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Atomistic modeling of interfacial and thermal transport properties of engineered graphene structures

Srilok Srinivasan
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Atomistic modeling of interfacial and thermal transport properties of engineered graphene structures

by

Srilok Srinivasan

A dissertation submitted

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Mechanical Engineering

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

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2018
DEDICATION

To Amma and Appa....
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ABSTRACT

The immense amount of research on graphene in the last decade has led to advancement in techniques to control the thermo-physical properties of graphene by making use of engineered graphene structures. Carefully designed defective graphene, van der Waals heterostructures, functionalized graphene and engineered graphene surfaces have potential applications in photoelectronics and thermoelectrics devices, as electrode materials, phase-change materials for thermal energy storage, sensors, coatings etc. In this study, we focus on the interfacial and thermal transport phenomena within these engineered graphene nano-structures.

The main objective of this dissertation is to understand the mechanism of heat transfer across the nano-structures and analyze the molecular interactions at the interface which governs the surface properties like interfacial thermal resistance, viscosity and wettability. We use atomistic modelling to evaluate these materials and compare the results with experiments. The degradation of thermal conductivity with concentration of isotope and vacancy defects in graphene was analyzed using molecular dynamics (MD). The results qualitatively match with collaborative experimental and theoretical efforts based on Boltzmann transport equation (BTE). We next investigate contrasting behavior of thermal conductivity and sheet conductance in graphene/MoS\textsubscript{2} van der Waals heterostructure. The phonon relaxation times and thermal conductivity in graphene are suppressed due to the weak van der Waals interaction with the adjacent layers. We also experimentally and computationally characterize thermo-physical properties of a mixture of \textit{n}-eicosane phase change material and graphite particles (GP). Our results show a large enhancement in $k$ (450\%) and $\mu$ (1200\%) for a 3.5\% vol. concentration of GP fillers. The surprising reduction in interfacial thermal resistance ($R_{\text{eff}}$) with increasing filler concentration, together with the high
thermal conductivity of GP contributes to the large enhancement in $k$. While the viscosity of the $n$-eicosane around GP increases, we explore graphene’s potential as a solid lubricant when used with nanodiamond. The frictional force at the atomic scale in nanodiamond wrapped with graphene and graphitized nanodiamond is studied using molecular dynamics. Our results show that the rotational degree of freedom of nanodiamond leads to a lower friction in graphene wrapped nanodiamond. Finally, we show that hydrophobicity of graphene surfaces can be tuned by changing the orientation of graphene flakes. Our results show that the hydrophobicity due to the graphene flake orientation determines the Kapitza resistance and evaporation rates of water over the surface. The faster heated evaporation over hydrophilic surfaces is attributed to the efficient heat transfer from the substrate to water. Our results matches with collaborative experimental observations.
CHAPTER 1. GENERAL INTRODUCTION

1.1 Graphene

Graphene is a two-dimensional (2D) allotrope of carbon with a hexagonal honeycomb lattice. The existence and the stability of free-standing graphene was first experimentally demonstrated by Novoselov et al in 2004[1]. Graphene’s unique properties arising from its 2D nature has attracted the interest of researchers over the last two decades. Graphene provides a very good alternative to carbon nanotubes with respect to their use in electronic devices [2, 3], sensors[4] and reinforcements of polymer matrices[5, 6] due to their superior physiochemical properties and abundance of its 3D counterpart: graphite.

Graphene finds applications in various sensor devices due to the distinctive physical and chemical properties viz. superior mechanical flexibility [7, 8], electrical and thermal conductivity [9-14]. Furthermore, the high surface area (2630 m²g⁻¹), remarkable mechanical strength[15] and high aromaticity of graphene makes it suitable to be used a pollutant adsorbent [16]. The above mentioned properties also make graphene a desirable catalyst for fuels and photo degradation of organics [17-21].

However, there are many engineering bottlenecks in effectively and economically utilizing graphene’s potential at the device scale. For example, although it is theoretically predicted that graphene has exceptional energy transport properties, the thermal and electrical conductivity measured in practice is much lower owing to the presence of defects [22-27]. Additionally, graphene’s interaction with the surrounding medium is found to depend on the number of layers
and the substrate [28-32]. In other words, the quality of the graphene determines its usage in an application. Depending on the quality the graphene sheet it can be broadly classified as [33]:

1. Graphene or reduced graphene oxide flakes – for composite materials, conductive paints.
2. Planer graphene – for lower performance active and non-active devices.

The dependence of thermo-physical properties of graphene on the defect density, type of defects, substrate etc. [22, 23, 34, 35] emerges due the deviation from the isolated pristine lattice at an atomic scale. The ability to tailor the unique properties of graphene, by controlled introduction of defects and by changing the surrounding environment, to make it suitable for a particular application will be extremely useful and will expand the spectrum of potential applications. We call such tailored graphene materials as “engineered graphene structures”. In this dissertation, the change in the thermal transport and interfacial properties of graphene due to the introduction of defects and its interaction with the surrounding medium is explored.

1.2 Organization of Dissertation

The current chapter (Chapter 1) gives some background about the various types of engineered graphene structures followed by a brief overview of the computational details. The second chapter deals with the effect of vacancy and isotope defects on the overall thermal conductivity of graphene. Our results show that a mean-field model is able to capture the relationship. The third chapter is a paper that analyzes the phonon dispersion, phonon lifetimes and the modal thermal conductivity of graphene/MoS2/graphene heterostructure using spectral energy density analysis. The fourth chapter is a paper that investigates the interfacial thermal resistance across few-layer-graphene and n-eicosane at temperatures above and below the melting point. The fifth chapter is a study on the frictional characteristics of graphitized nanodiamond and
graphene wrapped nanodiamond. The sixth chapter is a paper which investigates the wetting behavior of inkjet printed graphene. The seventh chapter investigates the effect of graphene flake orientation on the Kapitza resistance and the evaporation rates of water over the graphene substrate. Finally, a comprehensive summary and discussions about the future direction of research is proposed.

### 1.3 Engineered Graphene Structures

The advances in graphene synthesis over the last decade [36-40] has enabled researchers to control and modify the surface and transport properties of graphene using a variety of techniques. The most prominent techniques for tailoring the properties of graphene are:

#### 1.3.1 Defect-engineered Graphene

High quality graphene can be engineered to have the desired thermal conductivity and mechanical strength by using controlled low-energy electron beam irradiation to create vacancy defects [41, 42]. The density of the defects, \(N_D\), introduced due to the irradiation can be quantified using the conventional formula [43, 44]:

\[
N_D \text{(cm}^{-2}) = \frac{(1.8 \pm 0.5) \times 10^{22}}{\lambda^4} \left( \frac{I_D}{I_G} \right)
\] (1-1)

Selective areas in the graphene sheet can be preferentially irradiated to create a gradient in the defect density which can be useful for thermal rectification [45, 46]. Reduction of graphene oxide (GO) is also another way to produce defective graphene. However, it is difficult to quantify the density of defect density (\(N_D\)). Defect-engineered graphene also has potential application as anode materials for Mg and Li batteries, humidity and chemical sensor with enhanced humidity [47, 48].
1.3.2 Heterostructures and composites

The discovery of graphene and its unique properties owing to the 2D nature has triggered a lot of interest in exploring other graphene analogous free-standing 2D materials namely, hexagonal boron nitride (h-BN), transition metal di-chalcogenides (TMDCs), phosphorene, borophene, NbSe$_2$ etc. The possible list of 2D materials is huge with a wide spectrum of mechanical and transport properties: from the softest to strongest and from insulator to highly conductive[33]. Using a heterostructure of combination of 2D materials with complimentary properties is expected to expand the usability of these materials. 2D materials stacked on top of each other and held together by weak van der Waals forces are called van der Waals heterostructures[49]. For example, encapsulating graphene with h-BN results in heterostructure inert to environmental factors like chemical adsorbents while simultaneously improving the carrier mobility ($> 10^5$ cm$^2$V$^{-1}$s$^{-1}$)[50]. Similar enhancements where also observed when TMDCs are used for encapsulation[51]. Heterostructures composed of graphene and monolayer MoS$_2$ display excellent photo electronic properties desirable for applications like photodetectors[52], photoresponsive memory alloys[53] and transistor devices[54].

Composites are homogenous mixtures of graphene particles based additives in a host matrix of porous materials or polymers. The excellent mechanical and transport properties of graphene results in enhanced overall thermophysical properties of the composite. Even very low concentration (~ 4 wt%) of graphene additives in 1-octadeconal phase change material leads to enhanced thermal conductivity[55]. Likewise, graphene aerogels when mixed with octadecanoic acid (OA) resulted in increased heat storage capacity[56].
1.3.3 Functionalized Graphene

Functionalization of sp²-bonded aromatic sequence and the dangling bonds on the edges of graphene is yet another way of tailoring the properties. Functionalization of graphene also prevents them from agglomerating when dispersed in composites. Polymer composites with functionalized graphene additives display significantly enhancement glass transition temperature, ultimate strength, storage modulus and thermal stability[5]. GO has been widely used as precursor while synthesizing functionalized graphene materials since it has a wide range of functional groups on its surface namely hydroxyl, epoxide, diol, ketone and carboxyl functional groups. These functional groups alter the van der Waals interaction and make graphene sheets soluble in water or other organic solvents[16, 57-62]. For example the presence of carboxyl groups on the edge of graphene sheets make them highly hydrophilic.

Surface functionalization leads to the sp³ hybridized carbon atoms and degradation of electrical conductivity[63]. Such covalent modification of the surface carbon atoms can be achieved in the following ways:

- Nucleophilic substitution
- Electrophilic addition
- Condensation
- Addition

Hydrogenated graphene structures close to full hydrogen coverage, also called as graphene, exist in buckled form due to the sp³ nature of the carbon-carbon bonds. Graphane exist in different isomer forms depending on the hydrogen arrangement, namely, chair, boat, twist-boat, stirrup, armchair[64]. While graphene has zero band gap, graphane possess a finite bandgap with bandgap value depending on the hydrogen coverage[65].
Fluorine functionalized graphene, also called fluorographane, is a direct band gap material with a band gap of $3.0 - 4.2$ eV\(^{[66]}\). The layered nature and low surface energy plays a significant role in its use as a lubricant\(^{[67]}\). Fluorographene, compared to that of pure graphene, has a substantially large specific capacity for Li-ion, improving the discharge and shelf-life of Li-ion based batteries\(^{[68]}\). Fluorographene has also been applied for electro chemical sensing \([69-71]\), solar cell technologies \([72, 73]\) and electro catalytic applications \([74-76]\). Due to the hydrophobic surface properties fluorographane also has applications in anti-corrosion and self-cleaning coatings\(^{[77]}\).

