dissipation can be well managed and controlled in microelectronics devices.

This thesis is mainly focused on the micro/nanoscale thermal conductivity and interfacial thermal resistance characterization and optimization in two-dimensional (2D) nanostructures, such as graphene, C₂N, C₃N, phosphorene, stanene, molybdenum disulfide, and molybdenum diselenide. Various approaches including non-equilibrium
molecular dynamics (NEMD) simulation, equilibrium molecular dynamics (EMD) simulation, and transient pump-probe approaches have been utilized to explore the thermal properties. Phonon behaviors have also been studied to explain the mechanism of heat transfer. Then various machine learning (ML) models such as linear regression, polynomial regression, decision tree, random forest, and artificial neural network have been employed to predict the thermal properties of 2D materials. In a different area of research, the water desalination performance of carbon nanotube with rim functionalization has been systematically investigated using molecular dynamics (MD) simulations.
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CHAPTER 1: Introduction

Micro/nano-electronics are essential components used in everyday devices such as a personal computer, smartphone, tablets, and wearable electronics. Mobile apps, video games, spreadsheets, and accurate weather forecasts: that’s just a sampling of the life-changing things made possible by the reliable, exponential growth in the power of computer chips over the past five decades. Heat transfer issues are grand challenges for today’s electronic and optoelectronic devices. Thermal energies are being generated in smaller and smaller volumes as operating frequencies increase, and device dimensions shrink, making the development of high-performance and cost-effective thermal pathways at the nanoscales timely and urgent. Due to the constraints of experimental thermal measurement at sub-nm level, theoretical studies including ab initio calculations and classical molecular dynamics (MD) simulations have been widely used to characterize micro/nanoscale thermal properties. Classical MD simulation is a powerful tool to treat thermal transport problems at the micro/nanoscale. It intrinsically includes full anharmonicity in atomic interactions and does not make any assumptions on the thermodynamic limit. Since the description of atomic trajectories is achieved by numerically solving Newton’s equations of motion, the MD method can deal with thermal transport problem in systems containing millions of atoms. Therefore, MD simulations have been used in both thermal conductivity ($\kappa$) and interfacial thermal resistance ($R$) research.\textsuperscript{1-8} Tremendous efforts have been devoted to developing empirical interatomic potential (EIP) fields that can be adopted in MD simulation. One common strategy to develop an EIP is to first obtain the properties of the material, e.g., crystal structure, cohesive energy, or phonon dispersion, from either first-principles calculations
or experimental measurements, and then parameterize the potential by best fitting those properties.$^9,^{10}$

The objective of this thesis is to characterize the thermal transport in 2D nanostructures with classical MD simulations and understand, from the atomic level, how and to what extent boundary/interface scattering affects the lifetime of phonons of different modes and reduces the thermal conductivity of the material. In the following sections, the detail introductions and methods toward the characterization of thermal transport in 2D materials will be given in Chapter 2, and three related works will be discussed in detail. In Chapter 3, the heat conduction at the interface of 2D materials is studied and four related works are present. In Chapter 4, supervised machine learning (ML) techniques have been used to predict thermal resistance between graphene and hexagonal boron-nitride ($h$-BN) layers with the limited input information. Chapter 5 introduces the design of chemical functionalization to enhance the water desalination performance of carbon nanotube (CNT) membranes. This work is inspired by my Original Proposal Oral (OPO) exam.
CHAPTER 2: Thermal transport in 2D materials

2.1 Introduction

It is well documented that the thermal conductivity of nanoscale and nanostructured materials can be significantly reduced in comparison with that of the bulk counterparts due to the strong boundary scattering of energy carriers (phonons or electrons). The emergence of high thermal conductivity two dimensional (2D) monolayer structures, such as graphene, phosphorene, hexagonal boron nitride, some transition metal dichalcogenides (TMDCs) materials, and hole-free polyaniline (PANI) structures have attracted enormous attention in recent years. Among these 2D materials, graphene stands out by itself with novel thermal properties\textsuperscript{2, 6, 7} and superb thermal conductivities of 3000~5000 W/m·K at room temperature.\textsuperscript{11} It is considered as the most promising candidate for resolving the thermal dissipation problems in nanodevices.\textsuperscript{12} However, the zero band gap property limits its applications in nanodevices such as field effect transistors (FETs).\textsuperscript{13-15} Even though modeling graphene nanoribbon\textsuperscript{16, 17} and electrically gating bilayer graphene\textsuperscript{18} could raise its band gap up to 400 meV, on the other hand, its mobility will lose accordingly. Therefore, considerable efforts have been devoted to seeking other 2D materials with desired and tunable bandgaps as well as inherently good thermal properties. The 2D TMDCs, such as MoSe\textsubscript{2} and MoS\textsubscript{2} are a possibility to fill the role based on their large direct band gap and extremely high switching on/off ability.\textsuperscript{19-21} Another group of 2D PANI with tunable bandgap and ferromagnetic properties, such as C\textsubscript{2}N, C\textsubscript{3}N and C\textsubscript{3}N\textsubscript{4}, has also garnered intensive research efforts due to their extraordinary set of attributes.\textsuperscript{22-27} The 2D phosphorene is a good candidate as well owing to the layer-dependent direct bandgaps and high electron/hole mobility.\textsuperscript{28-30}
In Chapter 2.2, I will first introduce two major MD simulation approaches I used in my previous studies to characterize the thermal conductivity of 2D materials, i.e., steady-state equilibrium method and steady-state non-equilibrium method. Then, some analyses methods that reveal the mechanism of heat transfer and phonon properties of 2D materials will also be discussed. Finally, three related works will be present in Chapter 2.3 to 2.5.

2.2 Characterize thermal transport of 2D materials

2.2.1 Steady-state non-equilibrium molecular dynamics

The non-equilibrium molecular dynamics (NEMD) approach can be further split into two branches based on the way to generate steady-state heat flux. By applying two heat reservoirs at the opposite ends of the system, a temperature gradient can be built in the heat flux direction, which is also named the direct NEMD (d-NEMD) method. Alternatively, a heat flux can be directly imposed to the system by adding/subtracting kinetic energies to/from hot and cold particles i.e., the reverse NEMD (r-NEMD) method. In this way, the total energy and total linear momentum are conserved; hence, no external thermostat is needed. Once the system has reached steady-state under constant heat flux, thermal conductivity $\kappa$ can be calculated based on Fourier’s law of heat conduction

$$\kappa = -\dot{q} / \nabla T ,$$

(1)

where $\dot{q}$ is heat flux; $\nabla T$ is temperature gradient. The heat flux $\dot{q}$ is defined as

$$\dot{q} = J / A_c \cdot \ell,$$

(2)
where $J$ is the added/extracted thermal energy and $A_c$ is the cross-sectional area. It is worth noting that if the heat flux flows in two opposite directions symmetrically, the thermal energy needs to be divided by a factor of 2 for $\dot{q}$ calculations. After the system reaches steady state, atoms along the heat flux direction are grouped into equal thickness slabs per section with each slab contains at least one layer of atoms. The kinetic energies of each slab will be recorded and used to calculate the temperatures via the energy equipartition equation:

$$< E > = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 = \frac{3}{2} N k_B T$$

(3)

where $v_i$ is the velocity of atom $i$ and $N$ is the number of atoms in a slab. The calculated temperatures of each slab will be averaged and grouped as the temperature gradient $\nabla T$ profile. During the NEMD process, kinetic energies are constantly changed in the heating/cooling areas for temperature controls. In this ultrafast energy exchange process, kinetic energy and potential energy within the heating/cooling regions are in a non-equilibrium state and phonon boundary scattering is extremely rapid at the interface. Therefore the temperature drop is non-linear in these regions and should be eliminated from the thermal conductivity calculations.$^{32-35}$

### 2.2.2 Equilibrium molecular dynamics Green-Kubo method

Generally speaking, if the to-be-measured system has low thermal conductivity and large system dimension, the NEMD approach takes relatively long simulation time and has significant boundary condition issues at interfaces. On the other hand, results calculated from the equilibrium molecular dynamics (EMD) method depend sensitively on the
initial conditions of each simulation, thus necessitating a large ensemble of simulations to obtain the averaged result. The slow convergence of the autocorrelation function further increases the computational demand, requiring long integration time periods.

In EMD Green-Kubo method (GKM) calculations the 2D material’s thermal conductivity is given by heat current autocorrelation function (HCAF),

\[
\kappa_{xy} = \frac{1}{k_B T^2 V} \int_0^\infty < J_x(t) \cdot J_y(0) > dt
\]  

(4)

where \( V \) is the system volume; \( k_B \) is Boltzmann constant; \( T \) is the temperature of system and \( J_x, J_y \) are the heat current along \( x \) and \( y \) directions. The angular brackets denote the average over time. The upper limit of HCAF integral time in the Eq.4 is infinite, while the integration time is finite in MD simulations. Thus, as long as the integral time upper limit we chose is longer than the time takes the current-current correlations converge to zero, the results are meaningful.

### 2.2.3 Phonon density of states

To help analyze the thermal conductivity results, phonon density of states (PDOS) are calculated by taking the Fourier transform of the velocity autocorrelation function (VACF)

\[
F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt e^{i\omega t} \frac{\langle v(0) \cdot v(t) \rangle}{\langle v(0) \cdot v(0) \rangle}.
\]  

(5)

Higher values of PDOS for a phonon with frequency \( \omega \) means more states are occupied by it. And zero PDOS means there is no phonon with frequency \( \omega \) exists in the system.
The PDOS analysis provides a quantitative means to assess the power carried by different phonon modes in a system.

### 2.2.4 Maxwell–Boltzmann distribution

To assure the temperature distribution in the 2D sheet has reached steady state before and after the heating/cooling process, atom velocities are extracted from the MD system and compared with Maxwellian velocity distribution at the same temperature. Once the system reaches steady state, the velocities of atoms within the whole system should follow the Maxwell–Boltzmann distribution

\[
P_M = 4\pi v^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{\frac{-mv^2}{2k_BT}}
\]

where \( P_M \) is the probability of an atom with velocity \( v \), \( m \) represents atomic mass, and \( k_B \) is Boltzmann constant. The simulated velocity distribution and the Maxwell–Boltzmann distribution are compared to confirm that the system has reached steady state.

### 2.3 Thermal conductivity of two-dimensional phosphorene sheet: a comparative study with graphene

#### 2.3.1 Introduction

Phosphorene, a two dimensional counterpart of black phosphorus arranged in stacked honeycomb lattices, possesses novel structural and electronic properties, \( e.g., \) the layer-dependent direct bandgaps (1.51 eV to 0.59 eV with layer numbers from 1 to 5), high electron/hole mobility (up to 1000 cm\(^2\)/V·s), as well as high current modulation (up to
which can be exploited for nanoelectronic applications. Through a mechanical cleavage method, phosphorene has been successfully isolated from crystalline black phosphorus. Phosphorene-based FETs exhibit high carrier mobility and extraordinary on/off ratios, which suggest its potential applications in nano-electronic devices. Graphene, another 2D monolayer structure, is a single layer of carbon atoms densely packed in $sp^2$ bonded honeycomb lattices. The strong and anisotropic $sp^2$ bonding and low mass carbon atoms in the microscopic structure give graphene exceptional physical and chemical characteristics compared with traditional carbon- and silicon-based materials. These extraordinary properties, e.g., well deformation beyond the linear regime, superconductivity with proper gate voltage, ballistic electronic propagation, realizations of the Klein paradox, and metal free magnetism, etc., have made graphene a promising candidate for the next generation nano-electronics.

Thermal transport in graphene and graphene-based materials has been extensively investigated by both experimental and numerical studies. And recently, various numerical approaches have been applied to calculate the thermal conductivity in phosphorene. By combining the density functional calculations and Peierl-Boltzmann transport equation (PBTE), Zhu et al. discovered a peculiar coexistence phenomenon of size-dependent and size-independent thermal conductivities in phosphorene. The computed $\kappa$ for armchair and zigzag phosphorene are 24.3 and 83.5 W/m·K respectively. The anisotropy in thermal conductivity is attributed to the orientation dependent group velocities and relaxation times. Significant crystallographic orientation dependence of thermal conductance is observed using first-principles calculations combined with the non-equilibrium Green’s function method. It is found that the zigzag-oriented thermal
conductance is enhanced when a zigzag-oriented strain is applied but decreases when an armchair oriented strain is applied; whereas the armchair-oriented thermal conductance always decreases when either a zigzag or an armchair oriented strain is applied. In another first-principles calculation, $\kappa$ of phosphorene are predicted as 36 and 110 W/m-K at 300 K along with its armchair and zigzag directions respectively. By solving the phonon Boltzmann transport equation (BTE) based on first-principles calculations, Qin et al. computed the $\kappa$ of phosphorene as 13.65 W/m-K (armchair) and 30.15 W/m-K (zigzag) at 300 K, showing an appreciable anisotropy along with different directions.

In our work, thermal conductivities of 2D phosphorene sheet in the armchair and zigzag directions are computed using large-scale classical MD simulation. Various phosphorene structures with lengths up to 500 nm are constructed. Periodic boundary conditions are applied in the width direction of all cases to eliminate the size effect. Non-equilibrium molecular dynamics approach is used for the thermal conductivity characterization. As a comparative study, $\kappa$ of graphene in the armchair and zigzag directions with equivalent dimensions are computed. Detailed PDOS analyses are performed to help explain the thermal conductivity differences between phosphorene and graphene. Temperature dependence of thermal conductivity is explored from 100 to 400 K.

2.3.2 Methods

All MD simulations in this work are performed using the open-source classical MD code, large-scale atomic/molecular massively parallel simulator (LAMMPS). In this work, a Stillinger-Weber (SW) potential optimized and adapted using the valence force field (VFF) model is used to describe the phosphorene system. Atomic configurations of phosphorene are depicted in Fig. 1. Periodic boundary conditions are applied in the width
direction. To examine the effect of the size perpendicular to the heat flux direction, we varied the domain width from 5.1 to 20.4 nm. Similar thermal conductivities were obtained from the simulations with different widths. As a result, a moderate width of ~10 nm is chosen for all simulations to reduce the computational cost. In the SW potential, the top and bottom P atoms are treated as two atomic types. Thermal conductivities along with zigzag (x) and armchair (y) directions are calculated respectively in this work. The initial buckling distance is set as 2.13 Å. The second generation of the Brenner potential, reactive empirical bond-order (REBO) potential based on the Tersoff potential with interactions between C–C bonds, is employed to model the graphene system. The integration time step is 0.5 fs for all simulations in this work.

**Figure 1.** (a) Top view of the monolayer phosphorene structure. The zigzag boundary is along the x direction and armchair is along the y direction. (b) Front view of phosphorene
from the $x$ direction. The top and bottom P atoms are grouped as two atomic types for accurate inter/intra-layer interaction descriptions. (c) Side view of phosphorene from the $y$ direction.

The thermal conductivity of the 2D sheet is evaluated from the r-NEMD approached based on Fourier’s law. In previous experimental studies of graphene's thermal conductivity, Balandin et al.\textsuperscript{60,61} used the value of 0.35 ± 0.01 nm as the thickness of single layer graphene. Most of the numerical work studying the thermal conductivity of graphene chose the value of 3.35 Å as the thickness.\textsuperscript{2,62-65} Therefore, our calculation of graphene's thermal conductivity uses the same thickness value. This provides a common base when comparing our results with those by other researchers. The thickness of phosphorene is chosen as the bulk layer separation distance 5.25 Å, which is around the same value as used in previous studies.\textsuperscript{53, 54, 66, 67} Since the calculated thermal conductivity scales linearly with layer thickness, our results can be adjusted easily for other options.

\subsection*{2.3.3 Results and discussions}

\subsection*{2.3.3.1 The predictions of phosphorene and graphene’s $\kappa$}

Figure 2(a) illustrates the r-NEMD setup in the 9.9 × 40.2 nm$^2$ ($x \times y$) phosphorene for heat conduction in the armchair direction. Periodic boundary conditions are applied in the width ($x$) direction to eliminate the size effect. Free boundaries are used in the heat flux $y$ direction and out-of-plane $z$ direction. The outmost layers of P atoms denoted in black are fixed. For thermal equilibrium calculations, 500 ps canonical ensemble ($NVT$) and 500 ps micro-canonical ensemble ($NVE$) calculations are performed on the phosphorene system.
successively. After the system reaches thermal equilibrium at a given temperature of 300 K, four layers of atoms are grouped at each end to create the heat bath and heat sink respectively. Thermal energy $Q_{in} = 3.23 \times 10^{-8}$ W is added to the heat bath at each time step and the same amount $Q_{out}$ are subtracted from the heat sink constantly for another 2 ns. Temperature distribution along the heat flux direction at steady state is shown in Fig. 2(b). The calculated thermal conductivity of the $[9.9 \times 40.2 \text{ nm}^2]$ phosphorene in armchair direction is 3.9 W/m-K and $\kappa$ of similar sized $[39.9 \times 10.0 \text{ nm}^2]$ phosphorene in zigzag direction is 11.7 W/m-K. The thermal conductivity anisotropy can be quantified by the ratio ($\chi$) of maximum and minimum direction-dependent thermal conductivities. A factor of $\chi = 3$ anisotropy is attained from the above results, the same as shown in previous calculations. As a comparative study, thermal conductivities of graphene in armchair direction and graphene in zigzag direction of similar dimensions are calculated, which are 209.3 W/m-K and 213.6 W/m-K respectively.
**Figure 2.** (a) Illustration of the r-NEMD process. Black atoms at the boundaries of the system are fixed in position. Free boundary is used out-of-plane z direction. Periodic boundary condition is applied in the width (x) direction. Red and blue areas are denoted as heat bath and heat sink respectively. (b) Temperature distribution along the heat flux direction (y) in the 9.94 × 40.19 nm² (x × y) phosphorene in the armchair direction. The red solid line denotes the linear fitting results. Atomic configuration of phosphorene after the heating/cooling process is shown in the inset.

To assure the temperature distribution in the 2D sheet has reached steady state before and after the heating/cooling process, atom velocities are extracted from the MD system and compared with Maxwellian velocity distribution at the same temperature. Taking the [9.94 × 40.19 nm²] armchair phosphorene as an example, after successive *NVT* and *NVE*
simulations, a snapshot of the atom velocities is recorded. The statistical velocity distribution is mapped across the range from 0 to 1400 m/s, as is shown in Fig. 3(a). Another snapshot is taken after the 2 ns heating/cooling process is finished. Figure 3(b) demonstrates that the temperature gradient along the heat flux direction is constant before data collection.

![Figure 3](image.png)

**Figure 3.** Atomic velocity distributions in 9.94 × 40.19 nm² (x × y) armchair phosphorene. (a) Velocity distribution after 500 ps NVT and 500 ps NVE simulations. (b) Velocity distribution after 2 ns r-NEMD simulations.

**2.3.3.2 The length dependence of phosphorene and graphene’s κ**

In micro/nanoscale structures, the predicted thermal conductivities become dependent on system length (l) in the heat flux direction when the system dimension is comparable or smaller than the materials intrinsic phonon mean free path (MFP). Thermal transport
becomes ballistic at small length scales when $l < \text{MFP}$. Within the ballistic regime, certain phonon modes can transmit from the heat-source to the heat-sink without scattering. As the system length increases, the transport will gradually switch to diffusive. Due to their reduced MFP, the ballistic thermal transport contributes less to the overall thermal conductivity. Therefore the calculated $\kappa$ result changes with length at small scales. Length dependence of thermal conductivities for phosphorene in the armchair and zigzag directions and graphene in the armchair and zigzag directions are presented in Fig. 4(a). Lengths of 10, 20, 40, 80, 120, 160, 300, 400 and 500 nm are simulated. Widths of all 2D systems have the same value of $\sim$10.0 nm with periodic boundary conditions. Figure 4(a) shows that the thermal conductivities of phosphorene are around one order of magnitude lower than those of graphene. The computed thermal conductivity of phosphorene in armchair direction ranges from 2.0 to 21.7 W/m·K, and 6.2 to 73.6 W/m·K for phosphorene in the zigzag direction. On the other hand, the calculated $\kappa$ results of graphene in the armchair and zigzag direction range from 73.0 to 657.6 W/m·K and 75.0 to 690.6 W/m·K, respectively. The measured thermal conductivity of graphene from experiments is around 3000 – 5000 W/m·K for sample length of $\sim$10 µm.\textsuperscript{11,60} This high thermal conductivity exceeds that of graphite and is partly attributed to the long phonon MFP. Numerical simulations have reported much smaller $\kappa$ values of graphene due to the confined system sizes and stronger phonon boundary scatterings.\textsuperscript{68, 69} The calculation results in Fig. 4(a) indicate that the anisotropic thermal transport in phosphorene is much more significant than that in graphene. This high anisotropy is partially attributed to the direction-dependent group velocities and anisotropic phonon dispersion in phosphorene.\textsuperscript{53} A maximum factor of $\chi = 4.9$ anisotropy is observed in 300
nm length phosphoranes. It is speculated that the distinct pucker structures in the armchair and zigzag directions also contributes to the strong anisotropic thermal conductivities in phosphorene. As is shown in Fig. 1(b), the top and bottom P layers in phosphorene extend alternatively in the armchair direction. While in the zigzag direction shown in Fig. 1(c), the top and bottom P atoms are superposed in the out-of-plane direction continuously. On the other hand, the anisotropic thermal transport in graphene is attributed to two major factors: 1) different phonon boundary scatterings along with altered chiral directions; 2) strong localization of phonons in regions near and at the edges of graphenes, especially armchair graphenes, which suppresses thermal transport. 70-72
Figure 4. (a) Thermal conductivity of phosphorene and graphene in the armchair or zigzag directions versus length. Second order polynomial fittings (dashed lines) are applied to the data sets to guide the eye. (b) The corresponding linear relationship
between $1/\kappa$ and $1/L$ of 160 – 500 nm phosphorene and graphene. $a$- and $z$- stand for armchair and zigzag directions respectively.

The calculated thermal conductivity results are fitted using a linear function for lengths of 160 – 500 nm and the results are shown in Fig. 4(b),

$$\frac{1}{\kappa'} = \frac{1}{\kappa_\infty} \left( \frac{l}{L} + 1 \right),$$

where $l$ is effective phonon MFP and $\kappa_\infty$ is thermal conductivity for 2D sheet. The fitting results are shown in Fig. 4(b). It has been suggested that Eq. 7 is valid only when the system size is comparable or larger than the phonon MFP that dominates thermal transport. Qin et al. calculated the representative MFP of the armchair and zigzag phosphorene at 83 nm and 66 nm correspondingly. For confined graphene systems used in MD simulations, the effective phonon MFP ranges from 80 to 240 nm. Therefore, the system sizes used in the linear extrapolation fulfill the linear fitting requirement. The predicted thermal conductivities for infinite length armchair and zigzag phosphorene 2D sheets are 59.7 and 112.4 W/m·K respectively, which are on the same orders of magnitude with the first-principles predictions. To test the convergence of the predicted $\kappa$ results, extrapolations using only 300, 400 and 500 nm lengths are also performed. The calculated $\kappa$ results for phosphorene in the armchair and zigzag directions are 67.5 and 108.9 W/m·K. The fitting results using only 300, 400 and 500 nm points are shown in Fig. 4(c). The averaged thermal conductivity results for armchair and zigzag phosphorene 2D sheets can be presented as $63.6^{+3.9}_{-3.9}$ and $110.7^{+1.75}_{-1.75}$ W/m·K respectively. Similarly, the extrapolated $\kappa$ for armchair and zigzag graphene 2D sheets using four data points are
970.9 and 1027.8 W/m·K individually, and 1046.0 and 1145.9 W/m·K using only three data points. The averaged results are expressed as 1008.5$^{±37.6}$ and 1086.9$^{±59.1}$ W/m·K for armchair and zigzag graphene 2D sheets. The results deviations range from 1% to 6% for all cases, which can be considered as good convergences for the predicted $\kappa$ values of both phosphorene and graphene.

2.3.3.3 The PDOS of phosphorene and graphene

To gain further insights into the thermal conductivity differences between phosphorene and graphene, PDOS are calculated for armchair phosphorene and graphene with dimensions of $10 \times 40 \text{ nm}^2$. Due to the decoupled nature between in-plane and out-of-plane phonons in graphene, decomposed PDOS in $x$, $y$ and $z$ directions are calculated separately for both structures. The calculated results are shown in Figs. 5(a)-(d). The reported PDOS of graphene soundly matches previous MD simulations results,$^8, 76-78$ which illustrates that the flexural branch (ZA) dominates the low-frequency acoustic phonons while the in-plane longitudinal (LA) and transverse (TA) branches occupy the high-frequency phonons. Compared with graphene, the vibrational frequencies that can be excited in phosphorene are severely limited. The active phonon frequencies in phosphorene range from 0 to 15 THz, indicating a longer MFP compared with graphene and stronger phonon boundary scatterings, which may be the reason for the significantly lower thermal conductivities. While in graphene, the lateral phonons dominate the high frequencies up to 52 THz and flexural phonon occupies the low-frequency acoustical branches. The observed remarkable differences in PDOS could account for the vast disparity in the thermal conductivities of phosphorene and graphene. By measuring the
thermal transport of single layer graphene supported on amorphous SiO$_2$, Seol et al.$^7$ 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 BTE, Lindsay et al.$^{80,81}$ calculated the lattice thermal conductivity of graphene at 300 K and it turned out that the dominant contribution to $\kappa_L$ comes from the ZA branch, which is greater than the combined TA and LA contributions. Unlike those in graphene, the in-plane and out-of-plane phonons in phosphorene have the same PDOS frequencies in all directions, as is shown in Figs. 5(b)-(d). The differences from the flexural phonon contributions also contribute to the different $\kappa$ results in phosphorene and graphene.
Figure 5. (a) PDOS of armchair phosphorene and graphene, respectively at temperature 300 K. (b-d) Decomposed PDOS in $x$, $y$ and $z$ directions.

2.3.3.4 The temperature dependence of phosphorene and graphene’s $\kappa$

In practical applications, phosphorene and graphene could be placed in various working conditions at different temperatures. Therefore it is necessary to investigate the temperature dependence of their thermal conductivity. Aside from the 300 K used in previous calculations, temperatures of 100, 150, 200, 250, 350 and 400 K are applied and the calculated $\kappa$ results are shown in Fig. 6. Dimensions of phosphorene in the armchair and zigzag directions are $9.94 \times 40.19$ nm$^2$ and $39.93 \times 9.99$ nm$^2$; and $9.84 \times 40.05$ nm$^2$, $39.98 \times 10.01$ nm$^2$ for graphene in the armchair and zigzag directions, respectively. Quantum corrections are applied to the MD temperatures of graphene, as is shown in the top $x$ axis of Fig. 6. It is observed from Fig. 6 that $\kappa$ of both phosphorene and graphene decrease monotonically with temperature, which is as expected for phonon dominated crystalline materials. As the system temperature increases, higher frequency phonons become activated and the phonon population grows. As a result, the Umklapp phonon scatterings become more severe, which directly reduces the thermal conductivity in the 2D sheet. The maximum $\kappa$ reduction of phosphorene in the armchair and zigzag directions, graphene in the armchair and zigzag directions are calculated as 64%, 58%, 11%, and 13%. The calculated thermal conductivity results are fitted with an inverse relationship with temperature ($\kappa \sim 1/T$). It can be observed that the fitting curves soundly match the calculated thermal conductivities, indicating the Umklapp scattering is dominate at this temperature range.$^{82}$
2.3.4 Conclusion

Using large-scale classical MD simulations, thermal conductivities of monolayer phosphorene are computed and compared with graphene. Using a linear extrapolation method, thermal conductivities of the armchair and zigzag phosphorene 2D sheets are predicted as $63.6^{+3.9}_{-3.9}$ and $110.7^{+1.75}_{-1.75}$ W/m·K respectively. In comparison, $\kappa$ of the armchair and zigzag graphene are calculated to be $1008.5^{+37.6}_{-37.6}$ and $1086.9^{+59.1}_{-59.1}$ W/m·K individually. The calculated thermal conductivities of phosphorene are around one order of magnitude lower than those of graphene. On the other hand, the high scale of anisotropy exceeds...
that of graphene. Detailed PDOS analyses reveal that the in-plane and out-of-plane phonons in phosphorene share the same peak frequencies from 0 – 15 THz, while in graphene, the lateral phonons dominate the high frequencies up to 52 THz and flexural phonon occupies the low frequency acoustical branches. Therefore, it can be speculated that different thermal conductivities between phosphorene and graphene are mainly from two aspects: 1) severely limited vibrational frequencies in phosphorene compared with graphene; 2) fewer contributions from the out-of-plane flexural phonons in phosphorene. Temperature dependence of thermal conductivity is investigated and a monotonic decreasing trend is found for both structures. Our work provides a fundamental understanding of thermal transport in phosphorene and can be considered for improving certain nano-device performance with phosphorene-based thermal interface materials.

2.4 Thermal conductivity of monolayer MoSe₂: a comparative study with MoS₂

2.4.1 Introduction

A group of 2D materials is categorized as TMDCs, such as MoSe₂ and MoS₂. By mechanical exfoliating monolayer MoSe₂ and MoS₂ from their bulked structures, they can obtain direct band gaps of 1.55 eV and 1.8 eV respectively, which make them promising candidates in FETs and other optical devices. MoS₂-based FETs were reported to possess relatively low mobility of 100 cm²/V·s but an extremely high switching on/off (~10⁸) ability compared to graphene. The bandgap of MoSe₂ matches the optimum bandgap of single-junction solar cells and photoelectrochemical devices, enabling its applications of energy conversion involving the solar spectrum. As stated
by Huang et al.\textsuperscript{89}, the enhanced photoluminescence of in-plane heterojunctions between monolayer MoSe\textsubscript{2} and WSe\textsubscript{2} allows their usage as in-plane transistors and diodes. The good thermal stable direct semiconductor properties together with the unique physical and optical properties also facilitate the extensive employment of monolayer MoSe\textsubscript{2} and MoS\textsubscript{2} in sensors, saturable absorber of Q-switched Erbium-doped fiber laser, photocatalyst, and electroluminescence.\textsuperscript{90-95}

As monolayer MoSe\textsubscript{2} and MoS\textsubscript{2} are promising candidates for the next generation of nanoelectronics materials, the studies of their thermal conductivities become timely and crucial. Some former works have reported the thermal conductivity of monolayer MoSe\textsubscript{2} and MoS\textsubscript{2} at room temperature both theoretically and experimentally. Previous MD simulation studies usually underestimated the $\kappa$ of monolayer MoS\textsubscript{2} at around 1.35~5.8 W/m-K due to the potential employed.\textsuperscript{96, 97} While, first-principles calculations and experiments predicted relative larger values. From temperature-dependent Raman spectroscopy, Yan et al.\textsuperscript{98} measured the $\kappa$ of monolayer MoS\textsubscript{2} at 34.5 ± 4 W/m-K. With optothermal Raman Technique, Zhang et al.\textsuperscript{99} found the $\kappa$ of monolayer MoS\textsubscript{2} and MoSe\textsubscript{2} to be 84 ± 17 and 59 ± 18 W/m-K respectively. Cai et al.\textsuperscript{100} obtained a $\kappa$ of 23.2 W/m-K for monolayer MoS\textsubscript{2} using density functional perturbation theory (DFPT) based first-principles calculation. By combining PBTE and first-principles calculation, Li et al.\textsuperscript{101} predicted a $\kappa$ of 83 W/m-K for monolayer MoS\textsubscript{2}. With a similar method, Gu et al.\textsuperscript{102} estimated the $\kappa$ of monolayer MoS\textsubscript{2} and MoSe\textsubscript{2} equal to 103 W/m-K and 54 W/m-K correspondingly. In spite of the numerous studies on MoS\textsubscript{2}, however, to our best
knowledge, the thermal properties of MoSe$_2$ have not yet been investigated comprehensively by molecular dynamics approach.

In this work, thermal conductivities of monolayer MoSe$_2$ 2D sheet in the armchair and zigzag directions are studied r-NEMD approach$^{31}$ based large-scale classical MD simulation. Meanwhile, thermal conductivities of monolayer MoS$_2$ 2D sheet are also investigated for comparison. Size effects on the thermal conductivity of monolayer MoSe$_2$ and MoS$_2$ have been studied by analyzing the calculated thermal conductivities against the system length and width. Temperature and energy dependences of thermal conductivity for monolayer MoSe$_2$ and MoS$_2$ are also discussed in this work. Finally, the thermal conductivities of monolayer MoSe$_2$ and MoS$_2$ 2D sheet in both armchair and zigzag directions are confirmed by GKM calculations.$^{36}$

2.4.2 Methods

All MD simulations in this work are performed by LAMMPS.$^{55}$ The SW potential developed by Kandemir $et$ $al.$$^{103}$ is used to describe the interatomic interactions of monolayer MoSe$_2$ and MoS$_2$. In order to get an accurate description of the 3-body bond bending term, the top layer Se/S atoms are treated as different atomic type atoms from the bottom layer Se/S atoms. This SW potential was developed by fitting lattice constants, bond lengths, elastic constants and vibrational properties of monolayer MoSe$_2$ and MoS$_2$ via the particle swarm optimization method.$^{104}$ Thermal properties generated by this potential have good agreements with previous first-principles predictions$^{100-102}$ and experiment measured results$^{98, 105, 106}$, therefore it is credible to use this potential to evaluate the thermal conductivities of monolayer MoSe$_2$ and MoS$_2$. 
Atomic configuration schematics of monolayer MoSe$_2$ and MoS$_2$ are given in Fig. 7. Their thermal conductivities along with the armchair ($x$) and zigzag ($y$) directions are calculated by the r-NEMD method and verified by GKM method at the end of this work. For r-NEMD method, periodic boundary condition is applied to the width direction and fixed boundary condition is used in the heat flux direction. The out-of-plane $z$ direction is also applied with fixed boundary condition with 20 Å vacuum spacing to avoid layer-layer interactions. Atoms within the outmost layer at both ends are fixed. The next four layers of atoms at both sides are grouped together as heat bath and heat sink regions. The thicknesses of the monolayers are half of their vertical lattice constant $c$. For monolayer MoSe$_2$, the thickness is 6.469 Å$^{107}$ and for MoS$_2$ the thickness is 6.1475 Å$^{108}$. The atomic behaviors are integrated at each time step of 0.5 fs for all simulation works. At the beginning of MD simulation, the monolayer is placed under $NVT$ for 500 ps at 300 K and then moved to $NVE$ for another 500 ps. After thermal equilibrium calculations, the system remains in the $NVE$ ensemble and r-NEMD method is applied to the thermal conductivity calculations for additional 2.5 ns. At the last 500ps of NEMD simulation, the system temperature is averaged for thermal conductivity calculations.
**Figure 7.** (a) Top view, b) front view, c) side view of the monolayer MoSe$_2$ structure. The top and bottom Se atoms are treated as two different atomic types in the SW potential. (d) Top view, e) front view, f) side view of the monolayer MoS$_2$ structure. The top and bottom S atoms are treated as two atomic types as well.

### 2.4.3 Results and discussions

Figure 8(a) is the schematic of r-NEMD simulation in the armchair direction. Heat flux of $J_{in} = 9.74 \times 10^{-7}$ W is added to the heat bath at each time step and the same amount $J_{out}$ is subtracted from the heat sink simultaneously for 2.5 ns. Fig. 8(b) is an example of the temperature gradient along the heat flux direction for a 43.15 nm long armchair MoSe$_2$ nanoribbon. The black dots represent MD calculated temperatures and the red line stands for the linear fitting result based on Eq. (1).
Figure 8. (a) Schematic of the r-NEMD simulation method. The outmost layer black atoms are fixed. Periodic boundary condition is employed in the $x$ (width) direction. Free boundary is applied to $z$ (out-of-plane) direction. (b) Temperature gradient along the heat flux direction of 43.15 nm long armchair monolayer MoSe$_2$ nanoribbon. Red line stands for the linear fitting results of MD calculated temperature for each atom (black dot). Atomic configuration after heat flux reached steady state is shown in the inset.

2.4.3.1 Effects of system dimensions on $\kappa$

In order to analyze the size effect on the thermal conductivity of monolayer MoSe$_2$ system in the armchair and zigzag direction, two sets of models are made with different length, while the width is constant at $\sim$10 nm. Specifically, for the armchair direction $\kappa$ calculations, length varies from 10.64, 21.48, 43.15, 86.48, 163.46, 326.53, 433.16, to 519.83 nm. For the zigzag direction $\kappa$ calculations, length varies from 10.04, 20.25, 40.66,
81.48, 163.12, 326.40, 408.04, to 530.06 nm. As summarized in Fig. 9(a), the computed $\kappa$ shows a monotonic increasing trend with the length in both directions. For armchair direction, with the growth of system length, the $\kappa$ increases from 2.02 to 23.65 W/m·K. For zigzag direction with similar length changes, the $\kappa$ rises from 2.11 to 24.15 W/m·K, indicating the isotropy of thermal conduction for monolayer MoSe$_2$. To dispel size effect and predict the $\kappa$ of monolayer MoSe$_2$ 2D sheet, the linear function Eq.7 is used to fit the calculated $\kappa$ of limited length monolayer MoSe$_2$ nanoribbons.\textsuperscript{36} The fitting results of $1/\kappa$ with $1/L$ are given in Fig. 10(a). With 5 data points, the fitted $\kappa$ of monolayer MoSe$_2$ 2D sheet in the armchair and zigzag direction are 41.34 and 41.49 W/m·K respectively. With 4 data points, the fitted $\kappa$ of monolayer MoSe$_2$ 2D sheet in the armchair and zigzag directions are 43.29 and 42.43 W/m·K. The different between 4-points fitting and 5-points fitting are only 4.50% and 2.22% individually. Therefore, it is safe to conclude that, at room temperature, thermal conductivities of monolayer MoSe$_2$ 2D sheet are $42.31^{+0.98}_{-0.98}$ and $41.96^{+0.47}_{-0.47}$ W/m·K in the armchair and zigzag directions respectively. These values are very close to the first-principles $\kappa$ prediction of 54 W/m·K\textsuperscript{102} and experiment value of 59 $\pm$ 18 W/m·K\textsuperscript{99} at room temperature.
Figure 9. (a) Length dependence of thermal conductivities for monolayer MoSe$_2$ and MoS$_2$ nanoribbons in the armchair and zigzag directions. Second order polynomial fittings (dashed lines) are applied to provide a straightforward view. (b) Width dependence of thermal conductivity for 43.15 nm long armchair MoSe$_2$ nanoribbon, results converged at 5.90 W/m·K.

The size effect of monolayer MoS$_2$ is also studied. As shown in Fig. 9(a), the $\kappa$ with length of 10.22, 20.62, 41.43, 83.04, 160.23, 299.85, 415.92, and 499.50 nm in armchair direction and with length of 9.96, 20.07, 40.30, 80.76, 161.68, 303.30, 485.37 and 485.37 nm in zigzag direction are calculated. For the armchair direction, with larger system
length, the calculated \( \kappa \) increases from 5.51 to 62.23 W/m·K. For zigzag direction with similar length changes, the \( \kappa \) rises from 5.49 to 60.13 W/m·K, proving the isotropy of thermal conduction for monolayer MoS\(_2\). With 5 data points, the fitted \( \kappa \) of monolayer MoS\(_2\) 2D sheet in the armchair and zigzag direction are 99.50 and 103.31 W/m·K. With 4 data points, the fitted \( \kappa \) of infinite long monolayer MoSe\(_2\) are 106.50 and 109.05 W/m·K respectively. The different between 4-points fitting and 5-points fitting are 6.57% and 5.26% individually. Therefore, we can predict the room temperature thermal conductivities of monolayer MoS\(_2\) 2D sheets to be 103.00\(^{+3.50}_{-3.50}\) and 106.18\(^{+2.87}_{-2.87}\) W/m·K in the armchair and zigzag directions correspondingly. These values are consistent with the first-principles calculated monolayer MoS\(_2\) thermal conductivity of 103 W/m·K\(^{102}\) and the experiment value of 84 ± 17 W/m·K\(^{99}\) at room temperature.

We tested 5.10, 10.04, 20.25, 30.45 and 40.66 nm width monolayer MoSe\(_2\) structures with the same length of 43.15 nm. As presented in Fig. 9(b), the thermal conductivity is converged with system width. To reduce the computational cost, we used systems of 10.04 nm width with periodic boundary condition in monolayer MoSe\(_2\) and MoS\(_2\) thermal conductivity calculations.
Figure 10. (a) The linear fitting of $1/\kappa$ and $1/L$ for armchair and zigzag MoSe$_2$ nanoribbons based on 5 data points and 4 data points. (b) The linear fitting of $1/\kappa$ and $1/L$ for armchair and zigzag MoS$_2$ nanoribbons based on 5 data points and 4 data points.

2.4.3.2 Effects of temperature on $\kappa$

In order to determine the temperature effect, $\sim$160 nm long monolayer MoSe$_2$ and MoS$_2$ systems are put into 100, 200, 300, 400 and 500 K heat bathes separately and the
calculated $\kappa$ are summarized in Fig. 11(a). For monolayer MoSe$_2$, $\kappa$ in both armchair and zigzag directions have a monotonic decreasing trend with the increasing temperature. At high temperature, more phonons with higher frequency would be excited and involve in thermal transport, as a result, the total amount of phonon population is raised. Therefore, the Umklapp phonon scatterings become more active and prominently limit the thermal conductivity of monolayer MoSe$_2$ at high temperature. When the temperature of monolayer MoSe$_2$ increases from 100 to 500 K, $\kappa$ is reduced by 43.66% and 44.37% in the armchair and zigzag directions individually. The $\kappa$ is fitted with an inverse relationship with temperature ($\sim 1/T$) as shown in Fig. 11(a). The fitting curves well match the calculated results, indicating the Umklapp scattering is dominant at this temperature range. The decreasing speed and trend of thermal conductivity in armchair direction are similar to those in the zigzag direction, proving the isotropy of temperature effects on monolayer MoSe$_2$ thermal conduction. Likewise, the temperature effect on monolayer MoS$_2$ thermal conductivity is also isotropic. With the temperature of monolayer MoS$_2$ increasing from 100 to 500 K, $\kappa$ is reduced by 48.70% and 46.86% in the armchair and zigzag directions. As indicated in Fig. 11(a), the Umklapp scattering is the main cause at this temperature range for MoS$_2$ as well.

Besides, the influence of heat flux on the predicted thermal conductivity is investigated. By altering the added/subtracted heat flux of 43.15 nm long armchair MoSe$_2$ system from 2.99x10$^9$ to 29.90x10$^9$ W/m$^2$, the temperature gradient increases from 13 to 157 K. As presented in Fig. 11(b), the thermal conductivity is converged with heat flux. The change of added/subtracted heat flux amount to/from the system is associated with the change of temperature gradient; however, it has no influence on the result of thermal conductivity.
Figure 11. (a) Temperature dependence of thermal conductivity for ~160 nm long monolayer MoSe$_2$ and MoS$_2$ nanoribbons in the armchair and zigzag directions. Fitting results by the inverse relationship with temperature ($\kappa \sim 1/T$) are plotted with solid lines. (b) Energy dependence of thermal conductivity for 43.15 nm armchair MoSe$_2$ nanoribbons, results converged at 6.01 W/m·K, indicating thermal conductivity is independent of heat flux.

2.4.3.3 Comparative study with GKM

The thermal conductivities of monolayer MoSe$_2$ and MoS$_2$ 2D sheets at room temperature are also evaluated via GKM based on Eq. 4 to confirm our NEMD results. Once the
system reaches equilibrium, the heat current of each 10 time steps is saved for \(1.6 \times 10^6\) steps, giving an HCAF integration time of 800 ps. The MD simulation time is 8 ns which is 10 times larger than the HCAF integration time to obtain an accurate statistical average. To diminish the influence of HCAF noise on thermal conductivity predictions, for each monolayer, its thermal conductivity is calculated 10 times with different initial velocity seed. For GKM calculations, periodic boundary conditions are applied to both length and width directions, while the \(z\) direction is fixed boundary condition with 20 Å vacancy band. Therefore, the size effect of GKM method is much smaller than that of NEMD method.\(^{36}\) For size effect analysis, \(\kappa\) of monolayer MoSe\(_2\) and MoS\(_2\) systems containing 5×5 to 60×60 unit cells are calculated. As indicated in Fig. 12, \(\kappa\) of monolayer MoSe\(_2\) and MoS\(_2\) are both converged at 50×50 unit cells. So, the systems containing 50×50 unit cells, which are 34.02 nm and 32.76 nm long for monolayer MoSe\(_2\) and MoS\(_2\), are used for GKM method calculations.
Figure 12. GKM method size dependence of thermal conductivities for monolayer MoSe$_2$ and MoS$_2$ 2D sheets in the armchair and zigzag directions. Averaged thermal conductivities over the armchair and zigzag directions are shown in the solid line with a symbol to give a direct view of size convergence.

The averaged HCAF functions (Figs. 13(a) and (b)) of monolayer MoSe$_2$ decay to 0 after around 150 ps and the overall $\kappa$ of 10 trails are converged after 250 ps for both armchair and zigzag monolayer MoSe$_2$ as presented in Figs. 14(a) and (b). The $\kappa$ of monolayer MoSe$_2$ 2D sheet are then predicted by averaging the value of overall $\kappa$ from 250 to 800 ns and giving the results of $44.38_{-2.08}^{+2.08}$ and $44.63_{-2.50}^{+2.50}$ W/m·K in the armchair and zigzag directions. These are in good agreements with the NEMD method results of $42.31_{-0.98}^{+0.98}$ and $41.96_{-0.47}^{+0.47}$ W/m·K and only vary by 4.66% and 5.98% respectively.

For monolayer MoS$_2$, the averaged HCAF functions decline to 0 after 200 ps as shown in Fig. 13(c) and (d). The overall $\kappa$ of 10 trails are converged after 500 ps for both armchair and zigzag directions as shown in Figs. 14(c) and (d). The $\kappa$ of monolayer MoS$_2$ 2D sheet are evaluated by taking average of overall $\kappa$ from 500 to 800 ns and giving the results of $102.32_{-6.08}^{+6.08}$ and $108.74_{-6.68}^{+6.68}$ W/m·K in armchair and zigzag direction, which are quite close to the NEMD results of $103.00_{-3.50}^{+3.50}$ and $106.18_{-2.87}^{+2.87}$ W/m·K and only differ by 0.66% and 2.35% correspondingly. Although both methods show a ~0.3% variance of $\kappa$ in the armchair and zigzag directions, in practical applications, this small difference can be ignored. Besides, we can conclude that the thermal conduction of monolayer MoSe$_2$ and MoS$_2$ are isotropic.
Figure 13. GKM method simulation time dependence of HCAF function for monolayer MoSe$_2$ and MoS$_2$ 2D sheets in the armchair and zigzag directions. For both graphs, the HCAF functions decay to zero at the end of integration time 800 ps.
Figure 14. GKM method simulation time dependence of thermal conductivities for monolayer MoSe$_2$ and MoS$_2$ 2D sheets in the armchair and zigzag directions. Dashed lines stand for the thermal conductivities of 10 individual trials and solid lines represent the overall thermal conductivities. Dot lines indicate where thermal conductivity starts to converge.
2.4.4 Conclusion

Using large-scale classical MD simulations, thermal conductivities of monolayer MoSe₂ are computed and compared with monolayer MoS₂ by both NEMD method and GKM method. Thermal conductivities monolayer MoSe₂ 2D sheet predicted by NEMD method are $42.31^{+0.98}_{-0.98}$ and $41.96^{+0.47}_{-0.47}$ W/m·K in the armchair and zigzag directions respectively, which are similar to the GKM results of $44.38^{+2.08}_{-2.08}$ and $44.63^{+2.50}_{-2.50}$ W/m·K, the variances between two methods are 4.66% and 5.98% correspondingly. In comparison, thermal conductivities of the armchair and zigzag monolayer MoS₂ 2D sheet are $103.00^{+1.50}_{-3.50}$ and $106.18^{+2.87}_{-2.87}$ W/m·K by NEMD method as well as $102.32^{+6.05}_{-6.05}$ and $108.74^{+6.68}_{-6.68}$ W/m·K by GKM method, the difference between these two methods are only 0.66% and 2.35% individually. The thermal conductivity of monolayer MoS₂ 2D sheet is larger than that of monolayer MoSe₂ 2D sheet by a factor of two. Both materials show isotropic properties of thermal conduction. The thermal conductivity for both materials is monotonically increases with the system length and monotonic decreases with system temperature.

2.5 Monolayer and bilayer polyaniline C₃N: two-dimensional semiconductors with high thermal conductivity

2.5.1 Introduction

Monolayer C₃N, a 2D PANI with tunable bandgap and ferromagnetic properties, has garnered intensive research efforts due to its extraordinary set of attributes. Recently, 2D C₃N monolayer has been synthesized in the laboratory through the direct solid-state reaction of organic single crystals. Furthermore, controllable large-scale fabrication of
C$_3$N has been realized using polymerization of 2,3-diaminophenazine. In contrast to the Dirac band structure of the prototype 2D semimetal graphene, the as-synthesized 2D C$_3$N is a semiconductor with an indirect bandgap of 0.39 eV, and its bandgap can be tuned up to 2.6 eV by manipulating the quantum-dots sizes. The on/off ratio of the back-gated monolayer C$_3$N FETs is $5.5 \times 10^{10}$ with electron mobility of 1.2 cm$^2$/V·s and hole mobility of 1.5 cm$^2$/V·s. Surprisingly, it is found out that hydrogenation of C$_3$N can suppress the on/off ratio but increase its hole and electron mobility which initiate spontaneous ferromagnetism. The interesting physical properties such as quantum spin Hall, quantum anomalous Hall and spin-polarization effects exhibited by carbon nitride (CN$_x$) materials render them huge potentials for practical applications. For example, a FET device fabricated by C$_2$N has a high on/off ratio of $10^7$. Recent studies have revealed that the charged holey sites of C$_2$N provide a reactive ground for further functionalization by adatoms or molecules. The special holey structures make C$_2$N a sensitively selective filter for hydrogen purification, He separation and water desalination.

Thermal transport properties of CN$_x$ monolayers, such as graphene, C$_2$N, C$_3$N, and C$_3$N$_4$ have galvanized a new frontier of research in the scientific community. By combining first-principles calculation and phonon BTE, Ouyang et al. predicted the lattice thermal conductivity of monolayer C$_2$N to be 82.22 W/m·K at room temperature. Using EMD method, Zhang et al. calculated the thermal conductivity of C$_2$N at ~40 W/m·K in both armchair and zigzag directions at temperature 300 K. A similar study by Mortazavi et al. using NEMD method predicted the thermal conductivity for infinite-length C$_2$N to be 64.8 W/m·K at temperature 300 K. Also using NEMD method, Wang et al.
predicted $\kappa$ of infinite-length $C_2N$ van der Waals (vdW) bilayer at 80 W/m·K. Despite numerous studies on the thermal conductivity of $C_2N$, few investigations on the thermal properties of $C_3N$ and $C_3N_4$ are reported in the literature. Recently, using the NEMD method, the phononic thermal conductivity of free-standing monolayer $C_3N$ was predicted to be $815 \pm 20$ W/m·K. A much lower thermal conductivity is characterized by Kumar et al.$^{122}$ at 128 W/m·K using first-principles calculations. Given the aforementioned studies on CN$_x$ structures, to our knowledge, there are no experimental or theoretical investigations on the thermal transport properties of layered $C_3N$ structures.

In this work, the in-plane thermal transport in monolayer and bilayer $C_3N$ structures are systematically investigated using classical MD method. Effects of several modulators, such as system dimension, temperature, interlayer coupling strength and tensile strain on thermal conductivity are explored. Thermal conductivities of infinite-length monolayer and bilayer $C_3N$ are extracted based on a linear extrapolation method.

### 2.5.2 Methods

All simulations in this work are performed by LAMMPS.$^{55}$ Descriptions of carbon-carbon interactions are based on the optimized Tersoff potential by Lindsay and Broido.$^{123}$ The carbon and nitrogen atom interactions within $C_3N$ are modeled by the Tersoff potential developed by Kıncı et al.$^{124}$, which has been successfully employed to calculate thermal properties of various CN$_x$ structures such as $C_2N$,$^{119-121}$ $C_3N$,$^{125}$ and nitrogen-doped graphene$^{126-128}$. The vdW interaction between $C_3N$ layers is described by the 12-6 Lennard-Jones (LJ) potential.
\[ V(r) = 4 \chi \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \tag{8} \]

where \( r \) is the interatomic distance, \( \sigma \) is the length parameter and \( \varepsilon \) is the energy parameter. Parameter \( \chi \) is used to adjust the coupling strength. The energy and length parameters are extracted from the Universal force field (UFF) table,\(^{129}\) where \( \varepsilon_{C-C} = 4.56 \) meV, \( \varepsilon_{C-N} = 3.696 \) meV \( \varepsilon_{N-N} = 2.996 \) meV, \( \sigma_{C-C} = 3.431 \) Å, \( \sigma_{C-N} = 3.345 \) Å and \( \sigma_{N-N} = 3.261 \) Å. The cutoff distance \( r_c \) is set as 10 Å for all vdW interactions. The initial distance between adjacent C\textsubscript{3}N layers is set as 3.3 Å, which is also the thickness of graphitic carbon nitride.\(^{130}\) Atomic configurations of the monolayer and bilayer C\textsubscript{3}N structures are shown in Fig. 15. Time step is set as 0.5 fs.

\[ \]

**Figure 15.** Schematics of monolayer and bilayer C\textsubscript{3}N structures. (a) Top view of monolayer C\textsubscript{3}N. (b) Side view of bilayer C\textsubscript{3}N.
The in-plane thermal conductivities of monolayer and bilayer C\textsubscript{3}N are characterized by the steady-state r-NEMD method. The initial system is first placed in the \textit{NVT} ensemble for 500 ps to reach thermal equilibrium at a designated temperature. Then the system is switch to \textit{NVE} ensemble for NEMD calculations. Periodic boundary condition is applied to the width (y) direction and free boundary conditions are applied to the length (x) and cross-plane (z) directions. The outermost layer of atoms at each end of the length (x) direction is fixed. The adjacent four layers of atoms next to the fixed regions are grouped as heat reservoirs. After the initial thermal equilibrium calculation, a heat flux of 1.6×10\textsuperscript{11} W/m\textsuperscript{2} is imposed to the system continuously for 8 ns. Data from the last 2 ns are extracted to obtain the temperature distribution. The thermal conductivity can be calculated based on the Fourier law of heat transfer. To alleviate the data noise, each data point is obtained from three independent simulations with different initial conditions. The averaged value is taken as the final result, and standard deviations are extracted as error bars.

2.5.3 Results and discussion

To illustrate the principles of r-NEMD calculation, a bilayer C\textsubscript{3}N system with dimensions of 39.7 × 2.9 × 0.66 (x × y × z nm\textsuperscript{3}) is constructed. The steady-state temperature distribution along the heat flux direction in the bilayer C\textsubscript{3}N structure is shown in Fig. 16. The inset picture depicts the atomic configuration for the NEMD calculation. The predicted thermal conductivity for the 39.7 nm bilayer C\textsubscript{3}N system equals 262 W/m\cdot K, which is lower than that of semimetal graphene\textsuperscript{38} but significantly higher than other prototype 2D semiconducting materials such as silicene\textsuperscript{131}, phosphorene\textsuperscript{38} and monolayer MoS\textsubscript{2}\textsuperscript{132} and MoSe\textsubscript{2}\textsuperscript{1} at similar length scales. The system width for all structures is chosen
as 2.9 nm. Other system widths of 4.8, 6.8 and 8.8 nm are also tested and the calculated thermal conductivity results have negligible differences. Therefore, the smallest width value is chosen to save computational cost.

![Graph showing temperature distribution]

**Figure 16.** Steady-state temperature distribution in the C$_3$N bilayer. Inset figure illustrates the configuration of the NEMD simulation setup.