### 1.4 Computational Methods

Majority of this study is based on the results from computational analysis using atomistic modelling of engineered graphene structures. Molecular dynamics (MD) simulations \([78, 79]\) have been employed to investigate the thermal transport and interactions at the molecular interfaces of engineered graphene structures. MD involves solving the Newton’s equation of motion for all the atoms considered present in the system of interest. The interaction between the atoms are modeled using a potential suitable to describe the chemical interactions. The equations of motion of the \(N\) particles interacting with each other can be written as:

\[
m_i \ddot{r}_i(t) = F_i(t), \quad i = 1, 2, ..., N
\]

where \(r_i\) is the position of particle \(i\), \(m_i\) the mass of the atom \(i\), and \(F_i\) is the force experienced by the atom \(i\) under the potential due to the interacting atoms. Thus, \(F_i\) is calculated as:

\[
F_i(t) = \nabla \sum_{i=1}^{N} \sum_{j>i}^{N} U_{ij}(r_{ij})
\]

where \(U_{ij}\) is the pair-wise interaction potential between atom \(i\) and \(j\), \(r_{ij}\) the distance between atom \(i\) and \(j\). Newton’s equation of motion being second order differential equation with respect to time,
needs two initial values for each atom: \( r(t = 0) \) and \( \dot{r}(t = 0) \), in order to have a complete deterministic solution. Once the interatomic potential is defined, for a given initial condition of position and velocities of atoms, the subsequent position and velocities can be solved deterministically by computing the forces as the gradient the potential. The accuracy of the solution has a direct correlation with the choice of the interatomic potential used to describe the system. Although pair-wise interatomic potentials are sufficient and successful in describing the behavior of rare gases[80], they are poor in describing periodic crystal structures in general. This calls for a need to consider many-body potentials like 3-body Stillinger Weber potential[81], Tersoff potential[82] etc.

Before any data is collected from the simulation for analysis, the system under consideration needs to be equilibrated at the desired state variables (for example, the energy \( E \), volume \( V \), temperature \( T \), pressure \( P \) and the number of particles \( N \)). Depending on the state variables that are held constant the ensembles can be classified as:

- Microcanonical ensemble (NVE): The number of particles, system volume and the total energy of the system are held constant.
- Canonical ensemble (NVT): The number of particles and system volume are held constant. The temperature is held constant using an imaginary thermostat.
- Isothermal – Isobaric ensemble (NPT): The number of particles are held constant. The system volume is allowed to change in order maintain a fixed pressure and the temperature of the system is held constant using an imaginary thermostat.
- Grand canonical ensemble (\( \mu VT \)) – The chemical potential, volume and temperature are held constant.
The interatomic potentials and the exact computational schemes used varies from case to case depending on the analysis being performed. Although a broad overview of molecular dynamics is provided above, more specific description of the model for a particular analysis is given in the respective chapters.

1.5 References


CHAPTER 2. THERMAL TRANSPORT IN DEFECT ENGINEERED MONOLAYER GRAPHENE

Modified version of this chapter is published in *Chemical Physics Letters*\(^1\) and *Nanoscale*\(^2\)

2.1 Abstract

We employ molecular dynamics simulations to understand how presence of isotopes and vacancy defects influences thermal transport across graphene. We also investigate the thermal conductivity variation of graphene with density of vacancy defects, \(N_D\). The phonon spectra along with the variation of thermal conductivity reveal that out-of-plane modes are delocalized relative to the in-plane counterparts. The variation in thermal conductivity with isotope doping agree with results of an analytical model based on mean-field approximation. However, with the vacancy defects, the thermal conductivity reveals an intriguing saturation-type behavior at a higher defect density. The thermal conductivity dependence on defect density is also analyzed using the Boltzmann transport equation. The results from MD simulations match qualitatively with collaborative experimental efforts.

2.2 Introduction

Thermal transport in graphene, a planar sheet of sp\(^2\)-bonded carbon atoms in a honeycomb lattice, has been extensively investigated over the last decade using both experimental [1-6] and theoretical [6-9] approaches. Graphene\(^10\) has exceptionally high intrinsic thermal conductivity, \(k/3\)\(^11\). The measurements of thermal conductivity of large suspended graphene samples using the optothermal Raman technique revealed \(k\) values exceeding those of bulk graphite, which is \(k=2000\) W/mK at room temperature (RT)\(^11\). Independent measurements with the optothermal Raman technique\(^12, 13\) and the scanning thermal microscopy\(^14\) confirmed the excellent heat conduction properties of graphene. Theoretical considerations suggest that graphene can have
higher thermal conductivity than that of the graphite basal planes despite similar phonon
dispersions and crystal lattice anharmonicities. The latter is attributed to an unusually long mean
free path (MFP) of the long-wavelength phonons in two-dimensional (2-D) lattices [5, 6, 11].
Recent calculations by different methods suggested that the graphene sample size should be in the
100 µm[15, 16] or even 1 mm[9] range in order to fully recover the intrinsic thermal conductivity
limited only by the lattice anharmonicity, i.e. without phonon scattering by defects, polycrystalline
grains, and edges of the samples. The intrinsic $k$ values obtained in these works ranged from 4000
– 6000 W/mK near RT [9, 16, 17]. In other terms, the high intrinsic $k$ of graphene can be explained
by the fact that the phonon Umklapp scattering is less efficient in restoring thermal equilibrium in
2-D systems than in bulk three-dimensional (3-D) systems[15, 17, 18]

The thermal conductivity of graphene can be degraded by defects such as polymer residue
from nanofabrication[19], edge roughness[6], polycrystalline grain boundaries[20], and disorder
from contact with a substrate or a capping layer[2, 21, 22]. For this reason, the thermal conductivity
of graphene synthesized by the chemical vapor deposition (CVD) is always lower than that of the
mechanically exfoliated graphene from highly ordered pyrolytic graphite (HOPG)[1, 3, 12, 23,
24]. The loss of polycrystalline grain orientation in CVD graphene can lead to additional
degradation of the thermal conductivity[25]. The only reported experimental study of the phonon
– point-defect scattering in graphene utilized isotopically modified graphene[26].

Correlating the thermal conductivity variation with the changes in the phonon spectra due to
these defects is nontrivial and necessary to thoroughly characterize the thermal transport. Presence
of isotopes in a material structure induces mass disorder, reducing phonon thermal conductivity
($k$) due to enhanced energy scattering for even the smallest defect concentration. The reductions
in thermal conductivity for isotope substituted carbon and silicon nanomaterials have been
discussed in the literature [26-30]. In bulk 3-D crystals, the phonon scattering rate on point defects like vacancies, $1/\tau_P$, varies as $\sim 1/f^4$ (where $f$ is the phonon frequency)[31]. Owing to the changed phonon density of states (PDOS), the phonon scattering rate in 2-D graphene has a different frequency dependence, $1/\tau_P \sim 1/f^3$, which can, in principle, affect the phonon MFP and the thermal conductivity. In addition to the fundamental scientific interest, a quantitative study of the dependence of thermal conductivity on the density of defects is important for practical applications of graphene in thermal management.

Here, we employ molecular dynamics (MD) simulations to understand the physics of heat transfer in graphene, by examining the role of different vibrational modes in pure graphene, isotope substituted graphene and graphene with vacancy defects. Of the various isotopes of carbon, we substitute the $^{12}$C atoms in the corresponding 2D structures with the longest living $^{14}$C isotope. Our results, as elaborated below, show that the phonon scattering on isotope impurities is limited to the mass-difference term only. It does not include the local strain effects owing to missing atoms, bond breaking or presence of chemical impurities. We also investigate the variation of thermal conductivity with density of vacancy defects. The results from our MD study agree qualitatively with collaborative experimental and numerical study based on Boltzmann transport equation (BTE). The vacancy defects in experiments were introduced by electron beam irradiation with varying dosage and electron beam current.

2.3 Computational Methods

MD simulations are employed to investigate thermal transport in pure and defective graphene. The dimensions of graphene sheet for investigating the effect of isotope substitution is $140.24 \text{ nm} \times 4.68 \text{ nm}$, with the longer dimension being the armchair direction. The $z$- axis represents the out-of-plane direction and the in-plane axes are along the $x$- and $y$- directions. We
randomly substitute $^{12}$C atoms in the respective nanomaterials with their heavier counterparts, $^{14}$C isotope. For studying the effect of vacancy defects, simulations are performed on a pristine graphene sheet of size 319.5 nm $\times$ 54.1 nm containing 660,000 carbon (C) atoms. Defects (single and double vacancies) are introduced in the structure by randomly selecting and removing carbon atoms.

The dimension of the simulation box in the $x$- and $y$- directions corresponds to the length and width of the sheets, respectively. Periodic boundary conditions (PBCs) are imposed in all directions. Since the system is surrounded by the periodic images along the plane of the material, there are no unsaturated bonds on the edges. The $z$-wise dimensions of the simulation box are kept substantially large to prevent the sheets from interacting with their own periodic images along this direction. The interactions between C-C atoms in graphene are modeled using optimized Tersoff potential for thermal transport in graphene [32, 33]. All the simulations are performed with the highly parallelized LAMMPS package [34] and VMD tools are used for the visual analyses [35].

The graphene structure is first optimized by energy minimization. The resulting energy-minimized structures are shown in Figure 2-1. The optimized structures are then equilibrated at a temperature of 300 K and at a pressure of 0 bar under NPT ensemble for 4 ns using the Nosé-Hoover thermostat and barostat, each with a coupling constant of 0.1 ps. This is followed by 4 ns of equilibration in canonical (NVT) ensemble, using the Nosé-Hoover thermostat with coupling constant of 0.1 ps. The system is subsequently simulated without any constraints under the NVE ensemble for 2 ns to ensure energy conservation. The time step used in all our simulations is 1 fs.

Upon equilibration, we compute the mass-weighted velocity autocorrelation function (VACF) from the trajectories over the next 1 ns. The vibrational density of states (DOS) is obtained by considering the Fourier transform of VACF, as represented by
Figure 2-1: The equilibrated structure of graphene of length $L = 140.24$ nm and width $= 4.32$ nm along the $x$-$y$ and $x$-$z$ planes is shown in (a) and (b) respectively. C-C bond length in graphene is $0.142$ nm.

$$P(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{i\omega t} \left\{ \sum_{j=1}^{N} m_j v_j(t) \cdot m_j v_j(0) \right\} d\omega \quad (2-4)$$

where $\omega$ is the frequency of vibration, $m_j$ and $v_j$ are the mass and velocity of atom $j$. Thermal conductivity, $k$, is computed using the reverse non-equilibrium MD (RNEMD) technique by employing the Müller-Plathe method [36] with single kinetic energy swaps every 300 fs and the system divided into 100 bins along the direction of heat flow. The kinetic energy swaps are done for 7 ns before sampling the data for determining the temperature gradient in order to ensure that the system has reached steady state and a linear temperature profile is obtained. It is important to note that for the cross-section area used in the $k$ calculation, we simply consider a rectangular cross section of width ($y$-axis) equal to that of graphene, and thickness equal to the van der Waals diameter of the C atom. Although all our MD calculations are at 300 K, which is much below the Debye temperature of graphene (~2100 K [37]), the use of classical thermostats in equilibration process is justified since the relative change in thermal conductivity with isotope concentration at a fixed temperature remains unaffected even after quantum corrections. In addition, it has been shown that the difference between the thermal conductivity calculated using quantum corrections
and the classical thermal conductivity at 300 K and above are within an acceptable range [38]. The
errors in the predictions are obtained by applying ergodic hypothesis and computing $k$ at different
time intervals once steady state is attained.