### 2.5.3.1 Effects of system dimension and chirality on $\kappa$

To explore the effects of chirality on the thermal conductivity of monolayer and bilayer thermal conductivities, zigzag and armchair monolayer and bilayer C$_3$N structures of lengths 19.7, 39.7, 79.1, 118.7, 158.3 and 316.7 nm are constructed. Length dependence of thermal conductivity is shown in Fig. 17(a). Two phenomena are observed from the calculated results: 1) thermal conductivities of both monolayer and bilayer C$_3$N increase monotonically with system length and gradually converge at larger length values; 2) the calculated $\kappa$ values for monolayer and bilayer are very close, *i.e.*, the interlayer coupling
has negligible effects on the thermal conductivity of C$_3$N. Similar results have also been observed in monolayer and bilayer graphene. Using MD simulation, Rajabpour et al.$^{133}$ predicted the thermal conductivity of bilayer graphene to be 158 W/m·K, and 161 W/m·K for monolayer graphene, which is approximately the same. In a recent work, Zhang et al.$^{134}$ predicted the thermal conductivity for monolayer and bilayer graphene to be 135.01 ± 13.38 and 129 ± 8.45 W/m·K using NEMD method. For monolayer C$_3$N, the calculated κ increases from 196.8 W/m·K to 643.4 W/m·K with growing l values from 19.7 nm to 316.7 nm. While for bilayer C$_3$N, similar values are obtained from 173.5 to 636.4 W/m·K. Since the calculated thermal conductivities in armchair and zigzag directions have negligible differences, the following analyses focus on the predicted thermal conductivities in the armchair direction. The calculated thermal conductivity results are fitted using a linear function Eq.7. The fitted results for 1/κ and 1/l are shown in Fig. 17(b). The predicted thermal conductivities for infinite-length C$_3$N monolayer and bilayer are 820 and 805 W/m·K, respectively. The corresponding effective phonon MFPs are 84.1 and 79.5 nm. In a recent study, Mortazavi et al.$^{25}$ calculated the mechanical and thermal properties of monolayer C$_3$N. It was reported that the phononic thermal conductivity of free-standing C$_3$N was as high as 815 ± 20 W/m·K, which is very close to the reported value of 820 W/m·K in this work for infinite length C$_3$N monolayer.
The calculated $\kappa$ increases sharply with $l$ at small length scales and gradually converges at larger values. (b) Relationships between $1/\kappa$ and $1/l$ for monolayer and bilayer C$_3$N in both armchair and zigzag directions. Linear fittings are applied to both datasets to extrapolate the thermal conductivity for 2D sheets.

The reduction of thermal conductivity in C$_3$N compared to that of graphene can be attributed to the modification of phonon modes and the phonon scatterings around the nitrogen sites, which can be regarded as composition defects for pure graphene structures. In a recent study, Malekpour et al.\textsuperscript{135} investigated the thermal conductivity of suspended graphene as a function of the defect density from $2.0 \times 10^{10}$ cm$^{-2}$ to $1.8 \times 10^{11}$ cm$^{-2}$. The measured thermal conductivity of graphene decreases from $\sim(1.8 \pm 0.2) \times 10^3$ to $\sim(4.0 \pm \ldots$
The thermal conductivity of isotopically pure graphene determined by the opto-thermal Raman technique is around 4000 W/m-K at temperature 320 K, which is two orders of magnitude higher than that in graphene sheets composed of a 50:50 mixture of $^{12}$C and $^{13}$C. Using EMD simulations, Goharshadi et al. calculated the thermal conductivity of nitrogen-doped graphene. It was revealed that 1% of nitrogen doping can drastically diminish the thermal conductivity of graphene by 59.2% at 300 K.

Phonon behavior in C$_3$N can be further illustrated by phonon power spectra analyses. The PDOS can be calculated by Eq.5. Since the atomic structure of C$_3$N is similar to that of graphene, considering the anisotropic nature of different phonon modes in the latter structure, the overall and decomposed PDOS of both C$_3$N and graphene are calculated separately, as shown in Fig. 18. The two structures share similar active phonon frequencies. The high-frequency ranges in graphene are dominated by the LA and TA phonons whereas the ZA phonons dominate the low frequencies. In C$_3$N, the high-frequency domains are also dominated by in-plane LA/TA phonons but are softened compared to those of graphene. On the other hand, the low-frequency ZA phonons have an apparent blue shift compared to those graphene. The PDOS results shed some light on the discrepancies of phonon thermal transport between these two structures.
Figure 18. Comparison of phonon density of states between C$_3$N and graphene in (a) overall, (b) $x$ direction, (c) $y$ direction and (d) $z$ direction. The PDOS profiles have been smoothened by the Savitzky-Golay filter method.

Heat dissipations in C$_3$N can be directly observed by analyzing its spatiotemporal thermal transport. To visualize the thermal transport within C$_3$N, a 19.7 nm length monolayer system is used. After the thermal equilibrium calculations, a heat impulse of $1\times10^{12}$ W/m$^2$ is imposed at one end for 50 fs. The temperature within the heating area quickly rises to a much higher value and the accumulated thermal energies start dissipating through the system. Temperature evolution in the following 20 ps is recorded. Figures 19(a)-(d) depict the overall, $x$ direction, $y$ direction and $z$ direction heat transport in C$_3$N,
respectively. Interestingly, it can be observed from the results that the ZA phonons in C$_3$N carry more heat than LA/TA phonons. For example, the thermal energies shown in Fig. 19(c) have apparent accumulations within the heating area, whereas a strong thermal wave is observed in Fig. 19(d), indicating the ZA phonons dissipate thermal energies faster than LA/TA phonons. Similar conclusions have also been drawn from graphene.$^2$

![Figure 19](image.png)

**Figure 19.** Spatiotemporal thermal map of monolayer C$_3$N after a thermal impulse. The (a) overall temperature, and decomposed nominal temperatures for (b) longitudinal phonons, (c) transverse phonons and (d) flexural phonons are analyzed separately.

### 2.5.3.2 Effects of temperature and coupling strength on $\kappa$

To investigate the effects of temperature on the thermal conductivity of C$_3$N, monolayer and bilayer structures with lengths of 39.7 nm are selected and temperatures from 200 K to 600 K are used. Variations of thermal conductivity with system temperature are shown
in Fig. 20(a). It can be observed that the calculated $\kappa$ for monolayer C$_3$N decreases monotonically from 309 to 185 W/m-K with increasing temperatures. While those for bilayer C$_3$N decreases from 300 to 187 W/m-K in the same temperature range. The Umklapp phonon-phonon scattering plays a dominating role in thermal transport when the temperature increases, as higher frequency phonons are activated. The severe anharmonic scattering shortens the phonon MFP, which would limit the phonon transmission of C$_3$N. Besides, the phonon scattering around the nitrogen sites becomes stronger at the high temperature, which impedes the phonon transport. As a result, the increasing temperature hinders thermal transport, and the thermal conductivity of C$_3$N is reduced. To investigate the effect of contact pressure on thermal transport, different coupling strengths of $\chi = 0.5, 1, 2, 3$ and 4 are used in the bilayer C$_3$N system. The calculated dependence of $\kappa$ with $\chi$ are shown in Fig. 20(b). It can be observed from the calculated results that the increased coupling strength has a negligible effect on the lateral thermal conductivities of C$_3$N. The calculated $\kappa$ varies from 267 to 253 W/m-K based on the average of three independent simulations, with a discrepancy of 5.2%. In our cases, vdW interaction between C$_3$N interlayers is much weaker in comparison with the covalent bonding of the intralayer. Hence, although the coupling strength can enhance the atomic interaction between interlayers, it only exerts a small effect on the atomic interaction within the intralayer, which explains the independent basal-plane thermal conductivity with coupling strength.
Figure 20. (a) Dependence of monolayer and bilayer C$_3$N thermal conductivities on temperature from 200 to 600 K. (b) Dependence of bilayer C$_3$N thermal conductivity on interlayer coupling strength from 0.5 to 4.0.

2.5.3.3 Effects of tensile strain and defect on κ

In-plane mechanical stress within surface materials broadly exists in practical applications. Both uniaxial and biaxial tensile strains could affect the predicted thermal conductivities of monolayer and bilayer C$_3$N due to the variations of phonon dispersions and group velocities. Effects of biaxial strains on the thermal conductivity of various 2D
materials have been reported in previous studies. A 10-20% reduction in the thermal conductivity of MoS$_2$ can be achieved by applying a moderate biaxial tensile strain of 2-4%.\textsuperscript{136} It has been reported that biaxial tensile strains have more impact on the calculated thermal conductivity of graphyne compared with uniaxial tensile strain.\textsuperscript{137} Thermal conductivity of graphyne in the armchair direction decreases by 37.6% under the biaxial strain of 0.09 only reduces by 24.1% under uniaxial strain. Compared with uniaxial tension, the biaxial tension brings larger deformations in the 2D system and increases the lattice anharmonicity. The decreased mode-specific phonon group velocities and specific heat of each propagating phonon mode also contribute to the reduction of the predicted thermal conductivities.\textsuperscript{138} In this work, thermal conductivities of monolayer and bilayer C$_3$N under uniaxial and biaxial tensile strains are investigated using the $39.7 \times 2.9 \ (x \times y)$ nm$^2$ system. The predicted $\kappa$ with strain values from 0 to 8% are calculated and the results are shown in Fig. 21. It can be observed that the effects of biaxial tensile strain are greater than those of uniaxial tensile strain, which is consistent with previous studies. Specifically, the reductions of $\kappa$ for monolayer C$_3$N under biaxial tensions are slightly larger than those of bilayer C$_3$N. While the reductions of $\kappa$ for both monolayer and bilayer C$_3$N are the same under uniaxial tensile strain. The differences could be caused by the different levels of deformations in monolayer and bilayer C$_3$N under biaxial tensile strains. The biaxial tensile strains have a larger impact on the atomic configurations of C$_3$N and the monolayer structure could be more severely affected. Under uniaxial tensile strain, the predicted $\kappa$ decreases from 267 to 214 W/m-K for monolayer C$_3$N and from 262 to 219 W/m-K for bilayer C$_3$N with increasing tensile strains from 0% to 8%. Maximum reductions of 19.9% and 16.4% are calculated. Under biaxial tensile strain, the
calculated $\kappa$ decrease to 130 and 164 W/m·K for monolayer and bilayer C$_3$N, respectively, with maximum reductions of 51% and 38%. To have a better understanding of the phonon behavior changes, the overall PDOS for 8% strained monolayer C$_3$N is calculated, which is shown in the inset of Fig. 21. Compared to those in Fig. 18(a), it can be observed that the tensile strains soften the higher frequency peaks of the phonon spectra remarkably, which could slow down the phonon group velocities and result in a thermal conductivity decrease according to the classical lattice thermal transport theory.

**Figure 21.** Effects of uniaxial and biaxial tensile strain on the thermal conductivity of monolayer and bilayer C$_3$N from 0 to 8%. The inset figure shows the PDOS of 8% uniaxial strained monolayer C$_3$N.

The effect of the defect on the thermal conductivities of popular 2D materials such as graphene, hexagonal boron nitride, silicene, and phosphorene has been extensively studied. It was reported that $\kappa$ of suspended graphene decreases from 1800 to 400 W/m·K
with the existence of surface defect. It was found out that ~0.1% carbonyl pair defect can deteriorate the thermal conductivity of graphene by ~83%. The reduction of the thermal conductivity is mainly caused by the phonon-defect scattering process. In this work, the effect of the single-point defect on κ of C₃N is investigated. The carbon and nitrogen atoms were randomly removed from the 39.7 × 2.9 (x × y) nm² system to compose the defected C₃N structures with defect ratios ranging from 0.1% to 0.5%. The calculated thermal conductivities with different defect ratios are shown in Fig. 22. It can be observed that the thermal conductivity of C₃N is very sensitive to the variations of defect ratio. A small defect level of 0.5% can lead to maximum κ reductions of ~63% for both monolayer and bilayer structures. It is worth noting the carbon and nitrogen atoms need to be arranged in special patterns in the C₃N structure to maintain its structural stability. Therefore a larger defect ratio will lead to unstable systems.
Figure 22. Effect of defect on the thermal conductivities of monolayer and bilayer C$_3$N at temperature 300 K. Maximum reductions of $\kappa$ amount to $\sim$63% for both structures.

2.5.4 Conclusion

Thermal transports in monolayer and bilayer C$_3$N are systematically investigated in this work using classical MD simulation. The in-plane thermal conductivity for infinite-length monolayer and bilayer C$_3$N structures are predicted to be 820 and 805 W/m$\cdot$K, respectively, which are much higher than those of many prevailing 2D semiconducting materials such as phosphorene, hexagonal boron nitride, and TMDCs. Through detailed phonon power spectrum and spatiotemporal thermal dissipation analyses, it is revealed that the PDOS of C$_3$N share similar patterns as those of graphene, with LA/TA branches dominating the high-frequency domain and ZA phonons dominating the low-frequency range. Besides, it was discovered that ZA phonons in C$_3$N convey the most thermal energies during in-plane thermal transport, which is also similar to that of graphene. Effects of temperature, tensile strain and interlayer coupling strength on the predicted thermal conductivity are investigated. Monotonic decreasing trends of $\kappa$ with temperature and strain are observed while the negligible effect of coupling strength on $\kappa$ is reported. Results in this work provide fundamental knowledge to the design and application of C$_3$N-based electronic devices.
CHAPTER 3 Heat conduction at the interface of 2D materials

3.1 Introduction

When the device size is reduced to the length scales on the order of energy carrier’s MFP, device-level thermal transport is no longer determined by the thermal properties of the materials comprising the devices, but rather the energy transport across the interfaces between adjacent materials. Thermal contact resistance is a measurement of the interface’s resistance to thermal flow and it is the most common quantity used to characterize interfacial thermal transport. Understanding the thermal resistance between the two materials is of great significance to study their thermal properties.

Two-dimensional monolayers can be assembled into multi-layer heterostructures held together by vdW forces, resulting in new physical properties due to the formation of heterojunctions. Different combinations of vertical-aligned 2D heterostructures provide a way to take advantage of the best properties of different 2D materials together. For example, the graphene-based transistors with high carrier mobility have been realized by encapsulating graphene between two h-BN layers.\textsuperscript{140} The new electronic characteristics can be attributed to the improved dielectric environment provided by the full h-BN encapsulation of the graphene channel in conjunction with an optimized, self-aligned device structure. Modified band structure and the opening of several mini-band gaps have also been realized with the MoS\textsubscript{2}/graphene hetero-bilayer.\textsuperscript{141} The Fermi velocity of the graphene remains effective as pristine graphene. For phosphorene/graphene hetero-bilayer, the relative position of phosphorene's band structure with respect to the graphene's can be tuned by a normal external electric field.\textsuperscript{142} Moreover, by exploring the field dependent band structures and optical properties of the phosphorene/graphene
bilayer, the heterostructure may be applied as a high-speed device without using optical anisotropy.\textsuperscript{143}

The limited internal phonon coupling and transfer within graphene in the out-of-plane direction significantly affects graphene-substrate interfacial phonon coupling and scattering and leads to unique interfacial thermal transport phenomena. This is crucial for micro/nanoscale systems where interface phonon behaviors could directly affect properties relative to bulk materials. Recently there arises a strong motivation to study thermal properties of graphene and related composite materials, especially the graphene-based heterostructures.

In Chapter 3.2, two different thermal resistance calculation methods are discussed, \textit{i.e.,} the steady-state NEMD method and transient pump-probe approach. Then, the spectral energy density (SED) analysis is introduced as a common tool to reveal phonon behavior. Finally, five thermal resistance works will be present in Chapter 3.3 to 3.7.

### 3.2 Characterize heat conduction 2D materials’ interface

The NEMD simulation is one of the most commonly used simulation approaches for interfacial thermal resistance calculations, especially for bulk materials which contain tens of atomic layers in the heat flux direction.\textsuperscript{32, 144} By applying a heating source and heat sink separately at the opposite edges of the composite system, a temperature gradient can be created in the heat flux direction at steady state. The temperature drop occurring at the interface of the contact area can be used to determine the thermal resistance values as we discussed in the method part. However, for thermal contact resistance characterizations in 2D materials like graphene, the NEMD method should be used with
great caution. As we discussed above, the potential energy within the heating/cooling regions are in a non-equilibrium state and phonon boundary scattering is furious. Therefore, the temperature drop is non-uniform in these regions and should be eliminated from the thermal resistance calculations.\textsuperscript{31-33,145} To avoid this controversial situation, the 2D material can be put in the middle of a sandwiched structure.\textsuperscript{146-148} After the system reaches steady state, the temperature of the 2D material and its adjacent layers will be recorded and used for thermal contact resistance calculations. One possible drawback of this method falls on the temperature gradient building process, which could be extremely time-consuming, especially for large MD systems.

### 3.2.1 Transient pump-probe approach

Hence, in three of my following thermal resistance calculation works, a transient pump-probe approach is applied using MD simulations to mimic the experimental transient thermoreflectance (TTR) method, which has been previously applied to study the thermal transport in bulk materials and thin films.\textsuperscript{149-151} In the TTR technique, a laser pulse (pump) is focused onto a small spot on the surface of a thin film. Partial absorption of this pulse will lead to a quick temperature rise in the film, and then the film will be cooled via the heat conduction to the substrate. The change in the temperature of the thin film leads to a small variation in its optical reflectivity which can be measured by a second laser pulse (probe). The measured cooling profile of the thin film is used to determine the thermal contact resistance at the interface. Compared to traditional NEMD method, this pump-probe technique is focused on the dynamic thermal response of the hybrid system and can greatly reduce the computation time.
After the MD system reaches steady-state at designated equilibrium temperature, an ultrafast thermal impulse is applied to the top layer to increase its temperature to a much higher value. Meanwhile, the temperature of the bottom layer can be regarded as unchanged. Due to the ultrafast thermal excitation, a temperature gap between the top and bottom layers are created and thermal energies will dissipate from the higher temperature regions to the lower ones until thermal equilibrium is established again. During this process, heat conduction within the bilayer is the only thermal pathway for heat dissipation. Therefore, the interfacial thermal resistance ($R$) can be described as

$$\frac{\partial E_t}{\partial t} = \frac{A \cdot (T_{\text{top}} - T_{\text{bot}})}{R},$$

(9)

where $T_{\text{top}}$ and $T_{\text{bot}}$ represent the top and bottom layer temperatures respectively, $E_t$ is the total energy of the top layer at time $t$ and $A$ is the cross-plane area. During the interfacial thermal transport process, the energy decay of the top layer is only caused by its thermal energy loss to the substrate system. Therefore, given the energy and temperature evolutions of the top layer, the interfacial thermal resistance can be calculated using the equation

$$\frac{\partial E_t}{\partial t} = A \cdot (T_{\text{top}} - T_{\text{bot}}) / R.$$  

(10)

An instant $R$ can be calculated at each time step according to the local energy changing rate and corresponding temperature difference. We have tried this method and found it subject to the noise in the energy decay and the calculated interface thermal resistance has very large uncertainty. If $R$ has little variation within the temperature range during thermal relaxation, a constant $R$ value can be substituted into Eq.9 to predict the $E_t$ profile.
Under such a scenario, the interfacial thermal resistance can be calculated by the best fitting of the $E_r$ profile using the least square method.

### 3.2.2 Spectral energy density

The phonons behaviors of 2D materials can be revealed by phonon SED analysis, which is expressed as\(^{(152)}\)

$$
\phi(k, \omega) = \frac{1}{4\pi N \tau} \sum_{\alpha} \sum_{b} m_b \left| \int_{0}^{\tau} \sum_{n_{x,y,z}} \hat{v}_a \left( \frac{n_{x,y,z}}{b} ; t \right) \cdot \exp[i k \cdot r \left( \frac{n_{x,y,z}}{0} - \omega t \right)] dt \right|^2,
$$

where $N$ represent the number of total unit cells, $\tau$ the integration time, $\alpha$ the integration direction ($x$, $y$, $z$), $B$ the total number of atoms in a unit cell, $\hat{v}_a$ the velocity of atom $b$ in unit cell $n_{x,y,z}$ at time step $t$, and $r$ is the equilibrium position of unit cell $n_{x,y,z}$.

### 3.3 Tuning thermal contact conductance at graphene-copper interface via surface nanoengineering

#### 3.3.1 Introduction

As graphene is either supported or embedded in most applications like FETs or interconnects. A deep understanding of thermal properties at graphene-substrate interfaces is timely and crucial. Recently, the importance of thermoelectric effects, current crowding, and Joule heating has been studied at graphene-metal contact.\(^{(153-155)}\) In very large scale integrated circuits, graphene-metal contacts cannot be avoided in graphene and copper-based interconnects.\(^{(156)}\) Under such scenarios, thermal dissipation at graphene-metal contact becomes especially important in short channel transistors where
the electrode contact can turn into a crucial heat removal pathway. At high temperatures, graphene interconnects may become an important channel to spread heat inside an electronic package. However, in spite of the significant importance of the graphene-metal contact, the thermal contact resistance at the interfaces has not been well studied. In the following sessions, the dependence of interfacial thermal resistance on surface roughness’ dimension is investigated for various combinations of nanogroove depth and width. Effects of roughness formations on interfacial thermal transport are investigated for cylindrical and rectangular shaped nanobumps.

3.3.2 Methods
The second generation of the Brenner potential, \textsuperscript{57} REBO potential based on the Tersoff potential\textsuperscript{58, 59} with interactions between C-C bonds are employed to model the graphene system. The embedded atom method (EAM) potential is used to describe the Cu-Cu interactions. Graphene is proven to have a strong bonding with metals like Ti and Ni due to the coupling between open $d$-orbitals, but only interact weakly with Cu,\textsuperscript{157, 158} which justifies the application of 12-6 LJ potential for C-Cu interactions. The choice of the pair potential is also motivated by previous results that have indicated the LJ potential with parameters derived from quantum level simulations provide a reasonable approximation to the metal-carbon interactions.\textsuperscript{159} In this work, $\sigma$ and $\varepsilon$ are set as 3.0825 Å and 25.78 meV respectively.\textsuperscript{160, 161} The LJ potential is truncated at the cut-off distance of $r_c = 3.5\sigma$. A time step of 0.5 fs (1 fs = $10^{-15}$ s) is used in all MD simulations.

The most stable configuration of graphene nanoribbon (GNR) on the copper substrate is used.\textsuperscript{157, 158} The graphene honeycomb lattice is superposed on the copper (111) surface to match the triangular lattice with one carbon atom on top of a copper atom and the second
on a hollow site. Atomic configuration of the hybrid system is shown in Fig. 23. At the start of the simulation, the position of the GNR is located 3.46 Å above the upper layer of the Cu bulk. In the experiments, a metal substrate is usually much thicker than the graphene monolayer, thus the hybrid system characterizes a lattice constant close to that of the metal. Therefore, a pre-strain of 3.9% in graphene is introduced at the graphene-copper interface. According to the experimental evidence, this mismatch will not cause out-of-plane buckling in graphene and the copper surface will retain flat. Periodic boundary conditions are applied to the x and y directions and free boundary conditions to the z direction. Dimensions of the GNR are smaller than those of the copper substrate to avoid boundary interactions through the periodic boundaries.

**Figure 23.** Atomic configurations of the graphene-copper hybrid system. The GNR honeycomb lattice (red) is positioned to match the triangular lattice of Cu (111) surface (green) with one carbon atom on top of a Cu atom and the second carbon on a hollow site.

In this work, the transient pump-probe approach is applied to calculate the interfacial thermal resistance between GNR-Cu interfaces. After the MD system reaches the steady
state, an ultrafast heat impulse is imposed on the supported GNR for 50 fs. In the heating process, non-translational kinetic energy is evenly added to the GNR system in each direction by rescaling velocities of atoms. As is shown in Fig. 24, when the excitation is released, the temperature of the GNR ($T_{\text{GNR}}$) increases dramatically and then gradually decreases during the thermal relaxation process. In this work, three layers of Cu atoms adjacent to the supported GNR are grouped to calculate the surface temperature of the Cu bulk ($T_{\text{Cu}}$). $T_{\text{GNR}}$, $T_{\text{Cu}}$ and GNR system energy ($E_t$) are recorded each time step during the thermal relaxation.

**Figure 24.** Energy fitting of the supported graphene system for thermal resistance calculations. Temperatures of the GNR and top three layers of Cu substrate are recorded on the right $y$ axis.

The mechanism of energy transport across graphene interfaces can be diverse. For graphene/semiconductor interfaces, the main energy carrier in both graphene and
substrate is phonon. Therefore, the energy transport is mainly dominated by phonon transmission. When it comes to the graphene/metal interfaces since the electron is the main energy carrier in metals while phonon dominates heat transport in graphene, both phonon and electron participate in the interfacial energy transport. So phonon/phonon interaction, electron/phonon interaction and electron/electron interaction are all involved in the energy transmission across the interface. Koh et al.\textsuperscript{165} found that phonon/phonon interaction still dominates the thermal transport across graphene/metal interfaces at temperatures 50 – 500 K. In addition, Majumdar and Reddy\textsuperscript{166} concluded that the electron/phonon resistance only contributes to interfacial thermal transport when the phonon-mediated conductance is on the order of GW/K\textsuperscript{m}, which is over an order of magnitude greater than the values we report here for graphene-copper interfaces. Lyeo and Cahill\textsuperscript{144} experimentally determined that electron scattering does not affect thermal transport across metal/diamond interfaces. Previous studies on graphene-copper based thermal interface materials have also neglected the electron/phonon contributions to their calculated interfacial thermal conductance and thermal conductivity values.\textsuperscript{161, 167} Therefore, only phonon/phonon interactions are considered in this work to calculate the thermal contact resistances at the graphene-copper interface.

3.3.3 Results and discussion

3.3.3.1 Interfacial thermal resistance $R$

To understand the thermal transport across the graphene-copper interface, a copper substrate with dimensions of 5.7×20.1×3.8 nm$^3$ ($x\times y\times z$) is built. The area of the supported GNR is 4.2×18.5 nm$^2$ ($x\times y$). After 1 ns MD simulation in $NVT$ ensemble and another 1 ns in $NVE$ ensemble, the whole system reaches a steady state at 300 K. Then the GNR is
exposed to a thermal impulse $\dot{q}_{\text{in}}=6.24\times10^{-4}$ W for 50 fs. After the excitation, $T_{\text{GNR}}$ increases to 548 K and the adjacent copper surface temperature $T_{\text{cu}}$ is 301 K. In the following 100 ps thermal relaxation process, energy dissipation from graphene to the copper substrate is recorded and the interfacial thermal resistance is calculated. Energy and temperature results are averaged over 100 time steps for each data point in the calculation to suppress data noise. Temperature evolutions and energy fitting results are shown in Fig. 24. It is observed that after the 50 fs thermal excitation is released, the GNR’s energy goes down quickly due to the energy transfer to Cu-substrate. In the meantime, $T_{\text{GNR}}$ goes down accordingly and slight temperature rise is observed for the copper atoms adjacent to the interface. The energy decay fitting in Fig. 24 is performed based on Eq. 10. The calculated thermal resistance $R_{\text{\delta0}}$ is $2.61\times10^{-8}$ K·m$^2$/W, which is in the same magnitude with previous studies of graphene on Cu and Ni.$^{161}$ As shown in Fig. 24, the energy decay curve and temperature decay curve for the GNR are parallel to each other. At the beginning of the thermal relaxation process, a faster decay in GNR’s total energy is observed. This is caused by the strong energy disturbance induced by the thermal impulse to the system. During that period, the potential and kinetic energies have not yet reached equilibrium. Therefore, the initial part (5 ps) of the thermal relaxation profile is strongly dominated by the energy transfer from kinetic to potential energy in GNR. It can be observed from Fig. 24 that the fitting curve soundly matches the energy profile using a constant $R$. This leads to a strong point that the interfacial thermal resistance between GNR and Cu does not have large change over the relaxation temperature.
3.3.3.2 Effects of GNR dimensions

As a novel 2D material, it is found that the thermal conductivity of suspended graphene and GNR is also size dependent.\textsuperscript{168, 169} The length effect on the thermal conductivity of graphene is due to its intrinsically long phonon MFP, which is up to 775 nm at room temperature.\textsuperscript{11} The confined dimension in the lateral directions of supported graphene will greatly affect the phonon behaviors at the graphene-substrate interface. Therefore, it is of great interest to investigate the effects of dimension on the interfacial thermal resistance between graphene and copper.