2.4 Collaborative Efforts

2.4.1 Experiments

(Performed by H. Malekpour, P. Ramnani, A. Mulchandani and Alexander A. Balandin
from University of California, Riverside)

The single layer graphene samples were synthesized using ambient pressure chemical
vapor deposition (AP-CVD) on a Cu foil. Figure 2-2 shows a SEM image of the synthesized
graphene on gold TEM grid. The thermal conductivity of graphene samples were measured using
optothermal Raman technique. The optothermal Raman technique is a non-contact steady-state
technique, which directly measures the thermal conductivity [3, 11]. The samples were exposed to
20 keV electron beam (SEM XL-30) and the evolution of the Raman spectrum under irradiation
was used quantify density of defects [39, 40]. Further details on the experimental methods used
for graphene synthesis, thermal conductivity measurement and estimating the density of defects
can be found in Ref. [41]

2.4.2 Modeling using Boltzmann transport equation

(Performed by D.L. Nika from University of California, Riverside and Moldova State
University, Chisinau, Republic of Moldova)

In the framework of this Boltzmann Transport Equation under relaxation time
approximation the thermal conductivity can be written as [6, 42]:

$$
\kappa_c = \frac{1}{4\pi k_B T^2} \sum_{q \in \{LA,TA,ZA\}} \left\{ \left( \frac{d\omega_s(q)}{dq} \right)^2 \tau_{\omega_s}(s,q) \frac{\exp[\hbar \omega_s(q)/k_B T]}{[\exp[\hbar \omega_s(q)/k_B T] - 1]^2} q dq, \right. 
$$

(2-5)
where $h = 0.335$ nm is the graphene layer thickness, and the summation is performed over all acoustic phonon branches $s=LA$, $TA$ or $ZA$, $\omega_s$ is the phonon frequency of the $s$-th phonon branch, $q$ is the phonon wave number, $\tau_{tot}(s,q)$ is the total phonon relaxation time, $T$ is the absolute temperature, $\hbar$ and $k_B$ are Planck’s and Boltzmann’s constant, respectively. More information on the model details and the value of the parameter used can be found in Ref. [41]

![Figure 2-2: SEM performed by collaborators (H. Malekpour, P. Ramnani, A. Mulchandani and Alexander A. Balandin from University of California, Riverside). Scanning electron microscopy image of graphene transferred on gold TEM grid showing 7.5-$\mu$m array of square holes. Some holes are fully or partially covered with the graphene flake. The grid is depicted in gold color, the holes are shown in black and the almost transparent greenish areas are suspended graphene flakes.](image)

2.5 Results and Discussion

**Phonon density of states in isotope-substituted graphene:** Thermal transport in 2D nanomaterials is due to the three acoustic phonon modes: in-plane longitudinal mode along $x$-direction, in-plane transverse mode along $y$-direction and out-of-plane flexural mode in the $z$-direction. We examine the phonon spectra of the in-plane modes and the out-of-plane flexural modes for 0%, 10%, 25%, 30%, 35%, 50%, 60%, 80%, 90%, and 100% of isotope concentration.
For the sake of clarity, we show only the DOS curves for 0%, 25%, 50%, 80%, and 100% isotope substitution in Figure 2-3. The DOS curves for graphene sheets along the $x$-, $y$-, and $z$- directions are presented Figure 2-3(a), 2-3(b), and 2-3(c) respectively. Along both the longitudinal ($x$) and transverse ($y$) in-plane directions, the phonon spectra presented in Figures 2-3(a) and 2-3(b) shows that the prominent vibrational modes along the in-plane directions are high frequency localized modes, with peaks at around 50 Terahertz (THz) for pure $^{12}$C graphene sheets. On the other hand, the DOS spectra perpendicular to the direction of heat transfer in the out-of-plane direction peaks at much lower phonon frequencies of 11 THz and 25 THz for pure $^{12}$C graphene sheet as shown in Figure 2-3(c).

Isotope substitution induces mass disorder in the lattice that results in increased phonon scattering at the defective sites due to the difference in the characteristic frequencies. The effect of mass disorder is very conspicuous for the vibrational modes in all three directions. With increasing isotope fraction from 0% to 100%, there are two effects that can be observed from Figures 2-3(a), 2-3(b), and 2-3(c): (i) The frequencies of the vibrational modes are shifted to lower values (redshift) [43] with increasing isotope fraction and (ii) the intensity of peaks are reduced as the extent of mass disorder is increased in the lattice. The redshift of DOS can be explained by the increase in the effective mass with the inclusion of heavier isotopes. Under harmonic approximation, the frequency of vibration is proportional to $m_{\text{effective}}^{-0.5}$ [44]. The reduction in the peak intensities can be attributed to the mass disorder in the system.

The mass disorder increases for isotope substitution from 0% to 50%, lowering the intensity of the DOS peaks. The thermal conductivity reduces with increasing mass disorder as shown later in Figure 2-4. When the $^{14}$C concentration is more than 50%, the isotope becomes the major component in the lattice and the mass disorder decreases with further substitution. Beyond 50%
isotope substitution, the DOS continues to shift to lower frequencies but the intensity of the peaks increases, simultaneously improving thermal conductivity (Figure 2-4). Though the flexural modes have lower energies relative to the in-plane counterparts, we observe that the peak intensities are less affected by presence of isotopes in the lattice. Hence, the rather large reduction (around 70%) in thermal conductivity of graphene (Figure 2-4) can be attributed to the changes in the phonon characteristics of the short ranged in-plane modes. This also suggests that, though out-of-plane modes are relatively stiff [33, 45, 46] and delocalized in nature, the role of in-plane modes in heat conduction in graphene cannot be neglected.

**Thermal conductivity variation with isotope substitution:** We show in Figure 2-4 that with increase in isotope fraction ($\phi$), $k$ initially decreases until the isotope concentration is 50% where mass disorder is maximum. Beyond $\phi=0.5$, $k$ again increases representing the characteristic U-shaped curve [26, 44, 47]. The value of $k$ for graphene composed of pure $^{12}$C is 577.55 ± 41.70 W/m.K, which is in agreement to the value reported for graphene of similar dimensions in earlier MD based investigations [48, 49]. Increasing the fraction of isotopes from zero to 0.5 induces a gradual increase in mass disorder. Atoms in the lattice are either the lighter $^{12}$C (for graphene) or the heavier $^{14}$C. The vibrational frequencies of the 2D nanomaterial shift to lower values with increasing isotope fraction as discussed in Figure 2-3. Additionally, the characteristic vibrational frequencies of the heavier and lighter masses are different. When both of the isotopes are present in a lattice, phonons of different frequencies interact. $k$ decreases till it reaches a minimum at 50% isotope substitution. While the frequencies continue to shift to lower values with further increase of isotope concentration, in contrast $k$ increases for $0.5 < \phi < 1.0$. For isotope concentration between 50% and 100%, the heavier atoms comprise the majority of the 2D lattice structure. As mass disorder decreases, heat conduction is improved, as reflected in the increasing values of $k$. 
**Figure 2-3:** The phonon DOS for 0% (blue), 25% (red), 50% (yellow), 80% (violet) and 100% (green) isotope substituted graphene are presented: (a) in-plane longitudinal modes along the direction (x-wise) of heat transfer, (b) in-plane transverse modes (y-wise) and (c) out-of-plane flexural modes perpendicular (z-wise) to the direction of heat transfer. The DOS intensity represented along the vertical axes is in arbitrary units. The legends represent each graphene structure as $^{12}$C$_{(100-1000)}$ $^{14}$C$_{1000}$, where $\phi$ is the fraction of $^{14}$C isotope. The phonon frequencies shift to lower values (redshift) for both the in-plane and out-of-plane vibrational modes. The low frequency modes that are observed along the z-direction are delocalized. The intensity of the peaks decreases as mass disorder increases.
We observe that inclusion of a low fraction of mass disorder induces a relatively significant reduction in $k$, whereas the variations in thermal conductivity are relatively smaller for further increases in isotope concentration.

**Thermal conductivity predictions from mean-field approximation:** We compare our $k$ reduction predictions with a classical model based on mean-field approximation [44] which assumes that the heat transfer rate is proportional to the frequency, $\omega_x$ of a oscillator formed by connecting two different point masses, $M_\alpha$ and $M_\beta$. It follows from the mean-field approximation that the heat transfer reduction $k(\phi)$ can be given as [44]:

$$k(\phi) = \frac{k_\phi}{k_0} \sqrt{\frac{\varepsilon(1+\varepsilon)[(1-\phi+\varepsilon)M_\alpha+(\phi+\varepsilon)M_\beta]}{(\phi+\varepsilon)(1-\phi+\varepsilon)(1+\varepsilon)M_\alpha+\varepsilon M_\beta}}$$  \hspace{1cm} (2-5)

**Figure 2-4:** The variation of the thermal conductivity reduction $k(\phi)$ of mass disordered graphene is presented as the function of increasing isotope fractions ($\phi$) from 0.0 – 1.0 for nanomaterials simulated at 300 K. The error bars represent the standard errors as derived from the computations. Thermal conductivity calculations from the MD simulations show reasonable agreement with the predictions of mean-field model given by equation. The value of the parameters, $\varepsilon$ and $M_\alpha/M_\beta$, are 0.0297 and 1.1655. The model reproduces the sharp drop in $k$ for smaller isotope fractions (<0.3) as well as the maximum reduction in $k$ at 50% isotope substitution in both the nanomaterials.
where $k_\phi$ is the thermal conductivity of isotope substituted nanomaterial, $k_0$ is the thermal conductivity of the pure nanostructure, $\phi$ is the molar fraction of the isotope $\beta$ that replaces atom $\alpha$ in the nanomaterial and $\varepsilon$ is a dimensionless numerical parameter to prevent divergence for the limiting cases.

In a completely harmonic mean-field approximation the parameters $\varepsilon$ and $M_\alpha/M_\beta$ are determined using the following two boundary conditions: (1) $k(1) = (m_\beta/m_\alpha)^{1/2}$ where $m_\beta$ and $m_\alpha$ are the atomic mass of isotope $\beta$ and $\alpha$ respectively, (2) $k(x)$ obtained from [44]

$$k(x) = \frac{1}{\sqrt{x(m_\beta/m_\alpha) + (1-x)}} [x^2 + (1-x)^2 - x(1-x)]$$

(2-6)

The $k$ reduction with $\phi$ in equation (1) is presented in Figure 2-4. The values of the parameters, $\varepsilon$ and $M_\alpha/M_\beta$, are provided in Figure 2-4. The model predictions compare very well with the results calculated from the atomistic simulations. While remarkable qualitative agreement is observed, the minor quantitative differences exist due to the limited sampling data used for computing $k$ values, instead of averaging over a series of calculations with different spatial isotope arrangements. The mean-field approximation model reproduces the significant decrease in $k$ for low isotope fraction and the relatively lower reduction when the isotope substitution is between 30% and 70% for both the materials. Hence, if the thermal conductivity values for 0%, 50%, and 100% isotope substitution are only known, we can predict the approximate thermal conductivity for any isotope fraction using the mean field approximation. The predictions of the model, which requires only the masses of the atoms and fraction of isotopes for the isotope substituted graphene,
enable us to corroborate that it is the mass disorder and different effective masses of C and Si atoms in respective nanomaterials that is responsible for the reduction in thermal conductivity.

*Thermal conductivity variation with density of vacancy defects:* Let us now consider the thermal conductivity variation with density of vacancy defects as revealed from MD simulations. Our MD simulations show that a combination of single and double vacancy defects can also account for the experimentally observed thermal conductivity dependence on the defect concentration. As one can see from Figure 2-5, the thermal conductivity decreases drastically for $N_D$ increasing from $2 \times 10^{10}$ cm$^{-2}$ to $10 \times 10^{10}$ cm$^{-2}$ and subsequently reaches a near-constant value at the higher concentrations of defects. This value is substantially above the amorphous carbon limit – in line with the experiment (Figure 2-6).

![Figure 2-5](image_url)

**Figure 2-5:** Molecular dynamics simulation results for thermal conductivity of graphene with single and double vacancy defects. The simulated defect structures are depicted in the inset. The results show that the contributions of single and double vacancies are similar in reducing the thermal conductivity of graphene. The results are in line with the experimental trend.
The experimental procedures used in characterizing the thermal transport in defective graphene involves irradiating the sample with electron beam. The electron energies of 20 keV [41] used in the electron beam irradiation process are less than the knockout threshold energy of 80 keV [50-52]. Such irradiation is only sufficient to overcome the energy barrier required for breaking of the carbon-carbon bond and initiating reaction with any residual impurities such as H₂O and O₂ on the surface of graphene. This reaction results in functionalization of graphene with -OH and -C=O groups. Prior studies have shown that the –C=O configuration is energetically more favorable than –OH, and the transition of –OH and other functional groups into the energetically stable –C=O configuration can occur especially when they are annealed [53]. The energy barrier for the diffusion of -OH and epoxy groups is around 0.5-0.7 eV [54], which corresponds to a diffusion rate ~ 10² s⁻¹ as calculated from transition-state theory, assuming a typical phonon frequency range in graphene. For this reason, the functional groups can be mobile at the temperature of the thermal experiments (~350 K). Upon continuous electron beam irradiation, two epoxy or hydroxyl group can come together and release an O₂ molecule [54]. When the coverage of functional groups is high, detectable amounts of CO/CO₂ can be released creating vacancies in the graphene lattice [55]. The presence of -OH and -C=O functional groups can be the reason for stronger phonon – defect scattering than that predicted by BTE models with vacancies. The absolute value at the zero-defect limit is lower than the experimental due to the domain-size limitation in the simulation.

In order to understand the reason for the saturation behavior of k, we calculate the phonon density of states of graphene as a function of concentration of single vacancy (Figure 2-7) and double vacancy defects (Figure 2-8). While the peaks corresponding to the high frequency localized modes along the in-plane directions are suppressed with increase in concentration of
defects, the delocalized low frequency modes (both in-plane and out-of-plane) are relatively the same for all the defect density. According to this model scenario, upon irradiation, -C=O and other functionalized defects are formed that strongly reduce the thermal conductivity. Continuous irradiation results in the creation of single and double vacancies. The increase in their concentration does not lead to pronounced $k$ reduction, which approaches an approximately constant value for the $N_D$ range that was investigated. It can be explained in the following way. As more defects are introduced in graphene through irradiation the additional defect sites serve as scattering centers for phonons with wavelengths shorter than the distance between two vacancies. The delocalized long-wavelength phonons, that carry a significant fraction of heat, are less affected by extra defects that are closely spaced compared to those introduced at the previous irradiation step. At some irradiation dose, the increase in the phonon scattering rate of the delocalized modes due to extra defects is substantially smaller than that of the short-ranged localized modes.

![Graph](image.png)

**Figure 2-6:** This is a result of collaboration (Collaborators: H. Malekpour, P. Ramnani, D. L. Nika, R. Lake, A. A. Balandin from University of California, Riverside). Dependence of the thermal conductivity on the density of defects. The experimental data are shown by square, circle and triangle points. The solid curves are calculated using the BTE with different values of the specularity parameter $p$. 
Figure 2-7: Phonon density of states of graphene for different concentration of single vacancy defects
Figure 2-8: Phonon density of states of graphene for different concentration of double vacancy defects
Hence, after a certain critical $N_D$ the thermal conductivity effectively saturates. The weakening of the $k(N_D)$ dependence observed experimentally and revealed in the present MD simulation is in line with reported computational results performed for graphene and graphene ribbons under various assumptions about the nature of defects[28, 45, 56, 57]. The presence of vacancies in the irradiated graphene were confirmed by analyzing experimental Raman data[41] using the methodology developed in Ref. [58].

2.6 Conclusions

In summary, our computational investigation employing molecular dynamics shows that, in presence of isotopes that induces a mass disorder in the structure, thermal conductivity reductions in these nanomaterials is ascribed essentially to the perturbation of the phonon modes. The phonon DOS in all the three directions suffers a redshift with increase in the effective mass due to the inclusion of isotopes. While out-of-plane flexural modes are significantly stiffer and delocalized, the contribution of in-plane phonon modes to the overall thermal conductivity reduction in graphene cannot be neglected. A mean field approximation based on harmonic interactions simply employs the masses and fractions of the two isotopes to predict the $k$ variations. The model results are in strong agreement with our atomistic simulations. We have also explored the thermal conductivity variation with density of single and double vacancy defects. It was found that at higher defect density the thermal conductivity revealed an intriguing weakening of the $k(N_D)$ dependence. This behavior agrees with the results of Boltzmann transport equation and collaborative experimental efforts. The obtained results contribute to understanding the acoustic phonon – point defect scattering in 2-D materials.
2.7 References


CHAPTER 3. PHONON THERMAL CONDUCTIVITY AND SPECTRAL PHONON RELAXATION TIMES IN GRAPHENE/MoS$_2$ VAN DER WAALS HETEROSTRUCTURES

Modified version of this chapter is published in *Langmuir*\(^3\)

3.1 Abstract

The thermal conductivity of graphene encapsulated MoS$_2$ (graphene/MoS$_2$/graphene) van der Waals heterostructure is determined along the armchair and zigzag directions with different twist angle between the layers using molecular dynamics (MD) simulations. The differences in the predictions relative to those of the monolayers is analyzed using the phonon power spectrum and phonon lifetimes obtained by spectral energy density analysis. Thermal conductivity of the heterostructure is predominantly isotropic. The out-of-plane phonons of graphene are suppressed due to the interaction between the adjacent layers that results in reduced phonon lifetime and thermal conductivity relative to monolayer graphene. The occurrence of an additional non-zero phonon branch at the $\Gamma$ point in the phonon dispersion curves of heterostructure corresponds to the breathing modes resulting from stacking of the layers in the heterostructure. The thermal sheet conductance of the heterostructure being an order of magnitude larger than that of monolayer MoS$_2$, this van der Waals material is potentially suitable for efficient thermal packaging of photoelectronic devices. The interfacial thermal conductance of graphene/MoS$_2$ bilayer as a function of the heat flow direction show weak thermal rectification.

3.2 Introduction

Research in two dimensional (2D) materials has gained significant attention ever since the discovery of graphene and its unique mechanical[1, 2], thermal[3, 4] and electronic[5, 6] properties. While thermal transport in single and few layer graphene has been extensively investigated both theoretically[7-13] and experimentally[14-16], heat conduction through other 2D materials such as hexagonal boron-nitride (h-BN), transitional metal dichalcogenides (TMDs) and graphene-analogous nanostructures are relatively less explored[17]. Heterostructures that have been synthesized by stacking dissimilar 2D materials on top of each other are held together by weak van der Waals forces[18]. Such engineered 2D architectures are of interest due to their potential application in light emitting diodes[19], electrode materials[20], photovoltaics[21, 22] and photoresponsive memory devices[23]. For instance, the exceptional electronic and thermal properties of graphene albeit with the intrinsic zero band gap can be coupled with the nonzero bandgap of molybdenum disulfide (MoS$_2$)[24] for potential use in field effect transistor devices[25-29]. An earlier investigation suggests that graphene/MoS$_2$/graphene heterostructure has better photon absorption to produce electron-hole pairs compared to a single layer MoS$_2$[30].

Given the widespread potential application of graphene/MoS$_2$ heterostructures, characterizing the thermal transport properties and identifying the key phonon modes and scattering events influencing the heat conduction is critical for efficient thermal management of nanoelectronic devices fabricated with them. Heat conduction and interfacial thermal transport in these 2D materials is predominantly by lattice vibrations or phonons [13, 16, 31]. Although there have been computational studies in the past focusing on thermal transport in graphene/MoS$_2$ bilayer heterostructure [32-35] there has not been much effort to investigate the heat transport in MoS$_2$ encapsulated within graphene (graphene/MoS$_2$/graphene) heterostructures. We show that
thermal conductivity is predominantly isotropic. The variations in the vibrational properties as observed from the spectral energy density (SED) analysis and power spectrum relative to the single layer counterparts, suggest that the coupling of out-of-plane phonon modes due to the weak van der Waals forces between the layers is the primary cause for changes in thermal conductivity. We have also calculated the interfacial thermal conductance between graphene/MoS$_2$ interface and observe a weak thermal rectification across the interface.

3.3 Computational Methods

The dimensions of the unit cell of MoS$_2$ and graphene in the armchair direction are 0.541 nm and 0.431 nm, respectively, as shown in Figure 3-1(a). We consider two different configurations of the heterostructures, one with the armchair (or zigzag) edges of graphene and MoS$_2$ aligned ($\varphi = 0^\circ$) (Figure 3-1(b)) and the other with the zigzag edge of graphene aligned against the armchair edge of MoS$_2$ ($\varphi = 90^\circ$) (Figure 3-1(c)). For the $\varphi = 0^\circ$ case, a super cell of the heterostructure with almost zero strain is created by sandwiching 4 × 4 unit cells of MoS$_2$ between two 5 × 5 unit cells of graphene (Figure 3-1(a)). The spontaneous strain energy arising from the lattice mismatch of the graphene/MoS$_2$ in such a supercell has been shown to be almost zero [36]. The interlayer spacing between the graphene and MoS$_2$ layers is 0.363 nm[36]. In the case of $\varphi = 90^\circ$, a supercell with minimized strain can be similarly constructed by considering 15 × 30 unit cells of MoS$_2$ and 33 × 22 unit cells of graphene. For the $\varphi = 0^\circ$ case, heterostructure dimensions extending 5 × 5, 10 × 5, 15 × 5 and 20 × 5 supercells (equivalent to 10.82 nm × 6.25 nm, 21.65 nm × 6.25 nm, 32.47 nm × 6.25 nm and 43.30 nm × 6.25 nm, respectively) are considered for thermal conductivity ($k_{\text{armchair}}$) calculations along the armchair direction. Likewise, to compute $k$ along the zigzag direction ($k_{\text{zigzag}}$), the 2D material dimensions of 3 × 9, 3 × 18, 3 × 27 and 3 × 36 supercells (6.5 nm × 11.25 nm, 6.5 nm × 22.50 nm, 6.5 nm × 33.75 nm and 6.5 nm × 45.0 nm,
respectively) are considered. For the $\phi = 90^\circ$ case, heterostructure dimensions extending $1 \times 1$, $1 \times 2$, $1 \times 3$, $1 \times 4$ and $1 \times 5$ supercells (equivalent to 8.19 nm $\times$ 9.37 nm, 16.23 nm $\times$ 9.37 nm, 24.35 nm $\times$ 9.37 nm, 32.47 nm $\times$ 9.37 nm and 40.54 nm $\times$ 9.37 nm, respectively) are considered. The choice of these dimensions ensures that $k_{\text{armchair}}$ and $k_{\text{zigzag}}$ are computed for comparably sized heterostructures. The heterostructure is aligned along the $x$-$y$ plane of the simulation box. Periodic boundaries are imposed along the $x$ and $y$ directions while a fixed boundary condition is used for the out-of-plane $z$ direction. The length of the simulation box along the $z$-wise axis is kept significantly large (~20 nm) to prevent the atoms, oscillating about their mean positions, from escaping the boundary. The modified Tersoff potential is used to describe the interactions between the carbon atoms in graphene[37] in lieu of the AIREBO force field[38], which although employed in earlier graphene/MoS$_2$ heterostructure studies[32-34, 36, 39, 40], fails to reproduce the correct phonon dispersion and the density of states[37]. Atomic interactions in MoS$_2$ are modeled with the Stillinger-Weber (SW) potential[41]. The weak van der Waals forces between the adjacent layers are described by the 12-6 Lennard-Jones (LJ) function with $\epsilon$ (C-S) = 3.95 meV, $\sigma$ (C-S) = 0.3625 nm[36], and $r_{\text{cut-off}}$ = 1 nm. The above LJ parameters were parameterized by fitting the interlayer spacing and binding energy between graphene and MoS$_2$, to the study the mechanical properties of graphene/MoS$_2$ heterostructure[36].