To address this issue, GNR systems of length ($L$) 2.6 nm, 5.0 nm, 40.0 nm, 78.2 nm, and 156.6 nm are created. The width ($W$) of the GNR remains the same as 4.2 nm for all cases. Flat surface copper substrates are used in all calculations. Calculation procedures and data processing methods are the same as used in the manuscript. Calculated $R$ results are shown in Fig. 25. It can be observed from the results that the length of the supported GNR has a significant impact on the interfacial thermal resistance between GNR and Cu at short length scales from 0 to 40 nm. When the length is larger than 40 nm, the calculated $R$ tends to converge to a constant value. To elucidate this length effect, the actual energy exchange area on the Cu substrate is explored. It was mentioned in the manuscript that the cutoff distance $r_c$ between carbon and copper atoms is set as 3.5$\sigma$, which is 10.8 Å in all cases. The equilibrium distance between GNR and Cu substrate surface is smaller than $r_c$. This indicates that the actual surface areas involved in the thermal transport process are larger than the projected GNR areas on the Cu substrate, which is used in the overall energy fitting method to calculate the interfacial thermal resistance. This phenomenon is explained in the inset of Fig. 25. The relation between the
thermal resistance \( R \) calculated using the overall fitting method and the ideal one \( R_{\text{real}} \) without the edge effect is expressed as

\[
R = \frac{R_{\text{real}} \cdot W \cdot L}{(W+\xi)(L+\xi)},
\]

(12)

where \( W \) and \( L \) are the width and length of the supported GNR, respectively, and \( \xi \) is the effective distance extended from the edge of the projected area. Such an area extension is caused by the long-range vdW interaction. The interatomic forces in the extended areas are much weaker compared to those in the projected areas. However, the contributions from the extended areas cannot be neglected when the surface area of the supported GNR is small. Given the calculated thermal resistance values, we use Eq. 12 to fit the results in Fig. 25 to determine \( R_{\text{real}} \) and \( \xi \). The ideal interfacial thermal resistance without the edge effect is determined at \( 3.54 \times 10^{-8} \text{ K} \cdot \text{m}^2/\text{W} \) and \( \xi \) is determined at 11.6 Å.

**Figure 25.** Thermal resistance variations with GNR length.

**3.3.3.3 Effects of nanogroove dimensions and interface coupling strength**

Our previous research has revealed that when GNRs are bent to fit the substrate structure,
the thermal resistance can emerge in the bending area due to local phonon reflection and scattering. Aside from the bent structures in applications, the substrate surfaces are often engraved with patterns to achieve maximum thermal radiation and realize various electrical functions. In spite of the vast applications of graphene in nanoelectronics, however, to our best knowledge, the effects of substrate roughness on the thermal transport across graphene-metal interfaces have not been studied. Here, the interfacial thermal resistance between graphene and Cu-substrate with well-defined substrate roughness is studied.

In the rough substrate studies, physical domain dimensions of the GNR-Cu heterostructure remain the same as those in Fig. 23. Countless of roughness patterns can be engineered on the substrate surface and it’s impossible to address all of them. To simplify this study, first, prototype zebra-striped patterns with rectangular shaped nanobumps are engraved on the copper surface. In our pattern and system design, variations are made by changing the nanogroove width \(d\) and depth \(\delta\) in the \(x\) direction of the Cu-substrate. Interfacial thermal resistances for combinations of \(d = 1, 2, 4\) nm and \(\delta = 0.21, 0.42, 0.63, 0.83, 1.04, 1.25, 1.46\) nm are computed. Since the cut-off distance for the 12-6 LJ potential is only 1.08 nm, it is safe to speculate that the thermal resistance values will not change substantially for \(\delta > 1.46\) nm. Thus nanogroove depths larger than 1.46 nm are not investigated. Steady state atomic configurations of \(d = 2\) nm with \(\delta = 0.42, 0.83, 1.46\) nm systems are shown in Figs. 26(a), (b) and (c). It is observed that when \(\delta = 0.42\) nm, the whole GNR structure are deformed to fit the substrate surface and both the supported and suspended areas are in close contact with the underneath copper atoms. While for \(\delta = 0.83\) nm case, only a small part of the suspended GNR are in touch with the
nanogroove bottom. And all the suspended GNR regions are totally separated from the nanogroove for $\delta = 1.46$ nm case.

**Figure 26.** Atomic structures at steady state for $d = 2$ nm cases with $\delta = 0.42, 0.83$ and 1.46 nm. (a) The suspended GNR regions are bent to fit the surface nanogrooves on the Cu substrate. (b) GNR is partially in contact with Cu in suspended regions. (c) All suspended areas of GNR are separated from the Cu substrate.

Dependence of the thermal resistance on different combinations of nanogroove widths and depths are shown in Fig. 27(a). It is very surprising and interesting to observe that in all cases, the interfacial thermal resistance first decreases as $\delta$ becomes larger. For example, when $d = 2$ nm and $\delta = 0.63$ nm, the interfacial thermal resistance $R_{\delta=0.63 \text{ nm}}$ reaches the lowest value of $2.16 \times 10^{-8} \text{ K} \cdot \text{m}^2/\text{W}$, which is 17% smaller than $R_{\delta=0}$ under the same MD simulation procedures. This is contrary to the conventional view that compared with a flat surface; a rough surface tends to give a higher interfacial thermal resistance due to the poorer contact. Figure 27(b) shows the thermal contact resistances for $d = 2$ nm
cases with different scaling parameter $\chi$ of values 0.5, 1 and 2. It is known that the covalent bonding between graphene and its substrate can greatly reduce the thermal contact resistance, which indicates the stronger interatomic interactions are more effective for phonon transport across the interfaces.\textsuperscript{170, 171} The decrease in the thermal contact resistance with interface coupling strength $\chi$ can be explained from two aspects: (1) the phonon coupling between GNR and copper is enhanced, which directly reduces the interfacial thermal resistance; (2) the in-plane and out-of-plane phonons coupling in GNR become stronger, which indirectly boosts the efficiency of heat transfer from GNR to copper. In free standing graphene, the flexural phonon mode has been proven to dominate the thermal transport in graphene and the in-plane and out-of-plane phonons are well decoupled.\textsuperscript{172} With the existence of Cu-substrate, various symmetry rules, i.e., reflection, transmission, and rotation are broken. The phonon vibrations in carbon atoms are affected by the interactions between GNR and copper. Since the GNR honeycomb lattice is superposed on the Cu (111) surface to match the triangular lattice, the copper atoms underneath behave as scattering centers for the in-plane phonons in GNR, which unleashes the thermal energies stored in the in-plane phonons and transfers them into flexural phonon modes. This, as a result, strengthens the heat transfer between graphene and copper interfaces and reduces their thermal contact resistance. Unlike the vacuum circumstances used in MD simulation, in real-world applications, the effects of atmosphere pressures could enhance the contact pressure between GNR and Cu, which as a result leads to decreased thermal contact resistances. For the results in Fig. 27, the real contact areas of the graphene, not their projected areas on the Cu-substrate, are used for resistance evaluation.
Figure 27. (a) Thermal contact resistance variations with nanogroove width and depth. (b) Effects of the interaction strength ($\chi$) on the interfacial thermal resistance.

To explain these new findings, the interatomic forces between GNR and copper are calculated for the $\delta = 6.3$ Å case and the results are shown in Fig. 28(a). The supported and suspended areas are cross-adjacent and each region has a width of 2.0 nm. Due to the roughness of the copper surface, the interatomic forces are not evenly distributed in the supported GNR. For GNR over the nanogroove, most of the C-Cu distance is large,
beyond the repulsive force range. So the C-Cu interaction is attractive. When the nanogroove depth is small, this attractive force is strong enough to bend the graphene to fit the copper surface. Since the overall force on the GNR is zero on average, a net repulsive force will arise for the supported graphene areas. For example, at the location 14~16 nm in the length direction of the GNR [inset in Fig. 28(a)] the graphene is supported and the net interatomic force is calculated at +0.021 eV/Å. The positive sign indicates a repulsive force. This force gives a local pressure of 2.9 MPa for the supported graphene. Such high local pressure can significantly reduce the local interfacial thermal resistance. At the location of 16~18 nm shown in Fig. 28(a), the graphene is suspended. The net force is −0.01 eV/Å and the negative sign indicates an attractive force. The contact (local) pressure between the graphene and Cu-substrate increases greatly in the supported graphene region due to the significant attractive force in the suspended regions. This is like the supported graphene region is pulled down on both sides by the attractive force in the suspended regions. The significantly increased contact local pressure in the supported graphene region leads to a decreased thermal resistance between graphene and copper. This thermal resistance decrease offsets the thermal resistance increase in the suspended region, giving an overall thermal resistance decrease.

When $\delta$ becomes large enough, in the suspended region, a lot of graphene atoms have very weak or zero interaction with copper atoms. To elucidate this phenomenon, the radial distribution function (RDF) between graphene and copper for $d = 2$ nm cases are calculated and the results are shown in Fig. 28(b). It is observed that the $g(r)$ values are evidently larger at small nanogroove depths and drop to a much lower level when $\delta$ is increased from 0.63 nm to 0.83 nm. This corresponds to the interfacial thermal resistance
jump from $\delta = 0.63$ nm to $\delta = 0.83$ nm, as shown in Fig. 27(a). This again reinforces the fact that when the nanogroove depth is small, the supported graphene can stay closely with the dented Cu surface. When graphene in the suspended region is completely separated from Cu (weak/no coupling), the thermal resistance jumps suddenly. At the same time, the repulsive force in the supported area becomes smaller, and the local thermal resistance increases due to the reduced local pressure. Therefore the graphene can be hanged over the nanogrooves and the corresponding thermal resistance increases due to significant reduction in thermal contact area. As the nanogroove width $d$ grows larger from 1 nm to 4 nm, the suspended area of the GNR increases, which makes it easier for the top layer GNR to bend over to fit the surface patterns of the Cu-substrate. It can be concluded that for larger $d$ values, the carbon atoms will remain in close contact with the Cu-substrate for larger nanogroove depth, which leads to lower thermal contact resistances than the corresponding cases with a flat Cu-substrate.
Figure 28. (a) Interatomic force distributions in the GNR system at out-of-plane (z) direction for \( d = 2 \) nm, \( \delta = 0.63 \) nm hybrid system. (b) Radial distribution function between GNR and copper for different \( \delta \) cases at \( d = 2 \) nm.

### 3.3.3.4 Effects of nanobump formations

It can be seen in Fig. 26 that when the supported GNR regions are deformed into the substrate’s roughness patterns, the edges of the nanobumps are smoothened toward curved shapes. While for those fully separated regions between GNR and Cu, the nanobumps maintain their rectangular shapes with well-defined vertical edges. In this subsection, the effects of nanobump’s formations on the interfacial thermal resistance are
explored for $d = 2$ nm cases. To keep consist with previous calculations, the same set of nanogroove depth $\delta$ are used. Since the contact areas of rectangular nanobumps with GNR transient into curved shapes at steady state, it can be speculated that cylindrical shaped nanobumps can reduce the thermal contact resistances with better surface contacts. To prove this substrate design, cylindrical nanobumps with radius of 1 nm are carved from the rectangular models. Fig. 29(a) and (b) depict the steady state atomic configurations of two different nanobump formations at $\delta = 0.83$ nm. It is shown in Fig. 29(a) that all the supported GNR regions are bent over and remain in close contact with the substrate, which is significantly different from previous rectangular case under the same $d$ and $\delta$ conditions. Dependence of interfacial thermal resistance on nanogroove depth is shown in Fig. 29(c). It is concluded from previous rectangular nanobump results that when $\delta$ increases from 0.63 nm to 0.83 nm, the interfacial thermal resistance exhibits a sudden jump due to the separation of carbon and copper atoms. While for the cylindrical nanobump cases, this phenomenon disappears. The thermal contact resistance gradually increases for $\delta > 0.63$ nm cases and reaches the maximum value of $2.65 \times 10^{-8}$ K·m²/W when $\delta = 1.46$ nm. The atomic configuration in Fig. 29(a) clearly shows that the GNR monolayer remains in close contact with substrate when the nanobumps become smoother, which directly improves the surface contact conditions between GNR-Cu and results in smaller thermal contact resistances. While for $\delta \leq 0.63$ nm cases, the results do not have significant variations since the cylindrical and rectangular nanobumps have same/similar formations. To confirm the conclusion that interfacial thermal resistance reduction is induced by the high local pressure in supported GNR regions, interatomic forces at GNR’s out-of-plane ($z$) direction on 0.63 nm cylindrical nanobump Cu substrate
are calculated. Configuration of the hybrid structure and distribution of the interatomic forces are depicted in Fig. 29(d). The calculated interatomic force in the region of 14-16 nm is +0.021 eV/Å, which corresponds to a high local pressure of 2.9 MPa and is the same as that in the rectangular nanobump Cu substrate. This result provides a better approach to reduce the interfacial thermal resistance within a wider range of nanogroove depths.
(a) Cylindrical bump
δ = 0.83 nm

(b) Rectangular bump
δ = 0.83 nm

(c) Thermal Resistance (×10⁻⁸ K·m²/W)
- rectangular bump
- cylindrical bump

(d) Interatomic force (eV/Å)

Nanogroove depth δ (nm)
Length (nm)
Figure 29. Atomic configurations of (a) cylindrical nanobump and (b) rectangular nanobump for $d = 2$ nm, $\delta = 0.83$ nm heterostructures at a steady state. (c) Dependence of $R$ on nanogroove depth for cylindrical and rectangular shaped nanobump systems. (d) Interatomic force distributions in the GNR system at the out-of-plane ($z$) direction for $d = 2$ nm, $\delta = 0.63$ nm cylindrical nanobump system.

3.3.4 Conclusion

The interfacial thermal resistance between GNR monolayer and copper substrate is studied using classic MD simulations. A fast transient pump-probe technique is applied in this study to characterize the thermal contact resistance $R$, which can be determined from 100 ps MD simulation after the hybrid system reaches steady state. The effects of nanogroove dimensions, interface coupling strength and nanobump formations are investigated. The $R$ of flat surface substrate is calculated at $2.61 \times 10^{-8}$ K-m$^2$/W, which can be further decreased by 17% when nanogrooves of 2 nm width and 0.63 nm depth are engraved on the substrate surface. Compared with rectangular shaped nanobumps, a cylindrical nanobump formation can also effectively reduce $R$ values at large nanogroove depth. The thermal resistance decrease is caused by the high local pressures in the supported regions which enhance the thermal energy coupling and offset the thermal resistance increase in the suspended regions. Our study not only demonstrates an interface engineering method to improve the performance of micro/nano electronics but also provides new fundamental knowledge on the thermal transport between graphene and copper interfaces at sub-nm levels.
3.4 Interlayer thermal conductance within phosphorene and graphene bilayer

3.4.1 Introduction

Lately, it has been shown that stacking graphene/phosphorene vdW bilayer can preserve their properties in the ultimate heterostructure.\textsuperscript{142} The relative position of phosphorene’s band structure with respect to graphene’s can be tuned \textit{via} a vertical external electric field. Moreover, by exploring the electric field dependent band structures and optical properties of graphene/phosphorene bilayer system, Hashimi \textit{et al.}\textsuperscript{143} demonstrate that the bilayer heterostructure can be applied to high-speed device although the optical anisotropy in bilayer structure for in-plane electric field polarization has disappeared. Due to the presence of lone-pair state, monolayer phosphorene can be corrugated when in contact with common metal electrodes, which may degrade their performance. Conversely, graphene has excellent structural integrity with both metal electrodes and phosphorene due to its atomically smooth surface. Thus, graphene can serve as a perfect interfacial material between the phosphorene and metal electrode.\textsuperscript{173} In this work, the interfacial thermal transport at a graphene/phosphorene bilayer heterostructure is systematically investigated using classical MD simulations. To facilitate the thermal dissipation at the out-of-plane direction, several modulators, \textit{i.e.}, system temperature, contact pressure, surface defect and chemical functionalization, are considered and their effects on reduction of $R$ are significant. In the following sessions, the system construction and the approach for $R$ computation are explained. Detailed phonon power spectrum analyses are conducted for in-depth discussions.
3.4.2 Methods

The C-C interactions within graphene are described by the second generation of Brenner’s potential, i.e., REBO. The P-P interactions are modelled by a SW potential, which has been previously tested in the studies of phosphorene’s mechanical, thermal and optical properties. Coupling between graphene and phosphorene is described by the 12-6 LJ potential. The LJ parameters are taken from the UFF, where \( \varepsilon_{C-P} = 7.771 \text{ meV}, \sigma_{C-P} = 3.560 \text{ Å}, \varepsilon_{H-P} = 5.030 \text{ meV} \) and \( \sigma_{H-P} = 3.082 \text{ Å} \). To eliminate the size effects in lateral directions, periodic boundary conditions are applied to the in-plane \( x \) and \( y \) directions. Free-boundary condition is used in the out-of-plane \( z \) direction to allow full relaxation of the heterostructure during equilibrium simulation. Lateral dimensions of the heterostructure are 11.8 \( \times \) 12.2 (\( x \times y \)) nm\(^2\). Atomic configuration of the system is shown in Fig. 30. Time step in the MD simulations is 0.5 fs.

![Figure 30. Atomic configuration of the phosphorene-graphene bilayer heterostructure.](image-url)
3.4.3 Results and discussion

All MD simulations in this work are performed by LAMMPS. To characterize the interfacial thermal resistance within the bilayer structure, the system is initially placed into $NVT$ ensemble for 600 ps at temperature 300 K and then moves to $NVE$ ensemble for another 400 ps to reach thermal equilibrium. Temperature controls are applied to graphene and phosphorene monolayers separately to avoid internal temperature differences. After system reaches the steady state, a heat flux $\dot{q}$ of $8 \times 10^{12}$ W/m$^2$ is added to graphene monolayer for 50 fs. Temperature of graphene increases to $\sim 550$ K after excitation, while the temperature of phosphorene remains at 300 K. Values of $E_t$, $T_g$ and $T_p$ are recorded in the following 200 ps relaxation process. The energy decay data are fitted in Fig. 31(a) based on Eq. 10. The computed interfacial thermal resistance at 300 K is $8.41 \times 10^{-8}$ K-m$^2$/W, which is in the same order of magnitude as other vdW bilayer structures. The temporal evolution of $R$ is shown in Fig. 31(b). Since the energy decay is driven by the temperature difference $\Delta T = (T_g - T_p)$ as shown in Fig. 31(a), the phosphorene energy changes against $\int \Delta T dt$ is plotted. It is seen that the $E_t$ profile has a linear relationship with $\int \Delta T dt$. The $E_t$ profile is divided into many segments as shown in Fig. 31(b). For each segment ($t_1$ to $t_2$), $R$ can be treated as a constant, and can be determined by linear fitting of the curve. The fitted slope equals $A/R_{\text{low-frequency}}$ and can be used to determine $R$. As presented in Fig. 31(c), the calculated instant $R$ values vary slightly around the overall fitting results, indicating that the thermal resistance is constant during the transient process.
Figure 31. (a) Temperature evolution of the individual graphene, phosphorene monolayer, and the total energy change of graphene monolayer after introducing the thermal impulse. Atomic configuration of the heterostructure at stable state is shown in the inset. (b) Relations between the total energy of graphene and the temperature difference integration with time. (c) Segment interfacial thermal resistance values obtained in (b).
The phonon power spectrum analysis provides a quantitative way to assess the power carried by phonons in a system. The overall PDOS of graphene and phosphorene are depicted in Fig. 32(a). Due to the intrinsic anisotropic phonon properties of graphene, the decomposed PDOS in lateral and out-of-plane directions are calculated separately and the results are shown in Fig. 32(b) and (c). Thermal resistance is caused by the PDOS mismatch in graphene and phosphorene. Also, unlike graphene, the PDOS of phosphorene are isotropic in all directions and only appear in low frequency regions, which is the reason why phosphorene’s thermal conductivity is lower than that of graphene.\textsuperscript{38}

**Figure 32.** Phonon-power spectra of phosphorene and graphene. (a), (b), (c) denote the overall, lateral $xy$ directions, and out-of-plane $z$ direction PDOS, respectively. Integration area of each profile is normalized to unity for comparison.
3.4.3.1 Effects of temperature and contact pressure

Thermal interface materials embedded in FETs or other nano-devices are often placed under different working temperatures. The accumulation of thermal energies in these confined spaces could lead to possible structural failures. Besides, the condensed arrangement of thermal interface materials in layered structures can cause contact pressure variations and then affect the thermal transport efficiency. Thus, to effectively reduce the thermal contact resistance between graphene and phosphorene, effects of temperature and contact pressure on $R$ are investigated.

To be consistent with previous computations, the system configuration and simulation setup remain unchanged. Initial equilibrium temperatures are varied from 50 K to 350 K. Coupling strength $\chi$ is set to 0.5, 1.0 and 2.0 for each temperature value. Five independent simulations are performed for each case to obtain an accurate statistical average of $R$, as presented in Fig. 33. It is seen that the predicted $R$ values decrease monotonically with temperature. For $\chi = 1.0$ case, $R$ is reduced by 56.5% from $17.34 \times 10^{-8}$ K-m²/W to $7.55 \times 10^{-8}$ K-m²/W. As temperature increases, more phonons with higher frequency become active in both graphene and phosphorene, which results in higher phonon populations and directly facilitate the thermal transport across vdW interface. With increasing the temperature, the high frequency phonons might also break down into large volumes of low frequency phonons which have a higher probability to transfer through the interface compared to high frequency phonons. Besides, the more intensive three-phonon scatterings at higher temperatures can scatter the high frequency phonons within graphene into various low frequency branches, leading to the higher phonon transmission coefficients and enhanced phonon couplings between graphene and
phosphorene. The heat capacities of phosphorene and graphene are functions of temperature and will increase with temperature since more phonon modes will be excited, which as a result will lead to enhanced interfacial thermal conductance and reduced thermal resistance. In this work, the heat capacities are not directly involved in the thermal resistance calculations since $R$ is determined from temperature and energy correlations. Aside from the heat capacity effects, another important factor that contributes to the reduced thermal resistance is the increased inelastic phonon scatterings at the interface at higher temperatures. The interfacial thermal resistance calculated by the conventional acoustic mismatch model and diffuse mismatch model is independent of temperature within the classical high temperature limit. This is because the only temperature dependent parts for both models are the distribution functions, whereas inelastic scatterings are not considered at the interfaces. The transient method applied in this work accounts for both elastic and inelastic scatterings at the interface. It has been proved that at vdW heterojunctions, inelastic scattering provides the major contribution to the energy transport surpassing that of elastic scattering at high temperatures. The increase in the probability of inelastic scattering is due to the fact that, at high temperatures, the high frequency phonons might break down into large volumes of low frequency phonons. These low frequency phonons have a higher probability of getting transferred through an interface when compared to the high frequency phonons, leading to higher phonon transmission coefficients and a reduction in the overall interfacial thermal resistance for the system with increasing temperature.

When the coupling strength $\chi$ increases from 0.5 to 2, the predicted thermal resistance decreases by roughly the same ratio of 70.4% at all temperature values. For example, at
300 K, $R$ reduces from $16.2 \times 10^{-8}$ K·m$^2$/W to $4.8 \times 10^{-8}$ K·m$^2$/W when $\chi$ varies from 0.5 to 2. The $R$-decreasing trend coincides well with previous studies of SiO$_2$/Si$^{180}$ and silicene/SiO$_2^{38}$ interfaces. The enhancement of thermal transport across the interface mainly comes from two aspects. First, the increase in $\chi$ enhances the contact pressure, which directly strengthens the graphene/phosphorene phonon coupling, and reduces the thermal resistance. Second, the P atoms in phosphorene act as scattering centers of graphene. The enhanced coupling strength at interface makes graphene’s intrinsic coupling between lateral and out-of-plane phonons stronger, which indirectly facilitate the thermal dissipation.

**Figure 33.** Dependence of interfacial thermal resistance on temperature and coupling strength. The predicted $R$ decreases monotonically with temperature and the contact pressure.
3.4.3.2 Effects of vacancy defects

The exceptional mechanical, electrical, and thermal properties of graphene can be attributed to its unique sp$^2$ covalent bonds between carbon atoms.$^{181}$ However, some defects are still inevitable during the fabrication of graphene sheets.$^{182-184}$ The structural defects can significantly affect the chemical, electronic and magnetic properties of graphene.$^{185-187}$ However, the effect of surface defect on interfacial thermal transport, especially for bilayer vdW structures, has not been reported in the literature. Here, randomly distributed single-vacancy defects (inset of Fig. 34) are created on the graphene monolayer with 0.5% to 2.5% fraction of the defects. Figure 34 shows that the predicted thermal resistance $R$ decreases monotonically with increasing the fraction of the defects. A 34.8% $R$ reduction is seen when the fraction of defects increases from 0 to 2.5%.

![Figure 34](image.png)

**Figure 34.** Variations of thermal resistance with the fraction of defects in graphene. The calculated $R$ decreases with defect fraction due to the enhanced phonon coupling within the graphene monolayer.
The enhanced lateral and ZA phonon coupling in graphene is the major source of interfacial thermal transport. The phonon coupling between in-plane TA and LA phonons is proven to be much faster than those between TA/LA ↔ ZA phonons. Based on the dynamic excitation theory, the phonon-coupling time between TA/LA ↔ ZA is 4.7 times longer than that between TA ↔ LA. Since the kinetic energies are evenly distributed among all directions during the heating process, two thirds of the thermal energies are confined in the lateral directions after introducing the thermal impulse. The energy flow rates from the in-plane to out-of-plane phonons can be strengthened by producing defects to the graphene monolayer, thereby promoting reduction of interfacial thermal resistance between graphene and phosphorene. To quantitatively prove this point, the phonon power spectra of pristine and 2.5% defect graphene are calculated and the lateral/flexural PDOS are presented separately in Fig. 35. The overlap areas can be calculated as 

$$\delta = \int \omega A(\omega) d\omega$$

where $$A(\omega)$$ represents the intersection area at frequency $$\omega$$. The calculated $$\delta$$ for pristine graphene equals 0.348, whereas $$\delta$$ increases to 0.390 for 2.5% defected graphene. The increased overlap areas indicate better couplings between in-plane and out-of-plane phonons in defected graphene, which indirectly enhances the interfacial thermal transport.
**Figure 35.** Lateral and flexural phonon power spectra of graphene at (a) 0% defect and (b) 2.5% defect levels. The overlap areas become larger at higher defect level, indicating the enhanced phonon coupling between in-plane and out-of-plane phonons in graphene.

To further explain the decreasing trend of $R$ with increasing the fraction of defects, phonon-power spectra for both graphene and phosphorene under different defect levels are calculated and present in Fig. 36. The PDOS of phosphorene remain unchanged in all cases, indicating that the defects in graphene barely affect phosphorene. For graphene, the high-frequency $G$-band phonons exhibit significant blue-shift with increasing the defect levels. The calculation results are consistent with previous studies.\textsuperscript{69, 188, 189} This frequency blue-shift is an outcome of strong anharmonic phonon–phonon coupling in MD simulations, demonstrating that the single-vacancy defect improves the energy exchange between in-plane LA/TA phonons and out-of-plane ZA phonons.
Figure 36. Phonon-power spectra of (a) graphene and (b) phosphorene at different defect levels. Integration area of each profile is normalized to unity for comparison.