The initial geometry is first energy minimized by optimizing the atomic positions using conjugate gradient algorithm to ensure that the heterostructure attains the equilibrium interplanar spacing for the different twist angles used. Unlike first principle calculations, the thermal motion of atoms due to finite temperature in MD simulations implies momentary variations in the interlayer spacing. Hence a small change in our choice of initial interlayer spacing (0.363 nm) should not change the results. The system is equilibrated under an isothermal-isobaric (NPT)
ensemble at a temperature of 300 K and a pressure of 1 bar for 5 nanoseconds (ns) using Nosé-Hoover thermostat and barostat each with a coupling constant of 1 picosecond (ps). The barostat is removed and the structure is simulated under a canonical (NVT) ensemble at 300 K for another 5 ns. The heterostructure is subsequently simulated without any constraints under a microcanonical (NVE) ensemble for 4 ns. Subsequently, \( k \) is computed by reverse non-equilibrium molecular dynamics (RNEMD) technique by employing the Müller-Plathe[42] algorithm where the system is divided into bins along the direction of heat flow and the kinetic energies of the fastest atom in the extreme bins are swapped with that of the slowest atom in the central bin every 0.1 ps. Although the Debye temperature of graphene is much higher than 300 K (~2100 K [11]), the difference between the quantum corrected thermal conductivity and classical thermal conductivity are within the acceptable range around 300 K[43]. On the other hand, the Debye temperature of MoS\(_2\) is around 263.2 K[44]. Hence the vibrational modes of MoS\(_2\) are fully excited at 300 K and the use of classical simulations to estimate the thermal conductivity is justified. According to Fourier’s law, \( k = -\frac{\dot{Q}}{(w \times d) \nabla T} \), where \( \dot{Q} \) is the rate of heat transfer, \( w \) is the width of the cross-section, \( d \) the thickness and \( \nabla T \) is the temperature gradient along the direction of heat transfer. The rate of heat transfer \( \dot{Q} = E/2t \), where \( E \) is the total energy swapped and \( t \) the time for which RNEMD is performed. The factor of 2 accounts for the heat flow in two directions due to the use of periodic boundaries. Here, we use the van der Waals diameter of carbon (0.34 nm) as the thickness of monolayer graphene, the sum of the distances between the sulphur atoms in MoS\(_2\) and van der Waals diameter of sulphur (\( \approx 0.672 \) nm) as the thickness of monolayer MoS\(_2\), and the sum of the distances between the graphene layers in graphene/MoS\(_2\)/graphene heterostructure and the van der Waals diameter of carbon (\( \approx 1.377 \) nm) as the thickness of the heterostructure. The \( k \) values calculated from MD simulations depend on the choice of the thickness value. To compare the
thermal transport in the heterostructure with that of monolayers, we calculate thickness independent thermal sheet conductance $G_s = k \times d = -\left(\frac{\dot{Q}}{w}\right)/\nabla T$ [45].

![Diagram of MoS$_2$ and graphene lattice](image)

**Figure 3-1:** (a) Dimensions of MoS$_2$ and graphene lattice in one supercell. The lattice constant of the primitive unit cell (blue vectors) of MoS$_2$ and graphene is 0.312 nm and 0.249 nm respectively. The dimensions of the conventional unit cell (red vectors) of MoS$_2$ and graphene are 0.541 nm $\times$ 0.312 nm and 0.431 nm $\times$ 0.246 nm respectively. (b) Schematic representation of the graphene/MoS$_2$/graphene heterostructure when the armchair direction of graphene and MoS$_2$ are aligned, $\varphi = 0^\circ$. (c) Schematic representation of the graphene/MoS$_2$/graphene heterostructure when the armchair direction of graphene and MoS$_2$ are orthogonal, $\varphi = 90^\circ$.

We also perform non-equilibrium molecular dynamics simulation (NEMD) by placing separate thermostats on graphene and MoS$_2$ in the heterostructure thereby forcing them to have the same temperature gradient (see supporting information). A Langevin thermostat, with a damping parameter of 0.1 ps, is used to create a hot reservoir at the center and a cold reservoir at the extreme ends of the system by imposing thermostats to the corresponding regions at 325 K and 275 K. We analyze the trajectories sampled after 6 ns, sufficient for the system to attain steady
state. A time step of 0.001 ps is used in all our simulations performed with the LAMMPS\cite{46} package, while OVITO\cite{47} is employed to visualize the system.

3.4 Results and Discussion

The inverse $k$ predictions from RNEMD as a function of the inverse heterostructure length along the armchair and zigzag directions for $\phi = 0^\circ$, and the armchair direction of graphene for $\phi = 90^\circ$ are presented in Figure 3-2(a). The effective $k$ of the graphene/MoS$_2$/graphene ($\sim 17$–$65$ W/m.K) is higher than that of the monolayer MoS$_2$ of comparable dimensions ($\sim 4$–$11$ W/m.K), but significantly smaller than that of the graphene ($\sim 80$–$280$ W/m.K) (Figure 3-3). However, $k$ increases with length of the heterostructure (Figure 3-2(b)) suggesting that the effective phonon mean free path ($l_{mfp}$) is comparable to the maximum length between the heat source and heat sink ($\sim20$ nm corresponding to the heterostructure of length 40 nm) considered in this work. The findings suggest negligible anisotropy in heat conduction across the armchair and zigzag direction of the heterostructure for $\phi = 0^\circ$. Additionally, aligning the armchair direction of graphene with zigzag direction of MoS$_2$ ($\phi = 90^\circ$) does not change the $k$ values appreciably (Figure 3-2(b)).

In the Casimir limit\cite{48}, $k^{-1}$ can be approximated as $\frac{1}{k} = \frac{1}{k_\infty}\left(\frac{l_{mfp}}{L/4} + 1\right)$, where $L$ is the length of the heterostructure along the direction of heat transfer and $k_\infty$ is the thermal conductivity devoid of size effects as $L \to \infty$. The $k_\infty$ and $l_{mfp}$, estimated by an empirical curve fit to the results in Figure 3-2(a), are listed in Table 3-1. While the estimated $k_\infty$ of monolayer MoS$_2$ matches excellently with reported values of 19.76 W/m.K from MD simulations\cite{49}, and compares well with experimentally measured value of 34.5 W/m.K\cite{50}, the $k_\infty$ of monolayer graphene is significantly lower than the reported values of 3000-5000 W/m.K\cite{4, 16, 51}. This discrepancy can be attributed to the rather small system sizes considered that are unable to incorporate the effects of phonon modes with mean free paths much larger than the size of the simulated domain.
Figure 3-2: (a) $k^{-1}$ as a function of $L^{-1}$ for the heterostructures, and monolayer graphene and MoS$_2$. The discontinuous lines represent the curve fits to estimate length-independent thermal conductivity ($k_\infty$) and the mean free path ($l_{mfp}$). (b) Thermal conductivity along armchair ($k_{armchair}$) and zigzag ($k_{zigzag}$) directions as a function of the length of the heterostructure ($L$). (c) Thermal sheet conductance along armchair ($G_{s,armchair}$) and zigzag ($G_{s,zigzag}$) directions as a function of the length of the heterostructure. The subscripts in the legends indicate the direction of heat flow with respect to graphene, and $\phi$ represents the twist angle between the armchair directions of graphene and MoS$_2$. The error bars were estimated from $k$ calculated over different time intervals.
Figure 3-3  Thermal conductivity of the heterostructure along the armchair ($k_{\text{armchair}}$) and zigzag ($k_{\text{zigzag}}$) direction as a function of the length of the heterostructure, plotted alongside thermal conductivity of monolayer graphene and MoS$_2$. The legends indicate the direction of heat flow with respect to graphene, and $\phi$ represents the twist angle between the armchair directions of graphene and MoS$_2$.

The effective phonon mean free path of free standing graphene is $\sim 200 - 300$ nm[16], with 70% of the energy transported by phonons with mean free paths longer than 1 $\mu$m[52] and their collective excitations[10]. Also, the above predictions for $k^l$ are derived by assuming absence of any anharmonic phonon-phonon scattering between the heat source and heat sink[48]. The apparent reduction in $k$ of heterostructure when compared to free-standing monolayer graphene is expected due to the following reasons. First, the $k$ of MoS$_2$ is an order of magnitude lower than that of graphene. In other words, when the heterostructure is subject to a heat flux, graphene efficiently diffuses the heat while the thermal transport through MoS$_2$ is inefficient. This characteristic can be additionally noted from the temperature profile of individual layers in the heterostructure during RNEMD simulations (see figure 3-4).
Second, the thickness of the heterostructure is larger than the monolayers. For a given 2D material, $k$ predicted from MD simulations depends on the choice of thickness of the material ($k \propto 1/d$). Notably, researchers have resorted to other choices of thickness which yields different $k$ predictions for the same 2D material [53-55]. This ambiguity in the selection of 2D structure thickness contributes to the discrepancy in $k$ values. On the other hand, thermal sheet conductance [45], $G_s = k \times d = -\left(\dot{Q}/w\right)/\nabla T$ is a suitable alternative for comparing the heat transfer capability of 2D materials since it is independent of the thickness. Although $k$ of heterostructure is smaller than that of monolayer graphene, $G_s$ of the two structures of same dimensions are comparable (Figure 3-2(c)). The extrapolated value of $G_s$ when $L \to \infty$ is calculated from $k_\infty$ and is listed in Table 3-1. The thermal conductance ($G_{s,\infty}$) of the heterostructure is an order of magnitude higher than monolayer MoS$_2$, validating its usefulness for efficient thermal packaging while simultaneously utilizing the desirable photoelectronic properties [21-31] of the heterostructure.
Table 3-1: The empirically derived size effect independent thermal conductivity ($k_\infty$) and the effective phonon mean free path ($l_{mfp}$) for the simulated heterostructures and monolayers.

<table>
<thead>
<tr>
<th>Simulated material</th>
<th>Direction with respect to graphene</th>
<th>Twist angle ($\phi$)</th>
<th>$k_\infty$ ($W / mk$)</th>
<th>$l_{mfp}$ (nm)</th>
<th>$G_{s,\infty} \times 10^{-7}$ ($W / mk$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene/MoS$_2$/Graphene</td>
<td>Armchair</td>
<td>0°</td>
<td>112.51</td>
<td>10.73</td>
<td>1.55</td>
</tr>
<tr>
<td>Graphene/MoS$_2$/Graphene</td>
<td>Zigzag</td>
<td>0°</td>
<td>99.60</td>
<td>10.52</td>
<td>1.37</td>
</tr>
<tr>
<td>Graphene/MoS$_2$/Graphene</td>
<td>Armchair</td>
<td>90°</td>
<td>108.69</td>
<td>10.55</td>
<td>1.50</td>
</tr>
<tr>
<td>Monolayer graphene</td>
<td>Armchair</td>
<td>--</td>
<td>729.39</td>
<td>21.43</td>
<td>2.48</td>
</tr>
<tr>
<td>Monolayer MoS$_2$</td>
<td>Armchair</td>
<td>--</td>
<td>19.47</td>
<td>4.99</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 3-2: Thermal conductivity values computed using NEMD and RTA.