Due to the isotopic phonon power spectra in phosphorene, it can be speculated that defects in phosphorene will have less effects to the predicted interfacial thermal resistance compared to graphene. Since unlike graphene, the lateral and flexural phonons in phosphorene are well-mixed in the crystalline structures. To validate this presumption, extra calculations have been performed with a low defect ratio of 0.5% in phosphorene at temperature 150 K. The calculated result averaged from 5 independent simulations equals $11.490 \times 10^{-8}$ K·m²/W, which is very close to the zero-defect value of $11.332 \times 10^{-8}$ K·m²/W. Whereas for the same defect ratio of 0.5% in graphene, the interfacial thermal resistance is reduced to $9.614 \times 10^{-8}$ K·m²/W, which is 15.2% smaller than the zero-defect result.
3.4.3.3 Effects of hydrogenations

Chemical functionalization is an effective approach to modify the thermal, chemical, and mechanical properties of graphene. The fracture strain, shear modulus and shear strength of graphene can be reduced as much as 50\% with the hydrogen coverage at 30\%.\(^{190}\) Other mechanical properties remain insensitive to hydrogen coverage. It has been found that both concentration and configuration of hydrogen functional groups have significant influence on the thermal conductivity. By adjusting the coverage and distribution pattern of hydrogen adsorbates on graphene’s edge or surface, significant thermal rectifications can be achieved.\(^{191-193}\) Due to the significant effects of hydrogenation on thermal transport, it is necessary to investigate its impact on the interfacial thermal conductance between phosphorene and graphene.

In practice, hydrogen atoms can be attached to the single or both sides of graphene sheet. Therefore, all three cases, \(i.e.\) H-top (graphene is between H atoms and phosphorene), H-bottom (H atoms between graphene and phosphorene) and H-both (H atoms on both sides of graphene), are considered in this work with coverage ranging from 0\% to 12\%, while the pattern is random. Atomic configurations of the hydrogenated graphene monolayer are depicted in Figs. 37(a)-(c), respectively. It is worth noting that for H-both structure, the total number of hydrogen atoms from both side equals those of H-top/H-bottom from one side at the same coverage ratio. As shown in Fig. 37(d), the predicted interfacial thermal resistance \(R\) decreases monotonically with the hydrogen coverage. The minimum \(R\) occurs when hydrogen atoms are added to the bottom of graphene, \(i.e.,\) sandwiched between graphene and phosphorene. In this case, the maximum \(R\) reduction of 84.5\% is observed at 12\% hydrogen coverage. When H atoms are directly in contact with P atoms
in phosphorene; the phonon coupling between the two sheets is much stronger than other cases, and it offsets the enlarged distances between graphene and phosphorene.

**Figure 37.** Effect of hydrogenation on the interfacial thermal transport between phosphorene and graphene.

The enhanced thermal transport can be attributed to two main factors. First, the extra phonon coupling between H and P atoms directly facilitates the thermal transport at interface. Compared to individual graphene monolayer, an extra H-P heat dissipation channel is created in addition to that between C-P atoms. Contributions from this new heat dissipation channel can enhance the surface phonon coupling and reduce the
interfacial thermal resistance. Second, the hydrogenation can be viewed surface modification to graphene, which bear certain similar effects as single-vacancy defect. The absorbed H atoms on graphene can also behave as scattering centers, thereby enhancing the graphene’s lateral to flexural direction phonon coupling which indirectly strengthens the thermal transmission from graphene to phosphorene. The enhanced phonon couplings between graphene and phosphorene with hydrogenation can be further proved by the phonon power spectra analyses. H-bottom structure is selected for the PDOS calculations and the phonon power spectra of pristine graphene/phosphorene and 12% hydrogen doped graphene/phosphorene are shown in Fig. 38. It is observed that at 12% hydrogenation level, both the PDOS of graphene and phosphorene are broadened and a larger overlap is observed, indicating the enhanced phonon interactions between graphene and phosphorene.
Although the interfacial thermal resistance between graphene and phosphorene can be reduced by hydrogen functionalization, the quantitative contributions of H and C atoms to the thermal transport are still open questions. The effects of H atoms on the enhanced thermal transport can be understood by turning off the interactions between C-P atoms or H-P atoms. Since minimum R occurs when H atoms reside in the middle of graphene and phosphorene, the H-bottom configuration is used in the following calculations. The LJ parameters $\varepsilon_{C-P}$ and $\varepsilon_{H-P}$ are set to zero separately; the calculated R values are summarized in Fig. 39. $R$ reaches the lowest level when both C and H atoms are involved ($\varepsilon_{C-P} \neq 0, \varepsilon_{H-P} \neq 0$) in the thermal transport. When only H atoms are involved ($\varepsilon_{C-P} = 0, \varepsilon_{H-P} \neq 0$), $R$ increases significantly by two orders of magnitude. The $R$ values with only C atoms involved ($\varepsilon_{C-P} \neq 0, \varepsilon_{H-P} = 0$) are in between the two cases. The calculation results indicate that the thermal transport is still dominated by C-P interactions even with the hydrogenation. Interfacial thermal resistance is mostly dependent on the materials’ atomic mass ratio at the interface. The predicted $R$ value increases monotonically with atomic mass ratio, which further explains the greater contributions from carbon atoms since P/H mass ratio is 12 times higher than that of P/C.\textsuperscript{194}
3.4.4 Conclusion

Inter-plane thermal conductance at the phosphorene-graphene vdW interface is investigated using classical MD simulations. Several modulators such as system temperature, contact pressure, vacancy defect, and hydrogenation are explored, with which significant thermal resistance reductions are observed. The maximum $R$ reduction is predicted as 84.5% when the hydrogenation is applied on the near-phosphorene-side graphene surface. Other factors such as temperature, coupling strength, and fraction of single-vacancy defects have relatively weaker influences on $R$, which decrease $R$ values by 56.5%, 70.4%, and 34.8%, respectively. The PDOS mismatch in graphene and phosphorene appears to be the key factor to the thermal resistance. Note that unlike graphene, the PDOS of phosphorene are isotropic in all directions and only exist in low-frequency region. Reductions of $R$ at the interface can be attributed to several factors,
including increased phonon population, enhanced anharmonic phonon scattering at higher temperatures, as well as strengthened coupling between lateral and out-of-plane phonons of graphene with increasing fraction of the defect or functionalization. Our study provides new insights into thermal resistance in phosphorene-graphene bilayer, which can be useful for better design of heterostructures for nanoelectronic applications.

3.5 Lateral and flexural phonon thermal transport in graphene and stanene bilayer

3.5.1 Introduction

Recently, it has been reported that opening of an indirect band gap (~ 80 meV) can be realized in graphene/stanene hetero-bilayer. Combined with the extraordinary thermal conductivity of graphene, this new heterostructure may be promising for application in FETs. In particular, the high carrier mobility of graphene as well as the strong spin Hall effects of stanene can coexist in the bilayer, giving it an advantageous position as quantum spin Hall insulator and high-speed spintronic device. Despite of its excellent structural, electronic and optical properties, to our knowledge, the thermal properties of graphene/stanene bilayer heterostructure have not been investigated. It is important to thoroughly investigate both the in-plane and out-of-plane thermal conduction before their massive applications. In this work, the lateral and flexural phonon thermal transports in graphene/stanene hetero-bilayer are investigated using classical MD simulations. The in-plane thermal conductivity is characterized by the d-NEMD method. And the out-of-plane interfacial thermal resistance is calculated by the transient pump-probe method. The large $\kappa$ discrepancies between graphene and stanene are explained by phonon power
spectrum analyses and spatiotemporal temperature evolutions in overall/decomposed directions.

3.5.2 Methods

Periodic boundary conditions are applied in the lateral $x$ and $y$ directions to eliminate edge effects. Free boundary condition is used in the out-of-plane $z$ direction to allow the system fully relaxed. The initial distance between stanene and graphene is set at 4.1 Å. The second-generation Brenner potential, i.e., REBO, based on the Tersoff potential with interactions between C-C bonds is used to describe the graphene system. A Tersoff potential based on an ab initio derived training data set is used to model the stanene monolayer. The vdW interactions between graphene/stanene is described by the classic 12-6 LJ potential. The LJ parameters are taken from the UFF, where $\sigma_{C-Sn} = 10.58$ meV and $\sigma_{C-Sn} = 3.664$ Å. The cutoff distance $r_c$ equals $3.5\sigma_{C-Sn}$, which is 12.824 Å.

When calculating the in-plane thermal conductivity of 2D monolayer structures, the material’s thickness needs to be selected with great caution. Conventionally, the vdW distance between adjacent layers in the bulk structure is used as the layer thickness. Under such a scenario, the thickness of graphene $d_g$ is set as 3.35 Å, and thickness of stanene $d_s$ is 4.5 Å based on ab initio calculations. The overall thickness of the bilayer $d_b$ is the addition of $d_g$ and $d_s$, which equals 7.85 Å. On the other hand, Wu et al. in their recent publication argued that thickness is not a well-defined quantity for two-dimensional monolayer materials, and thus the same thickness should be used for all 2D materials when comparing their thermal conductivities. To avoid the ambiguous definition of thickness, Wu et al. proposed a new concept defined as
\[ \dot{\kappa} = -\dot{Q}/(w \cdot \nabla T) \], where \( \dot{Q} \) stands for heat energy; \( w \) is width of the system, and \( \nabla T \) is the temperature gradient. However, as stated by Wu et al., this new quantity \( \dot{\kappa} \) named as ‘thermal sheet conductance’ (W/K) is intrinsically different from the widely adopted definition of thermal conductivity \( \kappa \) (W/m·K) used by the academic thermal scientists. The thickness of 2D materials should be regarded as a numerator which needs be unified for fair comparisons of thermal conductivity. Therefore, Wu et al. used the thickness of graphene 3.35 Å to calculate the heat transfer capabilities of different 2D materials. Under this scenario, the thickness of graphene \( d_g \) and stanene \( d_s \) are both 3.35 Å, and the overall thickness of the bilayer \( d_b \) is 6.7 Å. In this work, both selections of thickness values are used and the corresponding in-plane thermal conductivities are calculated separately.

3.5.3 Results and discussion

3.5.3.1 Lateral phonon thermal transport

It is known that in-plane thermal conductivity of graphene is two orders of magnitude higher than those of stanene. Since stanene can lead to an indirect bandgap opening in the bilayer structure, it is interesting to know whether this bilayer structure can also inherit the high thermal conductivity of graphene. To address this issue, the overall thermal conductivity of the bilayer \( \kappa_b \), individual thermal conductivities of graphene \( \kappa_g \) and stanene \( \kappa_s \) are calculated using the d-NEMD method. The initial system is placed in a \( NVT \) ensemble for 1 ns to reach steady state. Next, the simulation system is changed to \( NVE \) for NEMD calculations. A heat source (a ribbon with 2 nm width) is created in the middle of the bilayer structure, and two heat sinks (each ribbon with a width of 1 nm) are
created at the two ends of the system. Temperature controls in the heat reservoirs are realized by the Langevin thermostat.\textsuperscript{199} Schematic of the system setup is shown in Fig. 40.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig40.png}
\caption{Atomic configuration of the graphene/stanene hetero-bilayer. Periodic boundary conditions are applied in lateral \textit{x} and \textit{y} directions. Free boundary condition is used in the \textit{z} direction.}
\end{figure}

For thermal conductivity characterizations, the heat source/heat sink temperatures are controlled at $T+\Delta T$ and $T-\Delta T$ respectively, where $\Delta T$ equals 50 K. Taking the 340.8\times 9.7 nm$^2$ system as an example, after the system reaches equilibrium at $T = 300$ K, temperatures of heat reservoirs at two ends are set at 250 K, and the middle at 350 K. Temperature distributions of the system at the steady state are shown in Fig. 41. Temperature regions within the black brackets in Fig. 41 are used for the $VT$ calculations. The predicted $VT$ for graphene, stanene and the bilayer are 0.430 K/nm, 0.422 K/nm and 0.428 K/nm, respectively. The inset of Fig. 41 depicts the atom configuration at the steady state. The planar structure of graphene and buckled structure of stanene are well preserved.
Figure 41. Temperature distributions of graphene, stanene, and bilayer at steady state. Discrepancies among $\nabla T_b$, $\nabla T_g$ and $\nabla T_s$ are within 1.9%. Inset shows the atomic structures at equilibrium state. Pink spheres represent graphene carbon atoms. Blue spheres represent stanene tin atoms.

The accumulated thermal energies added/subtracted to the heat reservoirs of graphene and stanene are shown in Fig. 42. It is observed that the energy needed to maintain a 100 K temperature difference in graphene is much larger than that of stanene, indicating that graphene has higher thermal transport capability which can dissipate thermal energies much faster from the heat source to the heat sinks. The slope of the energy profile can be used to determine the heat flux in each system. The calculated heat flux for graphene and stanene is 9.92 eV/ps and 0.21 eV/ps, respectively. Thermal conductivities of graphene, stanene, and the bilayer are predicted to be 569.7 W/m·K, 9.0 W/m·K and 241.5 W/m·K, respectively. The calculated $\kappa_g$ is two orders magnitude higher than $\kappa_s$, consistent with
Moreover, the thermal conductivity of graphene/stanene bilayer reaches a quite high value of 241.5 W/m·K for system length of 340.8 nm.

**Figure 42.** Accumulated thermal energies in heat reservoirs of graphene and stanene versus time.

Length dependence of thermal conductivity for graphene, stanene and the bilayer are shown in Figs. 43(a) and (b). Results in Fig. 43(a) are calculated based on the vdW thickness and Fig. 43(b) shows the results from a unified thickness of 3.35 Å. To better compare with existing literature, the following reported data values are based on Fig. 43(a). Each data point is taken from averaging over three independent simulations with different initial conditions. Aside from the 340.8 nm system, lengths (l) of 21.2, 42.5, 85.1, 170.3, 255.5 and 426.0 nm are simulated. Widths of all 2D systems have the same value of 9.7 nm with periodic boundary conditions. Since the heat current flows in two directions symmetrically, the effective heat conduction length is half the value of system length. It is observed that κ increases monotonically with system length and gradually
converges at the highest length values. Overall thermal conductivity of the bilayer increases from 85.9 W/m·K to 267.1 W/m·K with increasing \( l \). Since the heat flux in the bilayer equals to the sum of those from graphene and stanene, based on Eq. 1, correlations of \( \kappa_b \), \( \kappa_g \) and \( \kappa_s \) can be described by\(^{178}\)

\[
\kappa_b d_b \nabla T_b = \kappa_g d_g \nabla T_g + \kappa_s d_s \nabla T_s .
\] (12)

As shown in Fig. 41, the temperature gradients of the three systems only has 1.9% discrepancies, hence \( \nabla T_b \), \( \nabla T_g \) and \( \nabla T_s \) can be treated as equivalent. Besides, it has been proven that \( \kappa_s \) is two orders of magnitude smaller than \( \kappa_g \) and \( \kappa_b \), therefore, it can be safely neglected in Eq.12. Based on the above discussions, the thermal conductivity of the bilayer can be estimated from \( \kappa_b = d_g / d_b \cdot \kappa_g \). The predicted thermal conductivities of graphene/stanene bilayer are shown in Fig. 43, which coincides well with the NEMD calculation results. The relation between \( \kappa_g \) and \( \kappa_b \) provides an accurate and fast estimation of the bilayer thermal conductivity without using NEMD simulations on the hetero-bilayer. Besides, this empirical rule can be applied to other bilayer systems with large \( \kappa \) difference in the individual monolayer. The derivation of \( \kappa_b = d_g / d_b \cdot \kappa_g \) requires two simplifications: 1. The temperature gradient in all systems can be treated as the same, which gives \( \kappa_b d_b = \kappa_g d_g + \kappa_s d_s \). 2. Thermal conductivity in one monolayer is significantly lower than that of the other (\( \kappa_s \ll \kappa_g \)), which means the smaller value can be neglected and gives \( \kappa_b = d_g / d_b \cdot \kappa_g \). From the above discussions, it can be concluded that the derived equation is valid regardless of the layer thickness. The \( d_g \) and \( d_b \) values are numerators, which do not affect the correctness of the derived equation. This equation
only works for two monolayers which have distinct \( \kappa \) values and therefore cannot be used in bilayers consisted of the same material, e.g., two graphene layers.

**Figure 43.** Dependence of thermal conductivities \( \kappa_b, \kappa_g \) and \( \kappa_s \) with (a) vdW thickness and (b) unified thickness. Each data point is averaged over three independent simulations with different initial conditions. The predicted bilayer thermal conductivity \( \kappa_b \) from Eq. 12 coincides well with the simulation results.
The calculated thermal conductivity results are fitted using a linear function for lengths of 85.1 nm – 426.0 nm with Eq. 7. The fitted results for $1/\kappa$ and $1/L$ are shown in Figs. 44(a) and (b). Results in Fig. 44(a) and (b) are calculated based on the vdW thickness and unified thickness, respectively. As is shown in Fig. 44(a), the predicted thermal conductivities for infinite-length stanene and graphene are 13.4 W/m·K and 685.4 W/m·K, respectively. The thermal conductivity for the 2D graphene/stanene sheet is 311.1 W/m·K, which is higher than many monolayer structures, such as phosphorene,\textsuperscript{38} h-BN,\textsuperscript{203} MoS\textsubscript{2}, and MoSe\textsubscript{2}.\textsuperscript{1}

To demonstrate the phonon frequency differences in stanene and graphene, the overall and decomposed partial density of states of suspended structures in $x$, $y$ and $z$ directions are calculated (see Fig. 45). The out-of-plane flexural phonon mode in graphene is highly anisotropic from the in-plane transverse and longitudinal phonon modes. It was tacitly accepted that the in-plane acoustic phonons are dominant in the thermal transport of graphene,\textsuperscript{204} yet recent studies have indicated otherwise. By measuring the thermal transport of supported graphene on amorphous SiO\textsubscript{2}, Seol et al.\textsuperscript{79} performed a revised calculation and showed that the ZA phonon 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.\textsuperscript{80} computed the lattice thermal conductivity of graphene at 300 K. It turned out that the dominant contribution to $\kappa$ stems from the ZA branch, which is greater than the combined lateral phonon contributions. A symmetry-based selection rule and an anomalously large density of states of flexural phonons are used to explain their results.
Compared to stanene, the unique properties of flexural phonons in graphene greatly contribute to the high thermal conductivity.

Figure 44. Relations of $1/\kappa$ and $1/l$ for graphene, stanene and graphene/stanene bilayer with (a) vdW thickness and (b) unified thickness.
Figure 45. Phonon power spectra of (a) overall, (b) x direction, (c) y direction and (d) z direction for graphene and stanene.

To achieve further understanding of thermal dissipations in graphene and stanene, the spatiotemporal temperature evolutions in both systems are investigated. The suspended systems with dimensions of 42.5×9.7 (x×y) nm² with periodic boundary condition in y direction and free boundary conditions in x and z directions are used. The outermost layers of atoms at two ends in the x direction are fixed in position, while the four layers of atoms at one end are grouped to intake the thermal impulse. After the system reaches thermal equilibrium at temperature 300 K, a large thermal impulse of $1\times10^{12}$ W/m² is added to the grouped atoms. The overall temperature and decomposed effective
temperature in \(x, y, z\) directions of graphene and stanene are shown in Figs. 46(a)-(d) and Figs. 46(e)-(h), respectively. It can be observed from Figs. 46(a)-(d) that after the thermal impulse, the heat energies quickly dissipate across graphene within several picoseconds. While for the stanene system shown in Figs. 46(e)-(h), the heat energies are accumulated in the heating area and do not evenly spread out after 50 picoseconds. The variation in the heat dissipation speed intuitively proves the thermal conductivity difference between graphene and stanene. Another important phenomenon is that in graphene, the heat energy conveyed by ZA phonons is greater than that by LA and TA phonons, which coincides with previous discussions. This can be directly proven by the enlarged red areas in Fig. 46(d). While in stanene, the thermal energies carried by flexural phonons do not have noticeable differences with lateral longitudinal and transverse phonons.

![Figure 46](image_url)

**Figure 46.** Spatiotemporal effective temperature evolution of graphene in (a) overall, (b) \(x\) direction, (c) \(y\) direction and (d) \(z\) direction from 0-10 ps. Corresponding effective
temperature evolution of stanene in (e) overall, (f) $x$ direction, (g) $y$ direction and (h) $z$ direction from 0-50 ps.

### 3.5.3.2 Flexural phonon thermal transport

The phonon thermal transport in graphene has over 100-fold anisotropy between the in-plane and out-of-plane directions\(^{205}\). While the in-plane thermal conductivity can be extremely high due to the covalent $sp^2$ bonding between C-C atoms; the out-of-plane thermal conductance is limited by the weak vdW interactions. For thermal interface materials such as bilayer graphene/stanene, they are often attached to substrates or embedded in the medium in practical applications, which could become a limiting heat-dissipation bottleneck in highly scaled graphene devices and interconnects. To characterize $R$ between stanene and graphene, a 42.5×9.7 nm\(^2\) system with periodic boundary conditions in $x$ and $y$ directions is used. After successive 500 ps $NVT$ and 500 ps $NVE$ MD simulations, the system reaches thermal equilibrium at temperature $\sim$300 K. A thermal impulse of $8\times10^{12}$ W/m\(^2\) is imposed on the graphene monolayer. System energy of graphene $E_t$, temperature $T_g$, and $T_s$ are recorded continuously for another $10^6$ time steps. Energy and temperature evolutions of the system are shown in Fig. 47. The total energy of graphene and the predicted profile are plotted against the left $y$-axis. Temperature $T_g$ and $T_s$ are plotted against the right $y$-axis. It can be seen that after the heat impulse, the temperature of graphene quickly rises to $\sim$550 K, while the temperature of stanene remains unchanged at $\sim$300 K. The temperature difference between stanene and graphene provides a driving force for thermal energy dissipation across the interface. The two systems reach thermal equilibrium around a final temperature of $\sim$490 K after 300 ps. Based on the temperature and energy profiles, the thermal resistance can be
calculated by Eq. 10. The fitted curve denoted in red color in Fig. 47 nicely matches the outputs from MD simulation. The predicted thermal resistance is $2.13 \times 10^{-7}$ K·m$^2$/W.

**Figure 47.** Temperature and energy evolution in the system after 50 fs thermal impulse.

The temperature profiles are shown in the right y-axis and energy profiles in the left y-axis.

To effectively reduce the thermal contact resistance between graphene and stanene, effects of temperature and contact pressure are investigated. Initial equilibrium temperatures are varied from 100 K to 500 K. Coupling strength $\chi$ is set to 0.5, 1.0 and 2.0, respectively, for each temperature value. Five independent simulations are carried out for each case to obtain an accurate statistical average of $R$, as presented in Fig. 48. It is seen that the predicted $R$ values decrease monotonically with temperature. For $\chi = 1.0$, $R$ is reduced by 50.4% from $3.47 \times 10^{-7}$ K·m$^2$/W to $1.72 \times 10^{-7}$ K·m$^2$/W. The $R$ reduction for $\chi = 0.5$ and $\chi = 2.0$ is 56.4% and 50.0%, respectively. As the temperature increases,
more phonons with higher frequency become active in both graphene and stanene, which results in higher phonon population and can facilitate the thermal transport across vdW interface.

The heat capacities of stanene and graphene are functions of temperature and also increase with temperature since more phonon modes are excited. As a result, they lead to enhanced interfacial thermal conductance and reduced thermal resistance. Here, the heat capacities are not directly involved in the thermal resistance calculations since $R$ is determined from temperature and energy correlations. Moreover, the more intensive three-phonon scatterings at higher temperatures can scatter the high-frequency phonons within graphene into various low-frequency branches, leading to the higher phonon transmission coefficients and enhanced phonon couplings between graphene and stanene.

It has been proven that at vdW heterojunctions, inelastic scattering provides the major contribution to the energy transport, surpassing that of elastic scattering at high temperatures.\textsuperscript{206} The increase in the probability of inelastic scattering is because, at high temperature, the high-frequency phonons might break down into large volumes of low-frequency phonons. These low-frequency phonons have a higher probability of being transferred through an interface when compared to the high-frequency phonons, leading to higher phonon transmission coefficients and lowered interfacial thermal resistance for the system with increasing temperature. It is worth noting that classical MD simulations do not include any quantum effect, and all vibrational modes are excited regardless of the temperature in the simulations. In reality, some high-frequency modes are not excited when the temperature is lower than the Debye temperature. Wu et al.\textsuperscript{207} investigated the role of anharmonicity in the thermal transport across a model interface consisting of a
monatomic lattice and a diatomic lattice. It is found that the anharmonicity inside the materials plays an important role in the interfacial thermal transport by facilitating the energy communication between different phonon modes. The anharmonicity at the interface has much less impact on the interfacial thermal transport. The stronger anharmonic scattering at higher temperatures leads to more efficiency energy redistribution to low-frequency phonons, which can transfer heat across the interface more efficiently.

When the coupling strength $\chi$ increases from 0.5 to 2, the predicted thermal resistance decreases monotonically with reduction ratios from 63.1% to 68.2%. The highest $R$ reduction occurs at temperature 100 K, where $R$ reduces from $6.12 \times 10^{-7}$ K·m$^2$/W to $1.94 \times 10^{-7}$ K·m$^2$/W when $\chi$ varies from 0.5 to 2. The decreasing $R$ trend coincides well with previous studies of phosphorene/silicon\textsuperscript{208} and silicene/SiO$_2$\textsuperscript{209} interfaces. The enhancement in thermal transport across the interface mainly comes from two aspects: First, the increase in $\chi$ enhances the contact pressure, which directly strengthens the graphene/stanene phonon coupling and reduces the thermal resistance. Second, the Sn atoms in stanene act as scattering centers of graphene. The enhanced coupling strength at the interface makes graphene’s intrinsic coupling between lateral and out-of-plane phonons stronger, which indirectly facilitates the thermal dissipation.
3.5.4 Conclusion

In the work, the lateral and flexural phonon thermal transport in graphene/stanene heterobilayer are studied using the NEMD simulation and transient pump-probe methods. The predicted thermal conductivity for graphene/stanene 2D sheet is 311.1 W/m·K, higher than many 2D materials such as phosphorene, h-BN, MoS$_2$, and MoSe$_2$. The calculated $\kappa$ for stanene is two orders of magnitude lower than that of graphene. The overall and decomposed PDOS analyses reveal that the active phonon frequencies in stanene are only from 0-8 THz, severely limited compared to graphene, which explains its low lateral thermal conductivity. The computed interfacial thermal resistance between graphene and stanene is $2.13 \times 10^{-7}$ K·m$^2$/W, which is on the same order of magnitude as other 2D bilayer structures. Both the system temperature and vdW coupling strength can effectively lower the $R$ value. The maximum $R$ reduction amounts to 56.4% and 68.2% with respect to temperature and coupling strength individually. The desirable thermal and

Figure 48. Interfacial thermal resistance variation with temperature and coupling strength.
electronic properties of graphene and stanene render the graphene/stanene hetero-bilayer promising as a high-performance thermal interface material or electronic material.

3.6 Phonon thermal transport in graphene/MoSe\textsubscript{2} van der Waals heterobilayer

3.6.1 Introduction

Recently, ultrathin few-layered graphene/MoSe\textsubscript{2} heterostructure has been successfully produced using an ionic liquid-assisted hydrothermal approach.\textsuperscript{210} Furthermore, the bilayer graphene/MoSe\textsubscript{2} heterostructure has also been synthesized by a series of CVD processes.\textsuperscript{211} The combination of the superior electrical conductivity from graphene and high lithium and Na-storage capacity from MoSe\textsubscript{2} can lead to a high performance Li-ion battery.\textsuperscript{210, 212, 213} It has been theoretically proven that MoSe\textsubscript{2} monolayer is an ideal substrate for potential graphene-based devices.\textsuperscript{214} The graphene/MoSe\textsubscript{2} heterobilayer exhibits a semiconducting behavior which origins from the inhomogeneity of the onsite energy of carbon atoms induced by the MoSe\textsubscript{2} monolayer. Moreover, Cheng \textit{et al.}\textsuperscript{215} proved that graphene/MoSe\textsubscript{2}/h-BN heterostructure had achieved high tunneling current on/off ratio ($5 \times 10^3$) and an ultrahigh current rectification ratio ($7 \times 10^5$), which exhibits great potential as high performance tunneling FETs. It also possesses high program/erase current ratio ($>10^5$), large memory window ($\sim 150$ V from $\pm 90$ V) and good retention characteristics, which make it a favorable candidate for 2D non-volatile memory devices.