<table>
<thead>
<tr>
<th>Simulated material</th>
<th>Method</th>
<th>$k$ ($W/mK$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene in heterostructure</td>
<td>NEMD</td>
<td>535.32</td>
</tr>
<tr>
<td>Monolayer graphene</td>
<td>NEMD</td>
<td>623.08</td>
</tr>
<tr>
<td>MoS$_2$ in heterostructure</td>
<td>NEMD</td>
<td>19.49</td>
</tr>
<tr>
<td>Monolayer MoS$_2$</td>
<td>NEMD</td>
<td>19.69</td>
</tr>
<tr>
<td>Graphene in heterostructure</td>
<td>RTA</td>
<td>479.44</td>
</tr>
<tr>
<td>Monolayer graphene</td>
<td>RTA</td>
<td>512.09</td>
</tr>
<tr>
<td>MoS$_2$ in heterostructure</td>
<td>RTA</td>
<td>132.25</td>
</tr>
<tr>
<td>Monolayer MoS$_2$</td>
<td>RTA</td>
<td>143.35</td>
</tr>
</tbody>
</table>

Next, we compare the $k$ of graphene and MoS$_2$ in the heterostructure against the monolayer graphene and MoS$_2$ respectively. The $k$ values calculated using NEMD along the armchair
direction of monolayer graphene, monolayer MoS$_2$ and graphene and MoS$_2$ in the heterostructure ($\varphi = 0^\circ$) of same dimensions (43.30 nm × 6.25 nm) are reported in Table 3-2. While the $k$ of graphene in heterostructure is reduced by ~14%, the $k$ of MoS$_2$ is almost unaltered. Figure 3-5 shows the average temperature profile and the temperature profile of the individual layers during NEMD simulation.

![Average temperature profile and the temperature profile of the individual layers during NEMD simulation](image)

Figure 3-5 Average temperature profile and the temperature profile of the individual layers during NEMD simulation

We analyze the phonon power spectrum (phonon density of states) of the individual layers of the heterostructure to explain the $k$ variation relative to the monolayer counterparts. The power spectrum $P(\omega)$ is determined from the Fourier transform of the mass weighted velocity autocorrelation function $P(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{i\omega t} \langle \sum_{i=1}^N m_i v_i(t) m_i v_i(0) \rangle dt$, where $N$ is the number of atoms, $v(t)$ and $m$ are respectively the velocity of an atom at time $t$, and its corresponding mass.
Figure 3-6: Phonon power spectra of monolayer graphene compared against that of the graphene in the heterostructure along the (a) out-of-plane and (c) in-plane directions. Phonon power spectra of monolayer MoS$_2$ compared against that of the MoS$_2$ in the heterostructure along the (b) out-of-plane and (d) in-plane directions. The overall intensity of the high frequency modes in graphene is reduced in the heterostructure while that of the out-of-plane modes of MoS$_2$ is increased due to the phonon coupling resulting from the weak van der Waals interaction between the layers. The non-zero intensity in the out-of-plane modes at 0 THz is a result of numerical approximation associated with binning. Intensity corresponding to phonon modes close to Γ point (0 THz) are binned at 0 THz.

Each velocity dataset was collected for 10 ps when the system was under equilibrium in NVE ensemble. The final power spectrum was calculated by averaging over 10 such velocity datasets collected at different time windows. The phonon power spectra of graphene and MoS$_2$ layers in the heterostructure are compared against the single layer nanomaterials in Figure 3-6. While the intensity of the in-plane modes is reduced in the heterostructure, we observe an overall increase in intensity of the out-of-plane modes (Figures 3-6: (a)-(d)). The population of the out-
of-plane modes in the heterostructure is enhanced due to the coupling between the layers and the intensity of the in-plane peaks are simultaneously reduced. A similar trend is observed in isotope substituted graphene and carbon nanotubes where the \( k \) reduction is associated with the perturbations in the phonon spectra [56-60]. On the other hand, the overlapping frequency range of the phonon modes of MoS\(_2\) and the out-of-plane modes of graphene allows them to be coupled. The out-of-plane modes of MoS\(_2\) are enhanced due to the coupling between the flexural phonon modes of the adjacent layers.

The phonon dispersion curves are generated by calculating spectral energy density (SED) of phonon modes at given wavevector \((q)\), phonon branch \((s)\) and frequency \((\omega)\) from[61]

\[
\Phi(q, s, \omega) = \frac{1}{4\pi^2N} \sum_{\alpha=x,y,z} \sum_{\beta=1}^{n_{\beta}} m_{\beta} e_s(q, \omega) \left| \int_0^r \sum_{n_{x,y,z}} v_{\alpha} \left( \frac{n_{x,y,z}}{\beta} ; t \right) \exp[iq . r(n_{x,y,z}) - i\omega t] dt \right|^2 ,
\]

where \( N = (N_xN_yN_z) \) is the total number of primitive unit cells, \( m_{\beta} \) the mass of the basis atom \( \beta \), \( n_b \) the number of basis atoms in the unit cell, \( e_s \) is polarization vector for the phonon branch \( s \) at wavevector \( q \) and basis atom \( \beta \), \( v_{\alpha} \) the velocity of the atom, \( r \) the position of the unit cell, and \( t \) is the time. The polarization vectors, \( e_s \), are obtained from lattice dynamics as implemented in GULP package[62]. The phonon dispersion curves of graphene and MoS\(_2\) in the heterostructure are compared against that of monolayer graphene and MoS\(_2\) (Figure 3-7). Figure 3-7(a) and 3-7(c) show the phonon dispersion of monolayer graphene and MoS\(_2\) respectively, along the \( \Gamma-M \) direction of the Brillouin zone. The dispersion curves reproduce results from earlier investigations based on first principles and lattice dynamics calculations [63-65], thus validating the implementation of the SED method. Figures 3-7(b) and 3-7(d) show the phonon dispersion along the \( \Gamma-M \) direction of graphene and MoS\(_2\) respectively, when they are in heterostructure. The difference between the phonon group velocity \((v_{ph})\) of the freestanding monolayers and the layers
in the heterostructure is negligible since the shape of the optical and the acoustic modes are largely unaffected.

Figure 3-7: Phonon dispersion curves along Γ-M direction of (a) monolayer graphene, (b) graphene in the heterostructure, (c) monolayer MoS$_2$ and (d) MoS$_2$ in the heterostructure. The x-axis represents the normalized wavevector along the Γ-M direction (q/q$_M$), and the y-axis represents phonon frequencies in THz. The color-bar represents the magnitude of SED in J.s. The shapes of the phonon branches remain the same in all cases, except near the Γ point.

Next, we compare the SED peaks of the low frequency modes of graphene and MoS$_2$ in the heterostructure against their monolayer counterparts at q/q$_M$ = 1/5 in Figure 3-8, where q$_M$ is length of the Brillouin zone along Γ-M direction. The phonon lifetime (τ) can be determined empirically from the SED peaks by curve-fitting a Lorentzian function $\Phi(q, \omega) = \frac{I}{1+(\frac{\omega-\omega_c}{\gamma})^2}$.
where \( I \) is the peak magnitude, \( \omega_c \) is the peak frequency and \( \gamma \) is the half-width at half-maximum which is related to the phonon lifetime by \( \tau = 1/2\gamma \) [61]. From Figure 3-8, we can see that SED peaks of graphene and MoS\(_2\) in heterostructure has broader peaks (higher \( \gamma \) value) than their monolayer counterparts, and correspondingly a slightly reduced \( \tau \) is observed for the low frequency acoustic modes (Figure 3-9).

**Figure 3-8:** (a) Spectral energy density of monolayer graphene and graphene in the heterostructure at \( q/q_M = 1/5 \). (b) Spectral energy density of monolayer MoS\(_2\) and that in the heterostructure at \( q/q_M = 1/5 \). Only the peaks corresponding to the acoustic modes are shown in these figures for visual clarity.

The phonon lifetimes of the full spectrum of graphene and MoS\(_2\) is shown in Figure 3-10. We observe noticeable reduction in the phonon lifetimes of graphene modes in the range of 0 THz – 6 THz, which is also the frequency range of acoustic phonon modes of MoS\(_2\). Due to the large group velocity of the acoustic modes close the \( \Gamma \) point, even a small reduction in phonon lifetime
in these modes (close to 0 THz) can result in a reduced thermal conductivity. This reduction in \( \tau \) can be attributed to the introduction of additional phonon scattering events due to the interaction with the adjacent layers. As a result, the phonon mean-free-path \( (l_{mf} = v_{ph}\tau) \) of graphene in heterostructure is smaller than the monolayer graphene.

![Figure 3-9](image)

**Figure 3-9:** Phonon lifetime of acoustic modes of (a) graphene and (b) MoS\(_2\) in the heterostructure compared against that of the corresponding freestanding monolayer. The reduced phonon lifetime in the heterostructure is attributed to the scattering of phonons at the interface due to the weak van der Waals interaction between the adjacent layers.

Furthermore, we observe new peaks around 1.5 THz in both graphene and MoS\(_2\) when they are in the heterostructure. A closer interrogation at the dispersion curves near the \( \Gamma \) point (Figure 3-11) reveals the appearance of a new optical mode in the dispersion of both graphene and MoS\(_2\) around 1.5 THz. These modes are due to the out of phase motion of the atoms in two adjacent layers, also called breathing modes. The occurrence of breathing modes has been previously reported in supported graphene[64], bilayer graphene[66] and few layer MoS\(_2\)[67]. A recent first principle study on graphene/MoS\(_2\) bilayer heterostructure reported the occurrence of breathing
mode at 2.1 THz [35]. A similar behavior was reported by a recent first principles calculation of van der Waals monolayers supported on amorphous substrates[68].