Previous studies have reported the $\kappa$ of suspended monolayer graphene and MoSe\textsubscript{2} at room temperature to be 1047.7 W/m-K and 44.51 W/m-K, respectively, based on classical MD simulations.\textsuperscript{1, 216} To our knowledge, the thermal properties graphene/MoSe\textsubscript{2}
heterobilayer have not been investigated. In this work, using classical MD simulations, we systematically evaluate the cross-plane and in-plane thermal properties of graphene/MoSe$_2$ heterobilayer. We first investigate the effects of several external modulators including temperature, contact pressure, single-point defect on the calculated interfacial thermal resistance to find efficient ways to reduce the $R$ of heterostructure. Meanwhile, the SED and PDOS analyses are performed to help understand the phonon behaviors of the heterostructure under various conditions. We also investigated the overall thermal conductivity of graphene/MoSe$_2$ heterobilayer and the decomposed thermal conductivity for graphene and MoSe$_2$ respectively. Finally, the effects of system dimension on in-plane thermal conductivity are explored and the extrapolated thermal conductivity for infinite length graphene/MoSe$_2$ heterobilayer is extracted.

3.6.2 Methods

The graphene/MoSe$_2$ heterobilayer is built by placing a graphene monolayer 3.41 Å above a MoSe$_2$ monolayer, as shown in Fig. 49. Graphene and MoSe$_2$ have different lattice constants, where $a_{GR} = 2.46$ Å and $a_{MoSe_2} = 3.29$ Å. To construct the bilayer structure, a lattice mismatch of 0.3% is applied to the MoSe$_2$ layer. The graphene/MoSe$_2$ bilayer supercell contains $4 \times 4$ graphene unit cells and $3 \times 3$ MoSe$_2$ unit cells, making a lattice constant of $a_b = 4a_{GR} = 9.84$ Å$^2$. Thickness of the bilayer ($d_b$) is given by the summation of the thickness of each layer, where $d_b = d_{GR} + d_{MoSe_2} = 3.35 + 6.496 = 9.846$ Å$^2$. The C-C atom interactions within the graphene layer are modelled by the adaptive intermolecular reactive empirical bond order (AIREBO) potential. The MoSe$_2$ system is described by a SW potential developed by Kandemir et al. The vdW
interactions between C-Mo and C-Se atoms are modelled by 12-6 LJ potential. The distance and energy parameters $\sigma$ and $\epsilon$ are calculated based on the UFF, where $\sigma_{\text{Mo-C}} = 3.054 \text{ Å}$, $\epsilon_{\text{Mo-C}} = 3.325 \text{ meV}$ and $\sigma_{\text{Se-C}} = 3.585 \text{ Å}$, $\epsilon_{\text{Se-C}} = 7.58 \text{ meV}$. Values of energy adapter $\chi$ are modified from 0.5 to 2.0 to mimic the contact pressure alternations from halving to doubling.

Figure 49. (a) Top and (b) side views of the graphene/MoSe$_2$ heterobilayer. Periodic boundary conditions are applied to the lateral $x$ and $y$ directions. A fixed boundary condition is used in the $z$ direction. Schematics of (c) transient pump-probe approach and (d) NEMD methods.

To calculate the interfacial thermal resistance between graphene and MoSe$_2$, a heterobilayer with dimensions of $20.2 \times 11.7 \text{ nm}^2$ ($x \times y$) is built. Periodic boundary conditions are applied to the lateral $x$ and $y$ directions. A fixed boundary condition is used in the cross-plane ($z$) direction with a 20 Å vacuum space to avoid cross-boundary
interactions. The energy and temperature profiles can be obtained from the transient pump-probe approach. The system is initially relaxed in $NVT$ ensemble at the desired temperature for 200 ps and then switched to $NVE$ ensemble for another 300 ps, with a time step of 0.5 fs. After the thermal equilibrium calculations, a large amount of heat energy is added to the graphene sheet for a short period of 50 fs. During the following 500 ps thermal relaxation process, temperature and energy evolutions of the system are recorded for $R$ calculations.

The in-plane heat conduction is defined by thermal conductivity, which is evaluated by the d-NEMD method in this work. The thermal conductivity is calculated based on the Eq. 1. As shown in Fig. 49(d), the outermost layers of C, Mo and Se atoms at each end of the system are grouped together as heat sinks, with the same width of 10.5 Å. Meanwhile, the middle-layer-atoms are grouped as heat source, with a width of 21 Å. After 1 ns thermal relaxation, Langevin thermostat is applied to control temperatures of the heat sinks and heat source at 250 and 350 K, respectively, for 2.5 ns. To obtain the temperature profiles, the system is uniformly divided into small slices along the heat flux direction, with the same width of 2.5 Å for each slice. The atomic temperatures and energies within each slice are recorded and averaged for the last 1 ns.

### 3.6.3 Results and discussion

#### 3.6.3.1 Interfacial Thermal Resistance

Based on the transient pump-probe approach simulation results, the cross-plane interfacial thermal resistance can be obtained from Eq. 10. The right y axis in Fig. 50 shows temperature evolutions of the system after a heat pulse of $q = 1.9 \times 10^{-3}$ W. As a
result of the pulsed heating, temperature of the graphene layer increases to 552 K while that of the MoSe$_2$ layer remains at 300 K. The final equilibrium temperature for the bilayer system is ~438 K. Energy evolution of graphene is fitted by Eq. 10 as denoted by the red line in Fig. 50. In this case ($T = 300$ K, $\chi = 1$), the calculated interfacial thermal resistance equals $1.91 \times 10^{-7}$ K·m$^2$/W.

Figure 50. Energy evolutions of graphene layer (left axis) and temperature changes of graphene and MoSe$_2$ layer (right axis) after 50 fs thermal impulse. The red solid line shows the fitting result of MD calculated energy.

To compare the phonons behaviors of the free-standing and supported graphene, phonon SED analysis is performed based on Eq. 11. The SED calculation is performed in $NVE$ ensemble with an integration time step of 0.1 fs for a total simulation time of 100 ps. The unit cell length $a$ is 2.46 Å. The calculated SED results for free-standing and supported graphene are shown in Fig. 51(b) and (c), respectively. The phonon dispersions from the SED analysis are compared to those from the lattice dynamics calculations with GULP$^{222}$,
as shown in Fig. 51(a). It can be observed that the flexural phonon mode in graphene at \( k_0 \) point shifts to a higher frequency in the bilayer structure, which has also been observed in previous studies of graphene, \( h \)-BN, and silicene.\(^{223-225}\) The variation is mainly attributed to the restricted phase space for phonon-phonon scattering in the out-of-plane direction and the weak vdW interactions between graphene and MoSe\(_2\), which could modify the interatomic force constants of graphene. The SED differences shed some light on the discrepancies of phonon behaviors in free-standing and supported graphene in graphene/MoSe\(_2\) bilayer.

**Figure 51.** Phonon SEDs of free-standing graphene from (a) lattice dynamics and (b) MD simulation. (c) The SED of supported graphene in graphene/MoSe\(_2\) bilayer from MD simulation. The shading area indicates the SED magnitude for 2D Fourier transform of each \( k \) and \( f \) combination with an integration time of 100 ps.

Figure 52 presents the calculated thermal resistance at different temperature and contact pressures. Each data point is averaged from 5 independent simulations. For all coupling
strengths, the predicted $R$ values decay with increasing temperature. At normal pressure ($\chi = 1$), when the system temperature changes from 100 to 600 K, $R$ reduces by 65% (from $3.54 \times 10^{-7}$ to $1.24 \times 10^{-7}$ K·m$^2$/W). While the enhanced contact pressure leads to the reduction of $R$ for all temperature values. At 300 K, $R$ decreases by 75% (from $4.16 \times 10^{-7}$ to $1.06 \times 10^{-7}$ K·m$^2$/W) with $\chi$ increasing from 0.5 to 2.

![Graph showing interfacial thermal resistance variations with temperature](image)

**Figure 52.** Interfacial thermal resistance variations with temperature from 100 to 600 K and coupling strength from 0.5 to 2.0.

To further understand the calculated results, PDOS is used to analyze the phonon behavior based on Eq. 5. As shown in Figs. 53(a)-(c), the ZA branch from graphene is highly anisotropic from its LA/TA phonons. The majority of ZA phonons occupy the low-frequency regions, while LA/TA phonons occupy the high-frequency regions. Also, the overlap area between graphene and MoSe$_2$ is mainly from the ZA phonon mode. Hence, phonon coupling between the ZA phonons in the graphene and MoSe$_2$ layers is the dominant thermal pathway at the interface. At higher temperature, phonons with...
higher frequency will become activated and involved in the heat conduction. As a result, overall phonon population will increase and promoting the interfacial thermal transport. At higher pressure, the stronger interfacial coupling will enhance couplings between ZA phonons in graphene and MoSe$_2$ layers and accelerate energy passage. Therefore, both high temperature and high pressure will enhance the thermal transport at the interface.
Figure 53. (a) Overall, (b) in-plane LA/TA and (c) cross-plane ZA PDOS of pristine graphene and MoSe$_2$ at 300 K. (d) Overall, (e) in-plane LA/TA and (f) cross-plane ZA PDOS of 2.5% single-point defected graphene and MoSe$_2$ at 300 K. The insets depict the enlarged areas from 0 to 10 THz.

We further investigate the effects of single-point vacancy defects on interfacial thermal resistance. Such defects are made by randomly removing carbon atoms from the graphene layer. As shown in Fig. 54, the predicted $R$ results decrease with defect ratio. As the defect ratio increases from 0 to 2.5%, $R$ reduces by 43% (from $1.91 \times 10^{-7}$ to $1.09 \times 10^{-7}$ K·m$^2$/W). To understand the reduction of $R$ with defect, PDOS for the heterobilayer with 2.5% defect ratio is calculated as shown in Fig. 53(d)-(f). To quantitatively evaluate the differences between phonon coupling of graphene and MoSe$_2$ layers, the PDOS overlap area for graphene and MoSe$_2$ is integrated for both defected and perfect systems. It is found that the intersection area of the defected system is 11%, 5%, and 14% greater than that of the perfect system for the overall, LA/TA and ZA phonon mode, respectively. The larger overlap area for a defected system means higher phonon coupling at these regions. An obvious increase of ZA phonon interactions between graphene and MoSe$_2$ layer can be observed from Fig. 53(c) and (f), indicating the direct enhancement of ZA phonon coupling. Meanwhile, as shown in Fig. 53(b) and (e), peaks of LA/TA phonons in defected graphene are much lower than those of perfect graphene, which means more LA/TA phonons in defected graphene layer occupy the low-frequency states. It is due to the single-point defects in the graphene layer raise the probability of the phonon scattering of carbon atoms and assist the high-frequency phonons in breaking down into low-frequency branches. The low-frequency LA/TA
phonons are more active than high-frequency ones, and they are easier to transfer energies to the ZA phonons. Hence, the better heat exchanges between LA/TA and ZA phonons in the graphene layer indirectly improves the heat conduction at the interface.

![Figure 54](image)

**Figure 54.** Interfacial thermal resistance variations with defect ratio from 0.0 to 2.5% at 300 K.

### 3.6.3.2 In-plane thermal conductivity

The in-plane thermal conductivity of graphene, MoSe\(_2\), and their bilayer are evaluated by the d-NEMD method. Figure 55 shows the temperature profiles obtained from MD simulation. Since the system is symmetric around the heat source, only the left profile is used to calculate \(\kappa\). The calculated \(\nabla T\) for graphene, MoSe\(_2\), and bilayer are 1.23, 1.44, and 1.33 K/nm, respectively. To calculate thermal conductivity, we also need the amount of heat flux (\(J/t\)) in the system. Figure 56 shows the evolution of kinetic energy in hot and cold regions. The \(J/t\) for graphene, MoSe\(_2\) and graphene/MoSe\(_2\) are 3.98, 0.26, and 4.24
\((\times 10^{-6} \text{ W})\), respectively. The calculated \(\kappa\) values are 401.94, 11.80 and 138.24 W/m-K for 82 nm graphene, MoSe\(_2\) and graphene/MoSe\(_2\), correspondingly.

**Figure 55.** Temperature profiles of graphene, MoSe\(_2\), and bilayer in an 82 nm long system at steady state. The brackets surrounded regions are used for linear fittings.

**Figure 56.** Accumulated thermal energy evolutions of graphene, MoSe\(_2\), and bilayer in an 82 nm long system.
At the micro/nanoscale, the thermal conductivity of a material is a function of system size. To evaluate the size effect, graphene/MoSe$_2$ systems with lengths of 20, 82, 163, 245, 307, 409 nm are studied. The system width is kept at 11.7 nm for all NEMD models. The predicted $\kappa$ of graphene, MoSe$_2$, and graphene/MoSe$_2$ are summarized in Fig. 57. It can be observed that $\kappa$ values monotonically increase with the system length. To predict the $\kappa$ value of infinite length bilayer system, a linear-fitting approach is applied to the finite $\kappa$ results based on Eq. 7. The intercept of the fitting line, as shown in Fig. 58 should be the reciprocal of infinite long thermal conductivity $1/\kappa_\infty$. With this approach, the $\kappa_\infty$ of the individual supported graphene, MoSe$_2$, and the bilayer system is evaluated to be $709.2$, $34.38$, and $280.9$ W/m·K, respectively. When compared with the $\kappa_\infty$ for free graphene (1047.7 W/m·K) and MoSe$_2$ (44.5 W/m·K) from previous literature, the $\kappa_\infty$ for both supported graphene and MoSe$_2$ decreases.$^{1,38}$ It indicates that the existence of substrate reduces the in-plane heat conduction for both graphene and MoSe$_2$ layers, whereas, the $\kappa_\infty$ of bilayer system is one order of magnitude greater than the single MoSe$_2$ sheet. As proven by Seol et al.$^{79}$, the ZA phonons attribute to as much as 77% of $\kappa$ for single layer suspended graphene, and when the MoSe$_2$ layer involved, the substrate interactions between them enhanced the Umklapp scattering for the ZA phonons in the graphene layer due to the breaking of ZA phonon reflection symmetry. Hence, Mo and Se atoms in the MoSe$_2$ impede the heat transport in the graphene layer and result in the reduction of $\kappa$. We could expect similar effects on the ZA branches in MoSe$_2$ layer, which could lead to the drop of its $\kappa$ too.
Figure 57. Thermal conductivity variations with system length for graphene, MoSe₂, and graphene/MoSe₂ bilayer at 300 K. The pink line stands for the thermal conductivity of bilayer system predicted by Eq. 15.

Figure 58. Relations of $1/\kappa$ and $1/L$ for graphene, MoSe₂ and graphene/MoSe₂ at 300 K.
To quantitatively understand the $\kappa$ relationship between graphene-MoSe$_2$ bilayer and single layer systems, we used an equation derived by Liu et al.$^{178}$ to predict the $\kappa$ of the bilayer system. For the NEMD method, the amount of heat flux added to the bilayer system equals the summation of heat flux added to every single layer,

$$\dot{q}_B A_B = \dot{q}_{GR} A_{GR} + \dot{q}_{MoSe_2} A_{MoSe_2},$$

(13)

where the heat flux density is given by $\dot{q} = -\kappa \cdot \nabla T$ and the cross section area is $A = dw$. Since the width ($w$) of all systems are the same and temperature gradient $\nabla T$ are pretty similar to each other as demonstrated in Fig. 55, we can assume that $\nabla T_B = \nabla T_{GR} = \nabla T_{MoSe_2}$. Hence, it is derived that

$$\kappa_B d_B = \kappa_{GR} d_{GR} (1 + \frac{\kappa_{MoSe_2} d_{MoSe_2}}{\kappa_{GR} d_{GR}}).$$

(14)

Liu et al.$^{178}$ found that the ratio of $\kappa_{MoSe_2} d_{MoSe_2} / \kappa_{GR} d_{GR}$ dramatically decreases with system length when the length is greater than 20 nm for the graphene/MoS$_2$ system. Based on our MD simulation results, a similar trend is also observed for graphene/MoSe$_2$ system. Therefore, we can assume the ratio equals to 0 for large system, and Eq. 14 becomes,

$$\kappa_B = \kappa_{GR} \frac{d_{GR}}{d_B} = 0.347 \kappa_{GR}.$$ 

(15)

According to Eq. 15, the $\kappa_B$ for various length systems are predicted based on the $\kappa_{GR}$ values. As shown in Fig. 57, these calculated $\kappa_B$ agree well with MD simulation result $\kappa_B$. 


We further studied the effect of $\chi$ on the thermal conductivities of 82 nm long graphene, MoSe$_2$, and bilayer system at 300 K. As shown in Fig. 59, the thermal conductivities of graphene, MoSe$_2$, and bilayer all show a declining trend with $\chi$. The decreasing rate is 19.8%, 2.5%, and 16.6%, respectively, when $\chi$ increasing from 0.5 to 4.

![Figure 59. Thermal conductivity variations with coupling strength for 82 nm graphene/MoSe$_2$ system at 300 K.](image)

### 3.6.4 Conclusion

In this work, the cross-plane interfacial thermal resistance and in-plane thermal conductivity of graphene/MoSe$_2$ heterobilayer are investigated with classical MD simulation. At 300 K, the predicted $R$ at graphene/MoSe$_2$ interface is $1.91 \times 10^{-7}$ K·m$^2$/W. Effects of temperature, contact pressure, and single-point vacancy defect on interfacial thermal resistance are explored. It is observed that $R$ decreases monotonically with increasing temperature, contact pressure, and defect ratio with maximum reductions
amount to 65%, 75%, and 43%, respectively. Phonon density of states is used to reveal the mechanism of heat conduction at the bilayer interface and explain the effects of surface defect on $R$. It is revealed that the cross-plane phonon coupling between graphene and MoSe$_2$ layers is the major thermal pathway for interfacial heat conduction. Moreover, the thermal conductivity of infinite length supported graphene, MoSe$_2$, and the bilayer system are evaluated at 709.2, 34.4, and 280.9 W/m·K, respectively. Compared with free-standing graphene and MoSe$_2$ systems, the predicted $\kappa$ in the heterobilayer is smaller. Our study offers effective ways to reduce $R$ at the graphene/MoSe$_2$ interface and provides reasonable guidelines for its future applications.

3.7 Thermal contact resistance across a linear heterojunction within hybrid graphene/hexagonal boron nitride sheet

3.7.1 Introduction

Due to the geometric resemblance, i.e., condensed honeycomb lattices and covalent $sp^2$ bonding, monolayer $h$-BN possesses some similar physical properties as those of graphenes, such as strong mechanical properties$^{226-228}$ and high chemical and thermal stability$^{229-231}$. Using the MD approach, the $R$ at graphene and silicon interface is calculated at 3.1–4.9×10$^{-8}$ K·m$^2$/W$.^{34}$ Zhang et al.$^{209}$ studied the thermal resistance between silicene and various substrates with a numerical pump-probe method. They find that the interface thermal conductance at amorphous interfaces is higher than that at crystalline interfaces. Thermal contact resistances between stacked 2D sheets such as graphene/silicene$^{77}$, graphene/$h$-BN$^{78}$, and graphene/MoS$_2$ have also been investigated.
The calculation results suggest that the interfacial thermal conduction has correlated positively with system temperatures and interaction strengths. Those above supported 2D structures are attached to the substrate via weak van der Waals interactions. However, in a hybrid sheet, atoms located adjacent to the heterojunction are often connected by the strong covalent bonds. The thermal transport mechanism and phonon interactions of hybrid sheets differ from those of the stacked sheets, and further investigations are needed. In this work, the thermal transport across the graphene/h-BN heterojunction is studied using MD simulations. The thermal energy dissipation at the contact areas is investigated comprehensively. Effects of system dimensions, heat flux direction, temperature, and tensile strain on interfacial thermal resistance are explored. Detailed spatiotemporal isotherm and phonon spectrum analyses are conducted to assist explanation of the computation results.

3.7.2 Methods
A schematic of the simulation domain is shown in Fig. 60. The periodic boundary is applied to the y direction, which is perpendicular to the heat flux q direction, to eliminate size effects. Free boundary conditions are applied to the in-plane x and out-of-plane z directions. A lattice mismatch of ~1% is applied to both graphene and h-BN sheets to construct a supercell with a lattice constant of 2.485 Å. A comparable lattice mismatch between graphene/h-BN is confirmed by *ab initio* density functional calculations.\(^{232}\) Slightly larger lattice mismatches of 2.5% and 1.9% are reported in graphene/silicene\(^ {77}\) and graphene/MoS\(_2\)\(^ {233}\) hybrid sheets from previous computational studies. Compared with other graphene-based hybrid sheets,\(^ {234-237}\) the lattice mismatch considered in this study has negligible effects on the heterojunction's thermal properties.
Figure 60. Atomistic configurations of the $h$-BN and graphene hybrid sheet. Heat bath ($Q_{in}$) and heat sink ($Q_{out}$) are placed on the two ends with four layers of atoms respectively.

All MD simulations in this work are performed by LAMMPS. The second generation of Brenner potential, namely, the REBO based on the Tersoff potential with interactions between C–C bonds, is applied to model the graphene system. Interactions between boron, nitrogen atoms, and $h$-BN/graphene are described by the Tersoff potential, similar to previous studies. The r-NEMD method is conducted to characterize the interfacial thermal resistance. For thermal equilibrium simulations, the hybrid sheet is first placed in $NVT$ for 600 ps and then turned into $NVE$ for another 400 ps. After the system reaches thermal equilibrium at a given temperature, heat flux controls are applied to the heating/cooling groups constantly for another 7 ns, which is long enough for the temperature gradient to reach steady state. The heat flux is calculated by the equation

$$\dot{q} = \frac{\Delta e}{AA\Delta t}, \quad (16)$$
where $\dot{q}$ is the heat flux, $\Delta \varepsilon$ the imposed heat energy, $A$ the cross-sectional area, and $\Delta t$ is the time step. The temperature drop occurring at the heterojunction can be used to determine the thermal resistance value according to the equation:

$$R = \frac{\Delta T \cdot A}{\dot{q}},$$

(17)

where $R$ is the interfacial thermal resistance and $\Delta T$ is the temperature difference/drop across the heterojunction. Time steps are 0.5 fs for all simulations.

### 3.7.3 Results and discussion

#### 3.7.3.1 Effects of system dimension and heat flux direction

The r-NEMD method is applied for the interfacial thermal resistance characterizations. Taking the 30.0×5.0 (x×y) nm$^2$ hybrid graphene/h-BN sheet as an example, the graphene and h-BN sheets each takes half of the length, respectively, as shown in Fig. 60. After the system reaches thermal equilibrium at temperature 300 K, a constant heat flux $Q_{in} = 1.85 \times 10^{-7}$ W is added to the heat bath at each time step and the same amount $Q_{out}$ is subtracted from the heat sink simultaneously for $1.4 \times 10^7$ time steps. After the system reaches steady state, another $4 \times 10^6$ time steps are performed for data collection. The temperature distribution along the heat flux direction is shown in Fig 61. The sharp temperature drop $\Delta T$ at the heterojunction is caused by the thermal contact resistance between h-BN and graphene. To obtain an accurate temperature difference, linear fittings are applied to the temperature profiles of the hybrid h-BN and graphene sheet, and the end values are used for $\Delta T$ calculations. The calculated interfacial thermal resistance using Eq. 17 is $4.0 \times 10^{-10}$ K·m$^2$/W for the 30 nm length system. Previous studies by Li et
indicated that the interfacial thermal resistance between graphene and substrate could be lowered by two orders of magnitude if the bonding type change from vdW to covalent. The strong $sp^2$ bonds among B-N-C atoms facilitate the thermal energy dissipation at the $h$-BN/graphene heterojunction, which results in lower thermal contact resistance compared to that at the vdW interfaces.

Figure 61. Temperature distribution in the length direction of a $30.0 \times 5.0 \ (x \times y) \ \text{nm}^2$ hybrid sheet at a steady state. Temperature difference $\Delta T$ at the heterojunction is characterized by linear fitting the temperature profiles of each material and measuring the endpoint difference.

Phonon mean free path of graphene is measured at ~775 nm near room temperature. The intrinsically long MFP induces a size-dependent thermal conductivity in the graphene system. The confined dimension in the lateral directions will greatly affect the phonon behavior at the graphene/$h$-BN heterojunction. Thus, it is of great interest to
investigate the effects of system dimensions on the interfacial thermal transport. Hybrid sheets with lengths from 20 nm to 100 nm are used in the simulations. The predicted results are shown in Fig. 62. The $R$ values are independent of the heat flux direction, but decrease trend with increasing system lengths. The length dependence of $R$ arises if the system size is smaller than the phonon MFP. When the system size becomes larger, more phonon modes with longer wavelengths will be excited. Such phonons can pass through the interface with fewer degrees of inelastic scattering and possess higher transmission rates, which can make additional contributions to the thermal conduction. Aside from the length effects on the interfacial thermal conductance, the in-plane thermal conductivities of the hybrid graphene/$h$-BN sheet are also dependent on system dimensions. It has been predicted that the system length has a significant influence on the thermal conductivity of $h$-BN. The calculated thermal conductivity for infinitely long $h$-BN is 277.78 and 588.24 W/m·K, respectively, along with the armchair and zigzag directions.\textsuperscript{240}

![Figure 62. Dependence of interfacial thermal resistance on the system length.](image-url)
Phonon power spectrum analyses are conducted to assist in the understanding of the predicted results. After the hybrid system reaches a steady state with constant heat flux, atom velocities of $h$-BN and graphene hybrid sheet are recorded continuously for 10 ps, which are then used for the PDOS computation according to Eq. 5. The computed PDOS results are plotted in Fig. 63. When the heat flux flows from $h$-BN to graphene, the PDOS profiles shown in Fig. 63(a) are nearly identical to those in Fig. 63(b) where the heat flux is reversed from graphene to $h$-BN, indicating that the thermal transport is independent of the heat flux direction. One of the crucial factors in determining the interfacial thermal resistance is the overlap of phonon states. If the phonon population at a certain frequency $\omega$ is low or zero, the energy propagation by phonons of that wave vector would be highly restricted. To quantify this variation, an arbitrary unit variable, which is defined as

$$\delta = \int \omega A(\omega) d\omega,$$

is introduced to help the analyses. $A(\omega)$ represents the intersection area at a frequency $\omega$. The area integration is proportional to the amount of energy transport across the linear heterojunction by phonons at these frequency intervals. The calculated $\delta_1$ for heat flux from $h$-BN to graphene is 67.2% and $\delta_2$ equals to 67.1% in the opposite direction. The equivalent overlap areas further prove the independence of $R$ on heat flux direction.
Figure 63. Phonon power spectra of the graphene/h-BN hybrid sheet. (a) Heat flux is from h-BN to graphene. (b) Heat flux is from graphene to h-BN. The integrated PDOS overlap areas are 67.2% and 67.1% respectively.

To take a further look at the thermal energy propagation within the hybrid sheet, the spatiotemporal temperature evolution is calculated for the 40 nm length hybrid sheet. After thermal equilibrium simulation at 300 K, an ultrafast thermal impulse with an interval of 50 fs is imposed at the end of the graphene. Atoms along the heat flux direction are divided into smaller slabs whose temperature is then calculated according to Eq. 3. The isotherm contours are shown in Fig. 64. The pictures depict how heat flows from the origin to the entire field. Previous studies argued that the thermal conductivity in single layer graphene is mainly contributed by the in-plane TA and LA phonons, while the out-of-plane ZA phonon contribution can be ignored due to its small group
velocity. However, a recent study shows that for suspended graphene, the ZA phonon modes can contribute as much as 77% at 300 K and 86% at 100 K of the thermal conductivity due to the high specific heat and longer mean phonon scattering time. By formulating the ballistic thermal conductance of phonons in a 2D system and using the phonon dispersion relation, Nakamura et al. calculated the contribution of the TA, LA and ZA phonons to graphene’s thermal conductance. They also concluded that the ballistic phonon conductance is determined by the ZA phonon modes below about 20 K, but the contribution of the TA and LA phonon modes cannot be neglected above 20 K while the ZA phonon contribution is still dominant. Besides, by numerically solving the phonon Boltzmann equation, Lindsay et al. derived a symmetry-based selection rule which significantly restricts anharmonic phonon–phonon scattering of the ZA phonons, and they showed that the lattice thermal conductivity of graphene is dominated by the ZA phonon modes. Although many studies have been done to analyze the ZA modes’ effect on the in-plane thermal conductivity of graphene, their effect on the interfacial thermal conductance has yet to be investigated. Here, one can see from Fig. 64(d) that a strong thermal wave (ZA mode) propagates through the spatiotemporal isotherms, while from Figs. 64(b) and (c), no evident thermal waves (LA and TA modes) are seen. When the thermal relaxation time of phonons is relatively long, the thermal-wave effect becomes more prominent. Hence, it appears that the ZA mode is more significant than the LA and TA modes with respect to graphene’s thermal energy dissipation. It can be also observed that the ZA phonons attribute the most energy transmission across the heterojunction towards the $h$-BN monolayer, indicating the flexural phonons play a vital role in the
interface thermal conductance of the hybrid graphene/h-BN sheet. The stress wave front and thermal energy reflections at the interface are denoted in Fig. 64(d).

**Figure 64.** Thermal wave propagation from graphene to h-BN in the hybrid sheet. (a) Total temperature evolution in spatiotemporal space. (b), (c), (d) Decomposed thermal energies in x, y and z directions, respectively.

### 3.7.3.2 Effects of temperature

Temperatures from 200 to 600 K with an interval of 50 K are chosen and the calculated $R$ values in both zigzag and armchair directions are displayed in Fig. 65, where the inset shows atomic structures of the system after reaching thermal equilibrium. Our results indicate that the interfacial thermal resistance decreases monotonically with increasing temperature. Besides, the predicted $R$ values are independent of the heat flux direction at different temperatures. The decrease of $R$ can be attributed to two major factors: (1) The
increase of overall phonon population. At low temperature, only a limited number of phonons are excited and involved in the thermal transport process. When the temperature increases, higher frequency phonons can be excited, giving more contributions to the interfacial thermal transport and thereby lowering the $R$ values. (2) The increase of inelastic phonon scattering at the interface (heterojunction here), which further facilitates the phonon transmission and enhances the anharmonic coupling. The interfacial thermal resistance calculated by the conventional acoustic mismatch model (AMM) and the diffuse mismatch model (DMM) is independent of temperature within the classical high temperature limit. This is because the only temperature dependents parts for both models are the distribution functions, whereas inelastic scatterings are not considered at the interfaces. The NEMD approach applied in this work accounts for both elastic and inelastic scatterings at the interface. It has been proved that at van der Walls heterojunctions, inelastic scattering provides the major contribution to the energy transport surpassing that of elastic scattering at high temperatures.\textsuperscript{206} The second factor of the increase in the probability of inelastic scattering is because, at high temperatures, the high-frequency phonons might break down into large volumes of low-frequency phonons. These low-frequency phonons have a higher probability of getting transferred through an interface when compared to the high-frequency phonons, leading to higher phonon transmission coefficients and a reduction in the overall interfacial thermal resistance for the system with increasing temperature.
Figure 65. Thermal resistance variations with temperature from 200 K to 600 K. Inset is the fully relaxed atomic structure after the hybrid sheet reaches thermal equilibrium.

3.7.3.3 Effects of tensile strain

Mechanical strains have been proven to be an effective approach to tune the thermophysical properties of nanomaterials.\textsuperscript{242-244} For pliable 2D materials, such as graphene and h-BN, the planar structures can be easily bent to fit various substrate formations. The deformation the monolayer membranes can induce high local strains.\textsuperscript{3, 34} Effects of stains on the in-plane thermal conductivity of graphene,\textsuperscript{245} silicene,\textsuperscript{246} phosphorene\textsuperscript{247}, and other 2D materials\textsuperscript{248-250} have been extensively studied. However, the effects of tensile strain on the interfacial thermal transport across hybrid sheets are still unclear, hence the present study.

The definition of strain is $\varepsilon = (l-l_0)/l_0$, where $l_0$ is the original length, and $l$ is the final length. Interfacial thermal resistance computations are performed with strain values
varying from 1% to 7%. The predicted $R$ values are shown in Fig. 66. Our results show that the interfacial thermal resistance increases with the tensile strain. Phonon power spectra analyses are also performed to further understand the results. Figure 67 shows the computed phonon spectra of the graphene at thermal equilibrium. A notable softening of the G-band is observed when the tensile strain increases from 1% to 7%. The redshift of the higher frequency peaks reduces the phonon group velocities and results in reduced thermal conductivity according to the classical lattice thermal transport theory.\textsuperscript{251} The reduced phonon group velocities render less contribution from the phonon couplings to the interfacial heat flux, leading to higher thermal contact resistance between $h$-BN and graphene. Similar softening of the G-band was also seen in the Raman spectra of graphene flake under uniaxial strain\textsuperscript{252} and in few-layer graphene sheets under uniform in-plane strain.\textsuperscript{253}

![Figure 66. Dependence of interfacial thermal resistance on the tensile strain from 0% - 7%](image)
3.7.4 Conclusion

Thermal transport across a linear heterojunction in the hybrid graphene/h-BN sheet is investigated using NEMD simulations. Effects of the system dimension, heat flux direction, temperature and tensile strain on interfacial thermal resistance $R$ are explored comprehensively. It is found that the predicted $R$ values are independent of the heat flux directions. When the hybrid sheet length increases from 20 nm to 100 nm, the interfacial thermal resistance decreased by 58% from $5.2 \times 10^{-10}$ to $2.2 \times 10^{-10}$ K.m$^2$/W. The spatiotemporal evolution of the thermal energies from graphene to $h$-BN indicates that the main energy carrier in graphene is the ZA mode, which also contributes the most energy transmission across the interface. Due to the increased phonon populations and higher inelastic phonon scattering rates, the $R$ values decrease monotonically from $4.1 \times 10^{-10}$ to $2.4 \times 10^{-10}$ K.m$^2$/W when the temperatures increases from 200 K to 600 K.

Figure 67. Phonon power spectra of graphene under different tensile strains from 1% - 7%. The higher frequency peaks denote the G-bands.
Lastly, we show that the interfacial thermal resistance increases with the tensile strain. Our study provides a fundamental understanding of thermal transport across the graphene/$h$-BN heterojunction, and theoretical guidance for the design and development of the hybrid sheet based nanodevices.
CHAPTER 4 Machine learning and artificial neural network prediction of interfacial thermal resistance between graphene and hexagonal boron nitride

4.1 Introduction

Machine learning is a field of study that gives computers the ability to learn without being explicitly programmed. Research on ML has been around for decades but remains stagnant due to the low horsepower processors and limited dataset. Similarly, the concept of artificial neural network (ANN) was first introduced in 1942 by McCulloch et al.\textsuperscript{254} but slowly progressed until recent years. Both ML and ANN have blossomed in the era of big data with the help of Moore’s law.\textsuperscript{255} In recent years, machine learning, and artificial neural networks have made great progress in the field of artificial intelligence (AI), such as image classification\textsuperscript{256}, speech recognition\textsuperscript{257}, customized advertisements, and videos recommendations\textsuperscript{258}. The enormous success made by ML and ANN models empowers researchers to conduct more data-driven studies in different disciplines such as bioinformatics\textsuperscript{259-261}, information technology\textsuperscript{262}, and materials science\textsuperscript{263}. Most of the emerging applications of ML and ANN are supervised learning, where the models are trained on a given dataset with desired outputs.\textsuperscript{264} Once properly trained, the models can be used to predict the target values given only the instance features.

Thermal transport in materials is drawing persistent attentions because of intriguing phonon physics at various dimensions, as well as the growing importance of heat management in electronic devices and electricity base. Although ML and ANN have been applied to tackle many research problems, they rarely have been used in the field of thermal sciences.
In this work, several supervised ML and ANN models have been trained to predict the interfacial thermal resistance between graphene and h-BN. Thousands of data points were collected via high throughput computations (HTCs). The training data were generated by classical MD simulations using a transient pump-probe method. The trained models are used to predict the $R$ between graphene and h-BN given only the system temperature, coupling strength, and tensile strains values.

4.2 Methods

4.2.1 Machine learning algorithms

The workflow of a machine learning project is described in Fig. 68. The training dataset is first fed into the ML model for training. After training, the model is measured against the validation dataset for evaluation. A typical performance measure for supervised regression problem is the mean square error (MSE), which is expressed as

$$MSE(X, h) = \frac{1}{m} \sum_{i=1}^{m} (h(x^{(i)}) - y^{(i)})^2,$$

where $m$ is the number of instances in the dataset, $x^{(i)}$ is a vector of all the features, for instance, $i$, $y^{(i)}$ is the label of instance $i$, $X$ is a matrix containing all the features of all instances, $h$ is the hypothesis. The performance measure is also referred to as the cost function. If the performance of the trained model meets the deployment standard, the ML model is launched. Otherwise, error analyses and modifications are made to the model for re-training and re-evaluation. In general, several iterations of training are required to obtain the desired model performance.
In this work, four different ML algorithms, i.e., linear regression, polynomial regression, decision tree, and random forest are explored. The linear regression model can be expressed as

$$\hat{y} = h_{\theta}(x) = \theta^T \cdot x,$$

where $\theta$ is the model’s parameter vector, including the bias term $\theta_0$, $x$ is the instance’s feature vector, $h_\theta$ is the hypothesis function. Polynomial regression is based on the linear regression, which adds powers of each feature as new features and trains the model on the extended features. When there are multiple features, polynomial regression not only explores the powers of each feature, it is also capable of finding relationships between different features.

Both decision tree\textsuperscript{265} and random forest\textsuperscript{266} are versatile ML algorithms. The decision tree method splits the dataset into binary tree structures, where all datasets are nested under a root node and riven into different leaf nodes. The classifications of each node are based on the cost function.

**Figure 68.** The workflow of a classical machine learning project.
where \( k \) is the splitting feature, \( t_k \) is the threshold, \( \text{MSE}_{\text{node}} \) is the same as Eq. 18, and \( m \), \( m_{\text{left}} \), and \( m_{\text{right}} \) are the total number of training instance, left-node, and right-node training instances, respectively. Random forest is an ensemble training method, which is based on the structures of decision tree. When growing a tree in random forest, only a random subset of the features is considered for splitting at each node. The random tree model is trained via the bagging and pasting method.\(^{267}\)

Training a model means searching for the best combinations of model parameters that minimize a cost function. The model parameters are searched amongst the feature space. Therefore, one of the most important transformations on the dataset is feature scaling. In most conditions, the ML and ANN algorithms cannot perform well if the numerical input attributes have very different scales. For example, if the input temperature ranges from 100 to 500 K, while the coupling strength ranges from 0.5 to 4, then the cost function is elongated in the temperature dimension which makes it harder for the cost function to converge. There are two common ways for feature space normalizations: min-max scaling and standardization. The former rescale the values between 0 and 1, while the latter does not bound values to a specific range. Since ANN often expects input values from 0 to 1, min-max scaling is used in this work for data normalization.

4.2.2 Artificial neural network

The basic unit of ANN is called artificial neuron, which has one or more binary inputs and one binary output. The simplest ANN architecture is called Perception, which is
composed of linear threshold unit (LTU) with numerical values as inputs and outputs. The LTU outputs the weighted sum of inputs with certain step functions. A multi-layer ANN is composed of one input layers, one or more hidden layers and one output layer. When there are two or more hidden layers, the ANN is called a deep neural network (DNN). A schematic of a two layers DNN is shown in Fig. 69. Each layer except the output layer contains a bias term which equals to 1. All neurons in a previous layer are fully connected to the neurons in the next layer.

![Schematic of a two-layer deep neural network structure.](image)

**Figure 69.** Schematic of a two-layer deep neural network structure.

The concepts of ANN are based on the biological neural networks, where the connection between two neurons becomes stronger when one neuron triggers the other. Similarly, ANN uses the errors generated in the network to reinforce the connections between different neurons. For example, when some neurons predict the wrong result, the network will reinforce the weights of inputs that have contributed to the correct result. The learning algorithm is represented as

$$w_{i,j}^{n+1} = w_{i,j}^n + \eta(y_j - \hat{y}_j)x_i,$$  \hspace{1cm} (21)
where \( n \) is the \( n \)th step, \( w_{ij} \) is the weight between \( i \)th input and \( j \)th output, \( x_i \) is the \( i \)th input, \( y_j \) is the target value of the \( j \)th output, \( \hat{y}_j \) is the predicted value of the \( j \)th output and \( \eta \) is the learning rate. The weight values are updated based on the backpropagation training algorithm. For each training case, the algorithm first calculates the output of each neuron and feeds forward the results until the last layers. Then it measures the differences between the predicted output and the target output in the last layer to determine how much each neuron contributes to the errors. The errors are backpropagated to the input layer, and the weights are updated based on gradient descent. In this work, the rectified linear unit (ReLU) activation functions are used in all neural networks.

### 4.2.3 Molecular dynamics for \( R \) prediction

The training samples for ML and ANN are generated by classical MD simulations. All MD simulations in this work are performed using LAMMPS. Atomic structure of the graphene/h-BN heterobilayer is shown in Fig. 70, where the carbon, boron and nitrogen atoms are represented by cyan, pink and blue solid spheres, respectively. The transient pump-probe technique is used to calculate the interfacial thermal resistance between graphene and \( h \)-BN. The heterobilayer is first equilibrated under \( NVT \) ensemble for 300 ps. Then another 200 ps \( NVE \) ensemble is applied for system relaxations. After the system reaches thermal equilibrium at a designated temperature, a 50 fs thermal impulse is imposed on the graphene layer. In the following thermal relaxation process, the energy of graphene, temperatures of both graphene and \( h \)-BN are recorded at each time step for 500 ps for \( R \) calculation. The C-C interactions within graphene are described by the optimized Tersoff potential. The interactions between B and N atoms in \( h \)-BN are
modeled by the Tersoff potential developed by Kinaci et al.\textsuperscript{124} for BN-C nanostructures. The vdW interactions between graphene and $h$-BN are described by the 12-6 LJ potential. The energy and length parameters are extracted from the UFF table,\textsuperscript{129} where $\varepsilon_{B-C} = 5.97$ meV, $\varepsilon_{N-C} = 3.696$ meV, $\sigma_{B-C} = 3.533$ Å and $\sigma_{N-C} = 3.345$ Å. The cutoff distance $r_c$ is set as 10 Å for vdW interactions.

**Figure 70.** Configuration of graphene and hexagonal boron nitride heterobilayer.

### 4.3 Results and discussion

A heterobilayer with a dimension of $101.4 \times 98.8 \times 3.35$ (x × y × z) Å³ is used to illustrate the calculation of interfacial thermal resistance. After the system reached thermal equilibrium at temperature 300 K, a thermal impulse of $1 \times 10^{13}$ W/m² is imposed on the graphene layer. After the thermal excitation, the temperature of $h$-BN remained unchanged at 300 K while the temperature of graphene was raised to ~600 K. It can be observed from Fig. 71(a) that during the thermal relaxation process, the increasing $T_{h-BN}$ and decreasing $T_g$ gradually converged after 350 ps. The MD generated energy evolution of graphene is depicted in Fig. 71(b) by the solid blue squares. The energy can be predicted by the integral form of Eq. 10. The predicted energy profile of graphene is shown in Fig. 71(b) by the solid pink line. The predicted energy profile soundly matches the MD generated results, which indicates the validity of the fitting method. The
calculated interfacial thermal resistance equals $1.5 \times 10^{-7}$ K·m$^2$/W with a coupling strength of 1.0 and zero tensile strains, which is very close to the previously reported result.$^{78}$

Figure 71. (a) Temperature evolutions of graphene and hBN after thermal impulse. (b) MD simulation generated energy and predicted energy profiles of graphene.

4.3.1 High throughput computations of $R$

High throughput computations in this work are realized by the combinations of shell scripting, LAMMPS computations, and MATLAB post-processing. To obtain thousands of data points for interfacial thermal resistance, shell scripting is used to layout the directory tree structures for each job submission. Then the jobs are submitted to the supercomputing resources for LAMMPS computations. Once the job finished, shell scripting is adopted again for result collections. The collected results are post-processed
with MATLAB scripts to obtain the interfacial thermal resistance and organized into a spreadsheet. The spreadsheet is used as input for the ML and ANN training models.

To generate the training data for ML algorithms and ANN, different combinations of system temperature, interfacial coupling strength, uniaxial and biaxial tensile strains are explored, and the predicted $R$ results are used to train the models. Five different temperature values from 100 to 500 K and five different coupling strengths from 0.5 to 4.0 are used. For each temperature and coupling strength combination, five different tensile strains from 0 to 8% are used. The uniaxial tensile strains are applied in the armchair and zigzag directions, respectively. The biaxial tensile strains are applied in both directions. To perform statistical analyses and data augmentation, each data point is averaged from five independent simulations with different initial conditions. In total, 1625 different $R$ values are calculated.

The MD calculated $R$ results with temperature and coupling strength are presented in Fig. 72. It can be observed that the interfacial thermal resistance decreases monotonically with both increasing temperatures and coupling strengths. The high-frequency phonons might break down into large volumes of low-frequency phonons at high temperatures, which will have a higher probability to transfer through an interface and lead to higher phonon transmission coefficients. On the other hand, the enhanced coupling strength can directly heighten the atom interaction between graphene and $h$-BN, promoting the lattice synergy vibration and energy transmission across the interface. Atoms in one monolayer, such as $h$-BN, will also act as phonon scattering sites of the other layer, which indirectly increases the anharmonicity in the system. The increased inelastic scatterings at high
The temperature will directly reduce the predicted $R$. The stronger anharmonic scattering at higher temperatures leads to more energy redistribution to low frequency phonons, which can transfer heat across the interface more efficiently. The maximum $R$ reduction with temperature amounts to 64% when $\chi$ equals 0.5. On the other hand, the maximum reduction of $R$ with coupling strength amounts to 79% when temperature equals 100 K. Based on the above results, it can be concluded that the coupling strength has stronger effects on interfacial thermal resistance than the system temperature, which will be proven in the following discussions.

![Graph showing the effect of temperature and coupling strength on interfacial thermal resistance between graphene and h-BN.](image)

**Figure 72.** Effects of temperature and coupling strength on the interfacial thermal resistance between graphene and h-BN.

Effects of uniaxial and biaxial tensile strains on the predicted interfacial thermal resistance are shown in Fig. 73. The calculated $R$ increases monotonically with tensile strains in all directions. Uniaxial tensile strains in both armchair and zigzag directions
have similar effects on $R$, whereas the biaxial tensile strains have the most significant impact. The maximum increment of $R$ amounts to 59%, 49% and 99% for uniaxial zigzag, uniaxial armchair and biaxial tensile strains, respectively. Strain engineering has long been used to manipulate the thermal properties of bulk and nanostructures.\textsuperscript{209, 271, 272} It has been proven that graphene has a peak thermal conductivity value at zero strain.\textsuperscript{138} When a tensile strain is applied to the monolayers, the ripples in the flexural direction gradually disappear, and the atomic bonds stiffen which suppresses the phonon thermal transport across the interface, and leads to increasing interfacial thermal resistance. A similar observation has also been made in multilayer molybdenum disulfide structures.\textsuperscript{273}

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure73.png}
\caption{Effects of uniaxial and biaxial tensile strains on the interfacial thermal resistance between graphene and $h$-BN.}
\end{figure}

\subsection*{4.3.2 $R$ predictions via machine learning and artificial neural network}

When training ML and ANN models, it is important to make sure that the training, validation, and test datasets are from the same distributions. For example, all datasets should include different categories amongst the feature space, which is constructed with
four different attributes, i.e., system temperature, coupling strength, zigzag direction tensile strain (strain-x) and armchair direction tensile strain (strain-y). To better understand the correlations of between each feature and the predicted interfacial thermal resistance, the standard correlation coefficients ($r$) between every pair of attributes are calculated, and the results are presented in Fig. 74. The calculated $r$ ranges from $-1$ to $1$ with $-1$ representing strong negative correlations and $1$ representing strong positive correlations. Five different attributes are used in the $r$ calculations, where temperature, coupling, strain-$x$, and strain-$y$ are features, and the resistance is the target value. The values in the upper-left to lower-right diagonal direction represent the attribute themselves and therefore have positive $r$ values of 1. In Fig. 74, it is observed that coupling strength has the most significant impact on $R$, which is consistency with the results presented in Fig. 72. Therefore, stratified sampling based on coupling strength is used to split the raw data into training, validation, and test dataset with portions of 72%, 8%, and 20%, respectively. All ML and ANN models are trained on the training dataset, optimized on the validation dataset and tested on the test dataset.
Figure 74. Calculated standard correlation coefficients between each pair of attributes. It can be observed that coupling strength has the strongest correlation with interfacial thermal resistance.

After the ML models have been trained, these models can be used to predict the interfacial thermal resistance between graphene and h-BN, given only the input features. The prediction by an ML model only takes a fraction of a second, in comparison with several hours by using MD simulation. The training results of each model are shown in Fig. 75. The x-axis and y-axis represent the target (black dots) and model-predicted R (red dots) values, respectively. It can be observed from Fig. 75(a) that linear regression cannot properly describe relationships between interfacial thermal resistance and the features. The calculated MSE equals $0.854 \times 10^{-7}$ K·m²/W, which is on the same scale of previously predicted R values. The second order polynomial regression algorithm is
selected to train on the dataset, and the obtained results are shown in Fig. 75(b). The model generated $R$ values are closer to the target values, compared to the linear regression model, but the MSE is still very high at $0.45 \times 10^{-7}$ K-m$^2$/W. We also tested higher orders of polynomial fitting on the training dataset but did not achieve desired performance enhancement. The predicted interfacial thermal resistance results by decision tree, and random forest models are shown in Figs. 75(c) and (d), respectively. It can be observed that the predicted $R$ results are significantly better than those of linear and second-order polynomial regression models. The MSE are 0.064 and $0.059 \times 10^{-7}$ K-m$^2$/W, which are one to two orders of magnitudes lower than the MD calculated $R$ results. The calculated MSEs are summarized in Table. 1.
**Figure 75.** Machine learning results of (a) linear regression, (b) 2\textsuperscript{nd} order polynomial regression, (c) decision tree, and (d) random forest algorithms. The red and black square dots represent ML predicted and the target $R$ values, respectively.

Next, we trained four different ANN models to predict the interfacial thermal resistance between graphene and $h$-BN. The first pair of models has one dense layer with 10 (ANN-10) and 20 (ANN-20) neurons, respectively. The second pair of models has two dense layers with 10 (DNN-10-10) and 20 (DNN-20-20) neurons in each layer. The adaptive moment estimation (Adam) optimization\textsuperscript{274} method is used for gradient descent. The learning rate is set as 0.001. The predicted $R$ results from four different ANN models are shown in Fig. 76. The prediction results from all ANN models are significantly better than those of linear and polynomial regression models. The MSEs for ANN-10 and ANN-20 are 0.075 and $0.061 \times 10^{-7}$ K·m$^2$/W, which are comparable to those of decision tree and random forest models. It also can be observed that the performance of two layers ANN models are better than those of one layer ANN models. The MSEs for ANN-10-10 and ANN-20-20 are 0.055 and $0.045 \times 10^{-7}$ K·m$^2$/W, respectively. Based on the above discussions, it is concluded that the two-layer DNN model with 20 neurons, each layer gives the best $R$ prediction performance with negligible MSE values.
Figure 76. Artificial neural network results of (a) 1-layer with 10 neurons, (b) 1-layer with 20 neurons, (c) 2-layers with 10 neurons each layer and (d) 2-layers with 20 neurons each layer. The red and black square dots represent the predicted and the target $R$ values, respectively.

The current ML and ANN models are trained particularly to conclude the effects of temperature, coupling strength, and tensile strains in different directions. Since other factors are not considered, the models will not work for new impact factors. It is worth noting that for a new feature added to the training set, each token in that new feature will need to be combined with all existing training samples. For example, if surface defect with single atom vacancy is considered, and the defect ratio ranges from 0 to 10% with 1% interval, then the training data will be expanded by 10 fold, which requires tremendous
computational efforts for just one defect scenario. The training features selected in this work are not specific to the solid-solid system and can be extended to other heterostructures such as solid-liquid systems. Using MD simulations, Han et al.\textsuperscript{275} examined the effect of nanopatterns on Kapitza resistance of water boiling on a gold surface. Recently, Niu et al.\textsuperscript{276} studied the effect of surface wettability on condensation heat transfer in a nanochannel. In another work, Niu et al.\textsuperscript{277} constructed a dropwise condensation heat transfer model considering the liquid-solid interfacial thermal resistance. For above solid-liquid systems, other factors such as liquid contact angle, charge variation, and dipole moment can also be used as training inputs. While there could be numerous impacting factors to include in the training model, priorities should be given to the most important ones considering both computational effort and model accuracy.

**Table 1.** Mean square errors of different ML and ANN models.

<table>
<thead>
<tr>
<th>Model</th>
<th>MSE (×10\textsuperscript{-7} K\textperiodcentered m\textsuperscript{2}/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Regression</td>
<td>0.854</td>
</tr>
<tr>
<td>Polynomial Regression</td>
<td>0.45</td>
</tr>
<tr>
<td>Decision Tree</td>
<td>0.064</td>
</tr>
<tr>
<td>Random Forest</td>
<td>0.059</td>
</tr>
<tr>
<td>ANN-10</td>
<td>0.075</td>
</tr>
<tr>
<td>ANN-20</td>
<td>0.061</td>
</tr>
<tr>
<td>DNN-10-10</td>
<td>0.055</td>
</tr>
<tr>
<td>DNN-20-20</td>
<td>0.045</td>
</tr>
</tbody>
</table>
4.4 Conclusion

In this work, the interfacial thermal resistance between graphene and h-BN is predicted using supervised ML and ANN models. Classical MD simulations were used to investigate the effects of system temperature, coupling strength, uniaxial and biaxial tensile strains on $R$. It was discovered that the interfacial thermal resistance decreases with increasing temperatures and coupling strengths, while increases with increasing tensile strains in both armchair and zigzag directions. The MD results are consistent with previous studies. The linear and second-order polynomial regressions were unable to predict the $R$ values with reasonable accuracies, whereas the decision tree and random forest algorithms can predict $R$ with small MSEs. Most of the ANN architectures outperformed the ML models in $R$ predictions, with the best performance given by the two-layer DNN structure with 20 neurons each layer. The trained DNN model can accurately predict the interfacial thermal resistance between graphene and h-BN with only the knowledge of system temperature, coupling strength, and tensile strains.
CHAPTER 5 Water desalination through rim functionalized carbon nanotubes

5.1 Introduction

Freshwater is an essential element of human society. With the rapidly growing global population, freshwater storage has deteriorated dramatically due to agricultural, industrial, domestic, and municipal water withdrawals. The fast-growing freshwater demand and the limited renewable water supply render freshwater shortage a serious global challenge. Currently, approximately one-third of the global population lives under freshwater stress.\textsuperscript{278-280} Since seawater and saline aquifers account for ~98\% of the world’s water storage, seawater desalination has become one of the most promising supply-side measures to address the global freshwater shortage.\textsuperscript{281} The two most widely used desalination techniques are reverse osmosis (RO) and thermal distillation (including multi-stage flash and multi-effect distillation).\textsuperscript{282} In the Arabian Gulf and adjoining areas, mainly thermal distillation has been used in desalination plants. Such an approach demands a substantial energy supply and, as a result, could aggravate the greenhouse effect.\textsuperscript{283,284} Outside the Gulf area, RO is the most widely applied desalination technique and constitutes ~50\% of the global market.\textsuperscript{285} RO membranes are several times more efficient than the thermal distillation method. Seawater desalination efficiency is mainly characterized by two factors, \textit{i.e.}, water permeability and salt rejection. RO membranes can separate and collect desalinated water from seawater with a salt rejection rate of ~98\%. However, RO still has several drawbacks, such as a low water flow rate and high cost of water conveyance, pretreatment and equipment maintenance.\textsuperscript{285,286} Since all state-of-the-art plants are energy- and capital-intensive, their applications in the world’s freshwater supply are still limited.\textsuperscript{287,288}
Nanoporous membranes open up new perspectives for seawater desalination due to their fast convective water transport and very small pore dimension. Nanostructures, including CNTs, graphyne, graphene, graphene oxide, single-layer MoS$_2$, and zeolite thin-film nanocomposite membranes, have shown excellent desalination performances, either in laboratory tests or from MD simulations.$^{289-297}$ Among these media, CNT membranes stand out due to their excellent water transport and unique mechanical properties.$^{298, 299}$ Holt $et$ $al.$$^{299}$ reported that aligned double-walled CNT membranes with a sub-2-nm pore diameter exhibit extremely fast water flow up to $\sim 6\times 10^3$ L/cm$^2$/day/MPa, which is five orders of magnitude greater than those of RO membranes ($\sim 2.6\times 10^{-2}$ L/cm$^2$/day/MPa).$^{300}$ The excellent flow rate of CNT membranes is attributed to the smooth inner hydrophobic surface, which lubricates and speeds up near-frictionless water transport.$^{302}$ However, the Na$^+$ ion rejection rate for non-functionalized sub-2-nm CNT membranes is typically lower than 40%$^{289, 303}$ due to the slightly larger pore size than the size of hydrated sodium ions. To achieve nearly complete salt ion exclusion, previous MD simulations have suggested that the diameter of CNTs has to be $< 0.9$ nm (sub-1-nm), based on computations of salt ion desolvation energy barriers.$^{304, 305}$ However, typical experimentally synthesized CNTs exhibit a wide range of diameter distributions, making the massive production of sub-1-nm CNTs with nearly uniform size a substantial challenge. Introducing functional groups at wider CNT (diameter $> 0.9$ nm) ends is an alternative approach to control the ion exclusion capability. For example, Fornasiero $et$ $al.$$^{289, 290}$ experimentally demonstrated that the solution ionic strength, pH value, and ion valence could affect the ion exclusion capabilities of functionalized CNT membranes. They found that the Donnan-type rejection mechanism is dominated by the interaction
between negatively changed carboxylic functional groups at CNT tips and mobile ions in seawater solutions. Chen et al.\textsuperscript{306} designed an asymmetric tip-functionalized CNT membrane with hydrophilic groups (carboxyl) on one tip and hydrophobic groups (trifluoromethyl) on the other. The driving force produced by the hydrophilic-hydrophobic groups facilitated water transport and effectively blocked salt ions for pore sizes of 0.81 and 1.09 nm. However, functional groups do not always incur positive effects on the ion-blocking performance of CNT membranes. Corry et al.\textsuperscript{303} examined a range of functional groups with different charges and polarities on the tip of a 1.1-nm-diameter CNT. They found that 8 negatively charged carboxylic groups prevent the passage of both Na\textsuperscript{+} and Cl\textsuperscript{−} ions, resulting in a 100\% salt rejection rate. However, the addition of 4 OH groups unexpectedly facilitates the passage of Na\textsuperscript{+} ions. Hence, careful design of chemical functionalization is required to optimize the desalination performance of CNT membranes.