**Figure 3-10** Comparison of spectral phonon lifetimes (τ) of graphene and MoS$_2$ monolayers with graphene and MoS$_2$ in the heterostructure

Using the relaxation time approximation (RTA), the anisotropic thermal conductivity can be calculated as 

$$k_{\alpha\alpha'} = \frac{1}{v} \sum_{s,q} \tau(s,q) v_\alpha(s,q) v_{\alpha'}(s,q) C_{ph}(\omega_s),$$

where $C_{ph}$ is the specific heat due to the phonons with frequency $\omega$, computed as

$$C_{ph}(\omega) = \frac{(\hbar \omega)^2}{k_B T} \frac{\exp(\hbar \omega/k_B T)}{[\exp(\hbar \omega/k_B T) - 1]^2}. $$

The difference between $k_{armchair}$ and $k_{zigzag}$ of graphene and MoS$_2$ being negligible, as shown above, we can assert that $k$ is isotropic. The summation over wavevectors in the above equation for $k$ can hence be replaced by an integration over cylindrical co-ordinates resulting in[13, 64]

$$k = \frac{1}{4\pi t} \sum_s k(s) = \frac{1}{4\pi t} \sum_s \int_{q_{min}}^{q_{max}} v_s(q)^2 \tau(s,q) C_{ph}(\omega_s) q dq.$$
Figure 3-11: Phonon dispersion curves along Γ-M direction near the Γ point of (a) monolayer graphene, (b) graphene in the heterostructure, (c) monolayer MoS$_2$ and (d) MoS$_2$ in the heterostructure. The width of the peaks increases near the Γ point (blurred) indicating that the phonon lifetimes are decreased. An additional non-zero frequency branch appears near the Γ point of the heterostructure that corresponds to the breathing mode arising from the out-of-phase vibrations of the atoms in the adjacent layers.

where $t$ is the thickness of the 2D material. The above equation is used to calculate the modal contribution of thermal conductivities of the freestanding monolayers, as well as the monolayers in the heterostructure. The $k$ values of free standing monolayer and monolayers in the heterostructures, calculated using RTA, are summarized in Table 3-2. We observe a $\sim 6\%$ reduction in $k$ of graphene and a $\sim 7\%$ reduction in $k$ of MoS$_2$. The normalized contribution of the acoustic phonon modes ($k(s)/k_{total}$) of the monolayers is compared against that in the heterostructure in Figure 3-12. The effect of the out-of-plane acoustic modes (ZA) is suppressed
in the heterostructure, while the contribution of the longitudinal acoustic (LA) modes are enhanced. Although the population of the out of plane phonon modes are enhanced, as seen in Figure 3-6, the presence of an adjacent layer restricts the out of plane motion and introduces additional scattering events of ZA modes resulting in reduced lifetime and $k$. This argument is further supported by the predictions of $k$ accumulation as a function of frequency (Figure 3-13), where 

$$k_{\text{accumulation}}(\omega) = \int_0^\omega \sum s k_s(\omega) d\omega.$$ 

The contribution of phonon modes of graphene whose frequency overlaps with the phonon power-spectra of MoS$_2$ are suppressed due to the coupling between ZA modes of graphene and MoS$_2$. Similar reduction in the contribution of ZA modes is observed in graphene supported on a substrate [64, 69, 70].

**Figure 3-12:** Normalized modal thermal conductivity ($k(s)/k_{\text{total}}$) of (a) freestanding monolayer graphene and graphene in heterostructure, and (b) freestanding monolayer MoS$_2$ and MoS$_2$ in heterostructure. The contribution of the out-of-plane ZA modes are suppressed because of the weak van der Waals interaction between the adjacent layers.
It is worth noting that the phonon power spectra and RTA analysis are performed using the velocities sampled at equilibrium conditions. Effectively no heat is transferred across the graphene-MoS$_2$ interface at equilibrium. However, we still observe a reduction in thermal conductivity which is purely due to the changes in the phonon spectra and phonon lifetimes induced by the presence of adjacent layers and not due to the high thermal resistance of MoS$_2$. In contrast, the $k$ values calculated in NEMD simulations are under non-equilibrium conditions that includes the effects of out-of-plane heat transport due to the mismatch in thermal conductivities. We attribute the differences between the $k$ reductions estimated by the two different methods (NEMD vs. RTA) to the difference in the simulation conditions (equilibrium vs. non-equilibrium).

**Figure 3-13:** Thermal conductivity accumulation ($k_{\text{accumulation}}$) as a function of frequency compared between (a) freestanding monolayer graphene and graphene in heterostructure, and (b) freestanding monolayer MoS$_2$ and MoS$_2$ in heterostructure. The contribution of graphene phonon modes with frequencies overlapping with the phonon power-spectra of MoS$_2$ are suppressed due to the coupling between ZA modes of graphene and MoS$_2$ vibrational modes.
Figure 3-14: Temperature profile in the graphene and MoS$_2$ of the bilayer during the thermal relaxation simulation: (a) heat flow is from graphene to MoS$_2$, and (b) heat flow is from MoS$_2$ to graphene. (c) and (d) show the temperature difference between the layers corresponding to the process represented by (a) and (b), respectively. The temperature difference between the layers decays exponentially. The relaxation time constant $\tau_r$ is determined empirically by a curve fit.

We also calculate the thermal conductance ($G$) across the MoS$_2$/graphene bilayer interface using a thermal relaxation method[71]. After the bilayer is equilibrated at 300 K, one of the layers is rapidly heated to a higher temperature (500 K) by velocity rescaling. The $\Delta T$ between the layers (200 K) is maintained for 1 ns by applying two separate Nosé-Hoover thermostats to graphene and MoS$_2$. Then, the thermostats are removed, and the layers are allowed to relax to thermal equilibrium. Using the lumped heat-capacity model[72] the interfacial thermal conductance can be calculated as $G = \frac{C_{\text{effective}}}{A\tau_r}$, where $A$ is the interfacial area, $C_{\text{effective}} = C_G C_M / (C_G + C_M)$ the effective volumetric heat capacity of the bilayer[73] and $\tau_r$ is the thermal relaxation time determined from a fit to $\Delta T(t) = \Delta T(t_o) e^{-(t-t_o)/\tau_r}$, $t_o$ being the time origin. Heat capacities of the graphene ($C_G$) and MoS$_2$ ($C_M$) are obtained from the Debye model for lattice vibrations as $C = \int_0^\infty C_{ph}(\omega) \, d\omega$. 
The superior thermal conductivity of graphene results in very low Biot number[72] that justifies the use of lumped heat capacitance model. Figures 3-14(a) and 3-14(b) show the temperature profile of the layers, as they relax to thermal equilibrium when graphene and MoS₂ are heated, respectively. The temperature difference between the layers decays exponentially. A fit to $\Delta T(t)$ predictions and the $\tau_r$ thus obtained are shown in Figures 3-14(c) and 3-14(d). The interfacial thermal conductance, $G = 0.90 \text{ MW/m}^2\text{K}$ when the heat flow is from graphene to MoS₂ and $0.76 \text{ MW/m}^2\text{K}$ when the heat flow is from MoS₂ to graphene, both being significantly lower than the $G$ calculated using AIREBO or LJ potential functions[34][33]. We note that the calculated $G$ depends on the strength of the van der Waals coupling (LJ parameters in our model) between the layers. The interfacial thermal conductance has a sub-quadratic dependence on the strength of the van der Waals interaction[68]. The rectification ratio, $\eta = \frac{G_{\text{Graphene-MoS₂}} - G_{\text{MoS₂-Graphene}}}{G_{\text{MoS₂-Graphene}}}$, for the bilayer is 0.178 similar to previous investigations of graphene based van der Waals heterostructured interfaces [71, 74].

3.5 Conclusions

In summary, we predict the in-plane thermal conductivity of graphene encapsulated MoS₂ van der Waals heterostructure using molecular dynamics simulations. Our results show negligible anisotropy in thermal conductivity ($k$) along the zigzag and armchair directions of the heterostructure. Also, $k$ of heterostructure does not change appreciably when the armchair direction of graphene is aligned with the zigzag direction of MoS₂ ($\varphi = 90^\circ$). $k$ of heterostructure increases with the material dimension suggesting that the effective phonon mean free path is comparable to the maximum scattering length considered ($\sim 20 \text{ nm}$). While the overall $k$ of the heterostructure is significantly smaller than monolayer graphene, we find that the thermal sheet conductance of the heterostructure is an order of magnitude larger than that for monolayer MoS₂.
Thus, encapsulating MoS$_2$ within graphene provides a way to efficiently manage thermal energy in MoS$_2$ based photoelectronic devices. Additionally, $k$ of the graphene and MoS$_2$ in heterostructure is reduced compared to that of their monolayer counterparts due to the suppression of the out-of-plane ZA modes, an overall blue shift in phonon power spectra, and reduced phonon lifetime and mean free path. We note the occurrence of a non-zero phonon mode at the $\Gamma$ point when stacked in the van der Waals heterostructure, implying an out-of-phase motion of the atoms in adjacent layers (breathing modes). The interfacial thermal conductance of graphene/MoS$_2$ bilayer predicts an insignificant dependence on heat flow direction with the rectification ratio being only 0.178.

3.6 References


CHAPTER 4. ENHANCED THERMAL CONDUCTIVITY AND VISCOSITY OF N-EICOSANCE PHASE CHANGE MATERIALS WITH GRAPHITE NANOPARTICLES

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4.1 Abstract

Organic materials like simple, long chain n-alkanes have high latent heat and find application as a phase change material (PCM). In this work, we measure the thermal conductivity, \(k\), and viscosity, \(\mu\), of \(n\)-eicosane (C\(_{20}\)H\(_{48}\)) as a function of temperature, and examine the effect of homogenously dispersed graphite particles (GP) in the PCM. Our results show a large enhancement in \(k\) (450\%) and \(\mu\) (1200\%) for a 3.5\% vol. concentration of GP fillers. The surprising reduction of the interfacial thermal resistance (\(R_{\text{eff}}\)) with increasing filler concentration, together with the high thermal conductivity of GP contributes to the large enhancement in \(k\). \(R_{\text{eff}}\) increases with temperature when \(n\)-eicosane is in solid phase and decreases after phase transition. The enhancement in \(\mu\) is attributed to the layering of liquid \(n\)-eicosane at the graphene surfaces, and agglomeration of GP at higher concentrations.

4.2 Introduction

Concentrating solar power (CSP) plants rely on radiative heat transfer from the sun to a working fluid for generating electricity by different power cycles. The intermittent, variable and unpredictable nature of solar radiation generally results in mismatch between the rates of solar

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Note: In this work, MD study and modeling using effective medium theory is my contribution.
energy collection and supply. One solution to improve the performance and reliability of a power plant through regular supply and distribution of the load is by employing a Thermal Energy Storage (TES) system. During the charging stage TES stores energy (as chemical, sensible or latent heat) when the collected amount is in excess of the requirement, and discharges when the supply is inadequate. Latent heat thermal-storage systems (LHTS) are superior due to their high storage densities and the ability to store and release energy with small temperature differences during the charging-discharging periods. LHTS use phase change materials (PCMs) that undergo solid to liquid phase change during charging, while the liquid phase solidifies during the discharging period as heat is extracted. PCMs are broadly classified as organic or inorganic, and are available for a wide range of melting-point temperatures. The choice of PCMs depends on the operating temperature of the intended application, viz., low (< 400 K), medium (400-575 K) and high temperatures (> 575 K).

We investigate the effect of temperature and graphite fillers on the transport properties of a low temperature organic PCM, \( n \)-eicosane (C\(_{20}\)H\(_{42}\)). While earlier studies\([1, 2]\) measured the effects of temperature and nanoparticles on the thermal conductivity \((k)\) of PCMs with graphene based additives, the literature on the viscosity \((\mu)\) of this PCM is sparse.\([3]\) Enhancing the transport properties can facilitate increased energy storage and efficient thermal discharge from \( n \)-eicosane. Furthermore, previous analytical models employed to predict the effective \( k \) of the mixture are based on an invariant interfacial thermal resistance for a given combination of materials.\([1, 4-7]\) However, for an interface between two dissimilar materials, the interfacial thermal resistance depends on multiple factors like geometry of the interface, presence of defects, size of the filler material, etc. Here, we examine the enhancement in \( k \) by using the interfacial resistance as a function of the concentration of graphite particle (GP) fillers. Our experimental measurements are
validated against predictions of classical atomistic simulations and compared against available literature. The increase in $k$ is attributed to the excellent conductivity of the filler materials and interfacial resistance being strongly dependent on filler concentration. In accord with previous experimental[8] and simulation studies,[9] $\mu$ increases with GP concentration due to the agglomeration of the filler particles and layering of the fluid molecules on the surface of GP. Our investigation offers a strategy of tuning the transport properties of organic PCMs by dispersing graphite particles within them.