In this work, our focus is placed on the effects of a dipole moment at the CNT rim on the water desalination performance. The CNTs are first functionalized by hydrogen atoms; the charge of carbon atoms at the CNT rim is $-0.115e$, and the charge of hydrogen atoms used to passivate these carbon atoms is $+0.115e$. We can tune the charges of carbon and hydrogen atoms to mimic the dipole moment changes between C-H bonds. Using classic MD simulations, both the salt rejection and water permeability performance of CNTs are examined, with charge variations from $-0.515e$ to $+0.515e$. In addition to the dipole moments, two different pore sizes and four different pressures are also investigated. The water permeability of (9,9) CNTs is 5-fold greater than that of (7,7) CNTs. While a low dipole moment can facilitate water transport in CNTs, a high dipole moment blocks the
passages of both water molecules and salt ions through the CNT due to the enlarged energy barriers, which lead to enhanced salt rejection efficiency and reduced water flow. Overall, the (9,9) CNTs with high dipole moments give rise to the best water desalination performance, with more than 95% of ions being blocked at 200 MPa, and high water permeability of 10.2 L/cm²/day/MPa.

5.2 Methods
A schematic of the system is shown in Fig. 77(a). The axial direction of the CNT is set along the z-axis, and both CNT ends are connected with graphene (perpendicular to the z-axis). Every other carbon atom on the left rim of the CNT is passivated by hydrogen atoms, as shown in Fig. 77(b) and (c). The simulated water solution contains 33 Na⁺ ions, 33 Cl⁻ ions and 998 water molecules, corresponding to a salt concentration of 123 g/L. This higher concentration than that of seawater (~35 g/L) was chosen to increase the encounter probabilities between salt ions and CNTs during the MD simulations. The simulation box has dimensions of 6.0 × 6.1 × 10.0 (x × y × z) nm³. Periodic boundary conditions are applied in all directions. A rigid piston (monolayer graphene) is placed on the left side of the CNT and is used to push the water towards the CNT. Initially, half of the water molecules and all salt ions are located in the left portion of the system between the rigid piston and CNT. The other half of the water molecules are placed on the right side of the CNT. A (9,9) armchair CNT with a length of 1.1 nm and a diameter of 1.2 nm is studied first. For comparison, a narrower (7,7) CNT with a 0.95 nm diameter is also investigated. Both diameters are comparable to the size of hydrated sodium (with a diameter of ~0.76 nm). Convergences of water flux and salt rejection rate with membrane thickness are tested. The results show that nano-scaled membrane thickness has a
negligible impact on desalination behavior. Therefore, to save the computational cost, the CNTs length is fixed at 1.1 nm in all simulations. To further explore the dependence of desalination performance on external pressure, the pressure applied to the rigid piston is varied from 200 MPa to 800 MPa with 200-MPa intervals.

Figure 77. Schematics of the simulation system. (a) Snapshot of the (9,9) CNT system after a 200-ps equilibration run in the NVT ensemble without applying external pressure. The red and white colors represent oxygen and hydrogen atoms, respectively, in the water molecule. The turquoise and yellow balls represent carbon atoms and hydrogen atoms, respectively, at the CNT rim. Na$^+$ and Cl$^-$ ions are denoted by green and blue, respectively. After the equilibration run, external pressure is applied to the seawater as denoted by the blue arrow. A top view of the b) (9,9) and c) (7,7) CNT rims passivated with hydrogen atoms.
The carbon-carbon interactions in graphene layers are described by a second-generation REBO potential. The water molecules are modeled by SPC/E potential. The rest of the system, including the CNT, the salt ions and the pairwise interactions between each species, are described by the 12-6 LJ potential with the Coulombic interaction term; the parameters are summarized in Table 2. The cutoff distances for both the Coulomb and LJ energy terms are set as 9.8 Å. Previous studies have shown that the dipole moment of functional groups attached to the CNT rim plays a key role in desalination performance. To understand the effect of dipole moment on desalination performance across CNTs, the charge parameter $q$ of the rim carbon atoms (CCH) and the passivation hydrogen atoms (HCH) is adjusted to implement the dipole moment change. Originally, the charge of CCH ($Q_C$) is $-0.115e$, while the charge of HCH ($Q_H$) atoms is $+0.115e$, as bolded in Table 2 with underlines. For later modeling purposes, $Q_C$ is modified from $-0.515e$ to $+0.515e$, and $Q_H$ is changed from $+0.515e$ to $-0.515e$ accordingly. Meanwhile, the bond length and tilt angle of the C-H bond are kept at 1.09 Å and 0°, respectively.

**Table 2.** Lennard-Jones potential and charge parameters used in this work.

<table>
<thead>
<tr>
<th>Element</th>
<th>C (sp2)</th>
<th>CCH</th>
<th>HCH</th>
<th>Hw</th>
<th>Ow</th>
<th>Cl⁻</th>
<th>Na⁺</th>
</tr>
</thead>
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<td>$\varepsilon$ (kcal/mol)</td>
<td>0.0859</td>
<td>0.046</td>
<td>0.0301</td>
<td>0</td>
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<td>0.1684</td>
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<td>$\sigma$ (Å)</td>
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<td>2.985</td>
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<td>3.16435</td>
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<td>2.2589</td>
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<tr>
<td>$Q$ (e)</td>
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<td>$-0.115$</td>
<td>$+0.115$</td>
<td>0.5242</td>
<td>$-1.0484$</td>
<td>$-1$</td>
<td>1</td>
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</table>
All MD simulations in this work are performed by using LAMMPS. The system is first equilibrated in the $NVT$ ensemble at 300 K for 200 ps with no external pressure. Next, a constant and continuous external pressure is applied to the rigid piston to push the water molecules through the CNT until at least half of the water molecules from the solution side are moved to the permeate side. When water molecules move to the permeate side, the concentration in the solution side keeps increasing. The concentration difference between two sides will cause an osmotic pressure pointing to the left. The magnitude of the osmotic pressure can be estimated by $\Pi = cRT$, where $R$ is the ideal gas constant, $T$ is the temperature and $c$ is the molar concentration of NaCl in the permeate side which is given by $c = N_{\text{salt}} / N_A V$. Here, $N_A$ is the Avogadro constant, $N_{\text{salt}}$ is the number of salt ion in the permeate side solution with volume $V$, and $V = N_{H_2O} M_{H_2O} / N_A D_{H_2O}$. Here, $N_{H_2O}$ is the number of water molecules in the permeate side, $M_{H_2O}$ is the molar mass of water molecule, and $D_{H_2O}$ is the density of water solution. Using the initial concentration of the salt solution $c = 123 \text{ g/L}$ and the estimated value of osmotic pressure is 5.25 MPa. Hence, in order to eliminate the influence of increased concentration on the simulation results, a very large external pressure (at least 200 MPa), which is 2 orders of magnitude higher than the osmotic pressure, is applied to the graphene piston in the forward direction. The simulation time step is 0.5 fs unless otherwise stated, and the simulation time varies according to the CNT size, applied pressure, and charge. Two independent MD simulations with different initial velocity seeds are performed, and the results are averaged to suppress statistical noise.
The potential of mean force (PMF) is used to evaluate the water desalination performance of CNTs under different conditions. The PMF of moving a salt ion or a water molecule along the $z$ direction is calculated based on the umbrella sampling method. A restoring force in the $z$ direction is applied to each atom in the target group; this force is expressed as

$$F_z = K_z(z - z_0)m_i / m,$$  

(22)

where $K_z$ is the spring constant, $m_i$ is the mass of the $i^{th}$ atom in the target group, $m$ is the total mass of the target group, $z_0$ is the target position for each umbrella sampling window, and $z$ denotes the $z$-direction coordinate of the target group mass center. For the (9,9) CNTs, $K_z$ is set as 2 kcal/mol Å$^2$, while for the (7,7) CNTs, $K_z$ is 4 kcal/mol Å$^2$. The spring constants in the $x$ and $y$ directions are kept at 2 kcal/mol Å$^2$ to keep the target particle moving along the central axis of the CNT. The umbrella sampling windows are separated by 1 Å intervals in the span of 14 to 30 Å, which cover the range from the bulk water to the center of the CNT. Simulations are performed for 6 ns with a time step of 2 ps. Data from the last 4 ns are collected and analyzed by the weighted histogram analysis method (WHAM) to obtain the PMF.

5.3 Results and discussion

5.3.1 Water permeability

First, CNTs with zero dipole moment at the rim are studied; both $Q_C$ and $Q_H$ are set to 0. Once external pressure is applied, water molecules start moving from the solution side to the permeate side. During this process, the number of water molecules filtered by the CNT is monitored, and the results are presented in Fig. 78(a). At the beginning of the
simulation, for both pore sizes, the number of filtered water molecules shows a linear increase with simulation time. When the simulation time is sufficiently long, the water profile levels off, which means that all water molecules have moved to the permeate side. By fitting the linear region, the water flow rate per unit time for the (9,9) CNT is 182 molecules/ns under 800 MPa. In contrast, the flow rate per unit time for the (7,7) CNT is only 32 molecules/ns, which is more than 5 times slower than that obtained for the wider CNT. The difference in the flow rate per unit time for the (7,7) CNT and (9,9) CNT is due to the different local structures of water molecules inside the CNTs, as shown in Fig. 78(b) and (c). The water transport in bare (7,7) CNTs is limited to single- or double-chain passages, while in bare (9,9) CNTs, the water molecules are allowed to transport through more than four pathways, resulting in a much faster water flux.

**Figure 78.** (a) The cumulative number of water molecules filtered in (9,9) and (7,7) CNTs with zero dipole moment at the rim vs. simulation time under an external pressure of 800 MPa. The linear region, as denoted with brackets, is fitted for the water flux.
calculation. Front and top views of water molecules inside the b) (9,9) CNT and c) (7,7) CNT at 200 MPa. The red and white balls represent water molecules. The turquoise and yellow balls represent carbon atoms and hydrogen atoms, respectively, at the CNT rims.

Second, the effects of external pressure on the desalination performance of (9,9) and (7,7) CNTs are studied. The results are shown in Fig. 79(a). For both CNTs, the water flux increases linearly with external pressure. As such, we can predict water transport behavior at low pressures, such as those in commercial RO plants (1 ~ 10 MPa). The water permeability ($A_m$) of CNTs, a pressure-independent variable, is defined as

$$A_m = \frac{N v \rho}{P},$$

where $v$ represents the volume of a single water molecule, $P$ is the applied pressure, $N$ is the water flux, and $N/P$ is the slope of the linear fitting profile in Fig. 79(a), which represents the normalized water flux per unit pressure. When the CNT pore density $\rho$ is set to the experimental pore density achieved by Holt et al. (2.5 ×10$^{11}$ cm$^{-2}$), the $A_m$ of (9,9) and (7,7) CNTs is 0.170 and 0.0201 L/cm$^2$/day/MPa, respectively. If the pore density reaches the theoretical maximum calculated by Sotomayor et al. (5.8×10$^{13}$ cm$^{-2}$), the $A_m$ for (9,9) and (7,7) CNTs amounts to 39.4 and 4.9 L/cm$^2$/day/MPa, respectively. The latter density is used in the following analyses.
Figure 79. (a) Water flux vs. applied pressure for (9,9) and (7,7) CNTs with zero rim dipole moment. Water permeability in b) (9,9) and c) (7,7) CNTs vs. the rim charge. The error bars are calculated based on the standard errors of the linear fitting.

Third, to evaluate the effect of dipole moment, $Q_C$ is adjusted in the range of $-0.515e$ to $+0.515e$. The charge of $Q_H$ has the same magnitude as $Q_C$ but the opposite sign. The water flux versus the external pressure at different $Q_C$ values and pore sizes is shown in Fig. 80. For both uncharged and charged CNTs, the water flux has a positive correlation with the applied pressure. Thus, we can predict the water permeability of charged CNTs based on Eq. 23. The relationship between the added charge and water permeability is presented in Fig. 79(b) and (c), where the water permeability profiles for the (9,9) and (7,7) CNTs exhibit similar overall trends. For both CNTs, the water permeability curves are not completely symmetric with respect to the zero-charge point. In general, when carbon atoms hold a partial negative charge and hydrogen atoms hold a positive charge, the water flux is slightly faster than in the opposite charge arrangement. The water
permeability performance is usually better with a small charge than in uncharged conditions. When the charge magnitude is greater than +0.215e, regardless of the sign of the charge, the water flow in the (9,9) CNT declines sharply with increasing charge. For (7,7) CNTs, the water permeability curve starts to drop at $Q_c = +0.215e$. The maximum water permeability $A_m$ is 40.6 L/cm$^2$/day/MPa for a (9,9) CNT with a $-0.115e$ charge on the rim carbon atoms. This permeability is much higher than that for commercial RO membranes ($\sim$2.6×10$^{-2}$ L/cm$^2$/day/MPa) and is comparable to the maximum water permeability achieved by other low-dimensional carbon materials, such as nanopore-containing graphene (129 L/cm$^2$/day/MPa) and graphyne-4 membranes (13.1 L/cm$^2$/day/MPa).$^{293,294}$

![Graph of water fluxes for CNTs](image)

**Figure 80.** Water fluxes for a) (9,9) and b) (7,7) CNTs versus external pressure for CNT rim charge varying from $-0.515$ e to $0.515$ e.
5.3.2 Salt rejection

In addition to water permeability, we also compute the salt rejection rate, defined as

\[ R_r = 1 - \frac{N_{1/2}}{N_0}, \]  

(24)

where \( N_0 \) is the number of salt ions in the solution before the pressure is applied; and \( N_{1/2} \) is the number of salt ions passed through the CNT when half of the water molecules have moved to the permeate side.\(^{293,294}\) Here, \( R_r = 100\% \) means that all salt ions are rejected by the CNT and the permeate-side salinity is zero, and \( R_r = 0 \) means that the CNT has no salt rejection function. Fig. 81(a) shows the pressure effect on salt rejection for zero-charged CNTs. For both CNTs, the salt rejection rate decreases with increasing pressure. Specifically, the salt rejection in the (7,7) CNT reaches 100% below 400 MPa but reduces to 85% at 800 MPa. The salt rejection performance of the (9,9) CNT is not as good as that of the (7,7) CNT since salt ions can pass through the former more easily. The salt rejection rate decreases from 80% to 53% when the pressure increases from 200 to 800 MPa.
Figure 81. (a) The salt rejection rate vs. the external pressure for (9,9) and (7,7) CNTs with zero dipole moment. The salt rejection rate vs. the rim charge for b) (9,9) and c) (7,7) CNTs under external pressures of 200 MPa and 800 MPa.

As shown in Fig. 82, for charged CNTs, the salt rejection rate generally decreases with applied pressure. The salt rejection rate versus $Q_c$ is shown in Fig. 81(b). All charged (7,7) CNTs can block nearly 100% of the salt ions when the external pressure is < 400 MPa. For higher pressures, only CNTs with a large $Q_c$ can still filter all salt ions, whereas, for CNTs with a small $Q_c$, the salt rejection rate can be as low as 73%. For wider CNTs, the situation is even worse. Under 200 MPa external pressure, the (9,9) CNT can only filter more than 95% of the salt ions (a condition for drinkable seawater) if $Q_c > 0.315$ e. Under high pressure, none of the charged (9,9) CNTs can meet the salt-rejection requirement for desalination.
Figure 82. Salt rejection rates for a) (9,9) and b) (7,7) CNTs versus external pressure for CNT rim charge varying from −0.515e to 0.515e.

5.3.3 Mechanistic investigation of dipole moment effect

To further understand the effect of dipole moment on water desalination performance, oxygen and hydrogen density maps at the pore ends were generated and are given in Fig. 83. The CNT dipole moment and pore size can significantly affect the water distribution near the pore rim. For (9,9) CNTs with $Q_C = +0.515e$, the water molecules are distributed in a circular pattern, while for $Q_C = −0.515e$, the oxygen atoms are arranged in one-to-one correspondence with rim H atoms; however, the maximum density area is located in the CNT center due to the strong repulsion between the +0.515e-charged H atoms at the CNT rim and the oxygen atoms in water molecules. Besides, when the pore rim has zero dipole moment, the distribution of oxygen atoms is a mixture of the above patterns, where water molecules are scattered uniformly over the edge and center. In contrast, the oxygen density map in (7,7) CNTs with $Q_C = −0.515e$ or $+0.515e$ exhibits circular shapes with highlighted spots facing towards the rim H atoms. However, the hydrogen density maps for the two cases exhibit different shapes. In CNTs with $Q_C = +0.515e$, the −0.515e-charged hydrogen atoms at the rim are tightly surrounded by the hydrogen atoms of nearby water molecules owing to strong attractive interactions. Since the water molecules are confined by the pore rim, the water permeability in this case is even lower than that in the case of the (7,7) CNT with $Q_C = −0.515e$. For wider (9,9) CNTs, water molecules in the centers of the CNTs experience less constraint from the dipole moment at the rim, so a similar phenomenon is not observed. In general, CNTs with large dipole moments can facilitate the breaking of in-plane hydrogen bonds in water networks close
to the pore rim and the partial stabilization of water molecules near the rim. Hence, water transport in these CNTs encounters a high energy barrier and has a small flow rate. Also, for CNTs with small dipole moments, such as \( Q_c = -0.115e \), the water molecules show similar patterns to those observed for zero-dipole-moment CNTs, suggesting that even small dipole moments can promote the breaking of hydrogen bonds, but water molecules are not retained around the CNT rim. Thus, CNTs with small dipole moments result in faster water flux than zero-charged CNTs due to the reduced energy barrier for water passage.
Figure 83. Oxygen (-O-) and hydrogen (-H-) density maps at the pore rim of a) to h) (9,9) and i) to p) (7,7) CNTs with $Q_c = +0.515e, -0.515e, 0$ and $-0.115e$ at 200 MPa. A cold (blue) color represents a lower density, and a warmer color indicates a higher density.

To further elucidate the physical mechanism regarding water and salt ion passage in CNTs, the PMFs of moving a single water molecule, a Na$^+$ ion, or a Cl$^-$ ion, through the (9,9) and (7,7) CNTs are calculated. As shown in Fig. 84(a) and (b), for the CNTs with zero dipole moment at the rim, the energy barrier of moving a single water molecule through either (9,9) or (7,7) CNTs is extremely low. Similar results have been found by Corry et al.$^{305}$, who observed that water-molecule passage encounters negligible energy barriers in bare (n, n) CNTs for n > 5. Such a low energy barrier is consistent with fast water flow in CNTs. Likewise, the energy barrier for Na$^+$ ions is only $0.8$ kcal/mol in (9,9) CNTs, as the CNT allows the entire hydrated sodium to pass through without distorting its first solvation shell. In other words, Na$^+$ ions transport almost barrier-free in wide CNTs.$^{305}$ In contrast, Cl$^-$ ion passage in (9,9) CNTs encounters a high energy barrier of $~2.5$ kcal/mol due to the larger hydration shell than that of Na$^+$. When the pore becomes narrower, the energy barrier for both ions greatly increases. The energy barrier of Cl$^-$ ions in (7,7) CNTs is nearly 3 times greater than that in (9,9) CNTs, and the energy barrier of Na$^+$ ions also increases to $2$ kcal/mol. This illustrates the reason why the salt rejection is only $53\%$ through (9,9) CNTs at 800 MPa but reaches $85\%$ in (7,7) CNTs. Figure 84(c) and (d) present the PMFs of moving a Cl$^-$ ion through (7,7) and (9,9) CNTs with different dipole moments. For a small charge of $Q_c = +0.05e$, both CNTs entail similar energy barriers as that in the case of zero dipole moment, and thus, the salt rejection efficiency for the $Q_c = +0.05e$-charged CNTs is similar to that for the non-
functionalized CNTs. The (7,7) CNT only requires a charge of $Q_c = -0.215e$ to approach 100% salt rejection, as reflected by the sharp PMF increase in Fig. 84(d). In contrast, for (9,9) CNTs, the rim charge must be reduced to $Q_c = -0.515e$ to reach the same energy barrier and achieve a ~100% salt filtration efficiency at 200 MPa. We also computed the PMFs of water molecules in (9,9) CNTs with different dipole moments. Regardless of the CNT charge, water transport always encounters small energy barriers of less than 0.7 kcal/mol.
Figure 84. Computed PMFs of moving a single water molecule or salt ion through (7,7) and (9,9) CNTs with differently charged rims.

The number of hydrogen atoms anchored at (9,9) CNT rims is 9, while (7,7) CNT rims hold 7 hydrogen atoms. Effects of hydrogen atom numbers and dipole moment densities on PMFs are further studied. The PMFs of moving a single Cl$^-$ ion through (9,9) CNTs
with different dipole moment magnitudes and densities are shown in Fig. 85. Regardless of the dipole moment magnitude, the PMFs through CNTs with smaller dipole moment density at the pore rim are lower than those with larger density. The reason can be explained from two perspectives: 1) as shown in the non-dipole moment cases ($Q_c = 0$), removing hydrogen atoms at the pore rim increases the effective pore area and thus reduces the cost of energy to pass through the CNTs; 2) with large pore dipole moment ($Q_c = -0.515e$), CNTs with the less dipole moment density exert smaller repulsion forces on the incoming $\text{Cl}^- \text{ ions and results in a lower PMF compared to the denser dipole moment ones.}$

**Figure 85.** PMFs of moving a $\text{Cl}^-$ ion through (9,9) CNTs with different dipole moment magnitude and density.

The salt rejection behavior can also be explained by the RDF, computed by quantifying the occurrence probabilities of water molecules in the vicinity of a single salt ion. A series of RDFs along the $z$-axis were calculated, covering the entire CNT length. The salt
ion hydration coordination number can be calculated by integrating the first peak. In Fig. 86, the salt ion coordination numbers in narrower CNTs exhibit larger drops in the rim region, indicating higher energy consumption to enter the (7,7) CNTs. For narrow CNTs, more water molecules associated with the salt ion hydration shell need to be stripped off when the salt ion passes through the CNT, giving the higher salt rejection rate in (7,7) CNTs. This phenomenon is clearer for Cl\(^-\) ions because hydrated Cl\(^-\) ions have a larger size and can less easily enter narrow CNTs than Na\(^+\) ions. The maximum coordination-number drop for the (7,7) CNTs is 3.1, whereas, for (9,9) CNTs, the coordination number is only lowered by 2.1. For Na\(^+\) ions, the (7,7) CNTs result in a greater coordination-number decrease than (9,9) CNTs, but the drop is not as conspicuous as that observed for Cl\(^-\) ions.

**Figure 86.** The ion coordination number along the \(z\)-axis for a) Cl\(^-\) and b) Na\(^+\) ions passing through (7,7) and (9,9) CNTs with zero external pressure and with a rim charge of \(Q_C = +0.515\)e. The shadow area represents the position of the CNT.
Two snapshots of Cl\(^-\) ions are presented in Fig. 87(a) and (d), where the salt ion enters the (7,7) CNT with \(Q_C = +0.515\)e at the rim. To make the transport process clearer, two extra figures with more details were generated based on Fig. 87(a) and (d). Initially, the Cl\(^-\) ion holds 7 water molecules in its first water shell when it enters the pore. However, three water molecules are stripped off from the hydration shell and form new hydrogen bonds with surrounding water molecules. Simultaneously, two water molecules in the center drag the Cl\(^-\) ion to the permeate side by forming new hydrogen bonds with the remaining water molecules in the first hydration shell. Last, as shown in Fig. 87(d), the Cl\(^-\) ion is only surrounded by four water molecules within the CNT. The transport process is consistent with the Cl\(^-\) ion coordination-number change, as shown in Fig. 86(a).

**Figure 87.** Snapshots of a Cl\(^-\) ion passing through a (7,7) CNT with no external pressure. The yellow hydrogen atoms hold \(-0.515\)e charges (\(Q_C = +0.515\)e), with which hydrogen
bonds can be formed with the hydrogen atoms (white color) of water molecules. (a) A Cl$^-$ ion with 7 water molecules before entering the CNT. (b) Three water molecules, denoted with a grey color, move away from the first water shell of the Cl$^-$ ion due to the interaction with nearby water molecules and the CNT rim. (c) Three water molecules move away, and water molecules in the CNT drag Cl$^-$ ions along by forming hydrogen bonds with remaining water molecules in the hydration shell.

5.4 Conclusion

In this work, the desalination performance of CNTs with tube diameters > 1 nm and with different dipole moments at the pore rim is systematically studied by using classical MD simulations. To investigate the effect of the dipole moment at the rim, the charge values on the carbon atoms at the pore rim and adjacent hydrogen atoms are systematically changed. CNTs with low dipole moments have little effect on the improvement in water transport and salt rejection efficiency, whereas CNTs with high dipole moments yield much better salt rejection performance but reduce water flow. A series of other physical properties, including the PMF, RDF, and oxygen and hydrogen density maps, are computed to further understand the mechanism of water flow and salt ion passage. The effects of pore size and external pressure on desalination performance are also investigated. High pressure is found to have positive effects on water permeability but negative effects on salt rejection efficiency. Water transport in (9,9) CNTs is much faster than that in (7,7) CNTs. However, the salt rejection ability of wider CNTs is worse than that of narrower CNTs. Considering the need for balance between water permeability and salt rejection in the design of membranes, the (9,9) CNTs with a large dipole moment seem to be a better choice. At a high pressure of 200 MPa, the (9,9) CNTs could block
more than 95% of NaCl salt ions yet maintain a high water permeability of 10.2 L/cm\(^2\)/day/MPa. Under practical working conditions, introducing high-dipole-moment functional groups to CNTs not only maintains superfast water flow but also provides better salt rejection performance, rendering the functionalized CNTs a promising candidate for seawater desalination.
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