4.3 Experimental and Computational Methods

Eicosane (99% pure, Alfa Aesar) is initially melted and poured in a test tube that is further heated or cooled using a constant temperature bath to measure the properties at different temperatures. Graphite particles (GP) (99.9% pure, US Research Nanomaterials Inc.), are chosen as filler material to enhance $k$. Figure 4-1(a) shows the SEM characterization of GP, obtained using FEI Quanta 250 FE-SEM that has a maximum resolution of the order of 1.0 nm. The in-plane diameter of random shaped GP ranges between 0.4 - 1.2 $\mu$m and the net surface area ranges between 6 – 8 $m^2/g$. GP is dispersed in molten $n$-eicosane at a given volume percentage (1%, 5%, 7.5%, and 10%). The mixture undergoes ultra-sonication in a sonicator (Q500, QSonica, LLC.) for 4 hours to ensure thorough mixing, followed by solidification within a short time (~3 minutes) to prevent the graphite powder from precipitating. Figure 4-1(b), that shows the SEM characterization of the mixture (10% wt. GP), illustrates that our sample preparation method synthesizes mixtures with evenly distributed GP in the $n$-eicosane matrix.

Thermal conductivity, $k$, is measured using KD2 pro thermal properties analyzer (Decagon Devices, Inc.) that has a sensor needle which contains both the heating element and thermistor. The sensor plates of the viscometer vibrate with the same frequency and the amplitude is
maintained at a constant value by electromagnetic force.\([8, 10]\) \(\mu\) is determined by a sine-wave vibro viscometer (SV-10, A&D Japan) from the correlation between electric current and the magnitude of the viscous force. Unlike a rotating drum viscometer, the energetic interference to the sample liquid is minimum in this method, thus enabling us to continuously measure \(\mu\) with temperature variations.

**Figure 4-1:** The SEM characterization of the (a) GP shows the representative particle sizes for the filler material while that for (b) the homogenous mixture of n-eicosane and GP suggests that the sample preparation method results in a uniform dispersion of the particles. The molecular illustrations of (c) the initial configuration used for MD simulations consisting of crystalline n-eicosane with triclinic structure (\(\alpha = 67.6^\circ\), \(\beta = 83.96^\circ\), \(c = 2.544\) nm, \(a = b = 0.5\) nm)\([11]\) and (d) the amorphous structure of n-eicosane at 300 K obtained by melting the crystalline structure and subsequent quenching of liquid n-eicosane.
Equilibrium molecular dynamics (EMD) simulations are employed on a 3.5 nm × 6 nm × 5 nm cuboid domain where crystalline \( n \)-eicosane is constructed as a triclinic structure\[11\] (\( \alpha = 67.6^\circ, \beta = 83.96^\circ, c = 2.544 \) nm, \( a = b = 0.5 \) nm) with 224 molecules as shown in Figure 4-1(c). Each molecule contains 68 atoms (\( C_{20}H_{48} \)). Although crystalline \( n \)-eicosane has a triclinic structure, in order to facilitate the computations, we employ a cubic simulation box and allow the molecules to move across the box boundaries under periodic boundary conditions in all the directions. The OPLS-AA force field is employed to describe both the bonded and non-bonded interactions.\[12\] Upon energy minimization, the structure is equilibrated at 300 K and 1 atm. under the isothermal-isobaric (NPT) ensemble for 1 ns using the Nosé–Hoover thermostat and barostat with coupling constants of 0.05 ps and 0.5 ps, respectively. After density equilibrates within ~1 ns, the system is rapidly heated to 600 K and held for 550 ps to ensure complete melting of \( n \)-eicosane. Since \( n \)-eicosane samples used in the experiments are amorphous, we generate comparable molecular structures by performing multi-stage cooling (quenching) to 300 K. Figures 4-1(c) and 4-1(d) show illustrative representations of the crystalline and the equilibrated amorphous structures of \( n \)-eicosane at 300 K. \( k \) of the amorphous structure is computed using the Green-Kubo method by averaging over the \( x \), \( y \) and \( z \) directions as

\[
k_{av} = \frac{V}{3k_BT^2} \sum_{\alpha=x,y,z} \mathbf{J}_{\alpha\alpha}(0) \mathbf{J}_{\alpha\alpha}(t) > dt,
\]

where \( V \) is the volume, \( T \) the temperature, \( k_B \) the Boltzmann constant, \( \mathbf{J}_{\alpha\alpha} \) the diagonal elements of the heat flux tensor and \( t \) the time. Assuming the structure to be homogenous and isotropic, \( k_{av} \) is the same as the bulk \( k \). Likewise, \( \mu \) of the PCM when in liquid phase is computed using the Green-Kubo formulation as

\[
\mu_{av} = \frac{V}{3k_BT^2} \sum_{\alpha=x,y,z} \mathbf{P}_{\alpha\alpha}(0) \mathbf{P}_{\alpha\alpha}(t) > dt,
\]

where \( \mu \) is sampled over the \( x \), \( y \) and \( z \) directions, and \( \mathbf{P}_{\alpha\alpha} \) represent the diagonal elements of the pressure tensor.
4.4 Results and Discussion

4.4.1 Pure \( n \)-eicosane

The calculated density of 0.760 g/cm\(^3\) at 1 atm. and 300 K is in close agreement to the experimentally measured density of 0.788 g/cm\(^3\), validating our choice of force field and the method of generating the amorphous \( n \)-eicosane. Figure 4-2(a) shows the \( k \) predictions for \( n \)-eicosane below its phase change temperature. Our experimentally measured \( k \) at temperatures around 300 K are lower than our corresponding computational predictions. Unlike the experimental \( n \)-eicosane samples, the system in our MD simulations is completely defect free (100% pure). The presence of contaminants and other functional defects, even by a minimal amount, cause a strong reduction in heat conduction by lowering \( k \).[13-17] Nevertheless, our results for \( k \) around 300 K and its negligible dependence on temperature concurs with earlier reports.[1, 6] Figure 4-2(b) shows the variation of \( \mu \) with temperature. With increase in temperature, experimentally measured \( \mu \) decreases from 4.65 \( \times 10^{-3} \) Pa.s at 310 K to 2.37 \( \times 10^{-3} \) Pa.s at 345.2 K. \( \mu \) predicted from EMD simulations, for instance 3.41 \( \times 10^{-3} \) Pa.s at 320 K, agrees strongly with the corresponding measurement of 3.64 \( \times 10^{-3} \) Pa.s, and shows similar temperature dependence as observed in experiments. Kinetic energy of the \( n \)-eicosane molecules increases with rising temperatures facilitating enhanced motion of the atoms, bonds and angles about their mean equilibrium positions. Such interactions contribute to an increased mobility of the organic fluid, resulting in a decrease in \( \mu \).

4.4.2 \( n \)-eicosane with GP fillers

The increase in \( k \) of \( n \)-eicosane with addition of GP at 300 K is shown in Figure 4-3(a) (black dots). An astonishing enhancement of 450% is observed for 3.5% volume fraction of GP (10% wt.) dispersed in \( n \)-eicosane, in agreement with earlier observations.[1] Such a remarkable
increment is attributed to the extremely high $k$ of GP. The $k$ enhancement with GP is higher than that due to carbon nanotubes (CNT) fillers. We conjecture that such an effect results from a relatively lower effective interfacial thermal resistance ($R_{\text{eff}}$) across $n$-eicosane and GP as compared to the PCM and CNT interfaces.[1, 7].

![Figure 4-2](image)

**Figure 4-2:** (a) Thermal conductivity, $k$, of pure $n$-eicosane presented as a function of temperature suggests a negligible temperature dependence of $k$ in agreement with the literature [1, 6, 18]. (b) $\mu$ of pure $n$-eicosane decreases with increasing temperature. The standard deviation in $\mu$ measurement is $0.02 \times 10^{-3}$ Pa.s ($< 1\%$). The kinetic energy and the mobility of the $n$-eicosane molecules increases with temperature resulting in a monotonically decreasing $\mu$ with rising temperatures. The experimental results strongly concur with the computational predictions.
We perform reverse non-equilibrium MD (RNEMD) simulations to predict the thermal resistance across \( n \)-eicosane/graphite interface and to understand the contribution of \( R_{\text{eff}} \). A 9 nm \( \times \) 6 nm \( \times \) 5 nm simulation domain is used, as shown in Figure 4-3(b), where six graphene layers are sandwiched between the amorphous \( n \)-eicosane. The distance between the graphene layers is 0.34 nm. We employ the Müller-Plathe algorithm\([19]\) where the system is divided into bins along the \( x \) direction and the kinetic energy of the fastest atom in the extreme bins is swapped with that of the slowest atom in the central bin of the simulation box, thus imposing an artificial heat flux. Additional details on employing the technique are discussed elsewhere \([14, 20]\). Figure 4-3(d) shows the temperature distribution of a system equilibrated at 250 K after it has attained steady state (linear temperature variation with position). The non-linear profile at the center and the edges of the simulation domain are attributed to energy scattering due to lattice vibrations near the heat sink and heat source.\([21]\) The interfacial thermal resistance \( R_{\text{eff}} = A\Delta T/J \), where \( J \) is the imposed heat flux, \( A \) the cross-sectional area perpendicular to the heat flux and \( \Delta T \) the temperature difference at the interface calculated as the average of \( \Delta T_1 \) and \( \Delta T_2 \) illustrated in Figure 4-3(d). We note from Figure 3(c) that the calculated \( R_{\text{eff}} \) increases with increasing temperature. At higher temperatures, the contributions of the lattice vibrations due to anharmonic interactions increase, resulting in a higher resistance to heat flow across the solid-solid interfaces\([22, 23]\).

However, beyond the phase change temperature, \( n \)-eicosane undergoes solid-to-liquid transition and \( R_{\text{eff}} \) decreases abruptly. The drop in \( R_{\text{eff}} \) is attributed to liquid \( n \)-eicosane forming molecular layers adjacent to graphene surfaces resulting in enhanced interfacial heat conduction. We support our analysis by computing the density variation of \( n \)-eicosane in the simulation domain at 350 K (temperature chosen to ensure complete melting). The simulation box is divided into 0.2 Å wide bins in a direction orthogonal to the graphite surface. The density profile in Figure 4-3(d)
is obtained by sampling the mass density of $n$-eicosane in each bin over a span of 1 ns. The peaks of the density distribution near the interface are characteristic of fluid layering on graphene. Away from the interface, the density converges to the bulk value with a homogenous distribution.

\[ \text{Figure 4-3: (a) Enhancement in } k \text{ at 300 K is shown as a function of the GP concentration in } \% \text{ vol. (filled circles in black). The lines represent the increase in } k \text{ as predicted by the EMT model for different values of } R_{\text{eff}}. \text{ As the concentration of GP increases } R_{\text{eff}} \text{ increases initially due to increased number of interfaces. At sufficiently large concentration, the GP form a percolating network resulting in a significant reduction in } R_{\text{eff}}, \text{ suggesting that } R_{\text{eff}} \text{ strongly depends on the filler concentration. (b) The simulation domain for RNEMD simulations illustrates six layers of graphene sandwiched between amorphous } n\text{-eicosane along the x-direction. (c) The variation of } R_{\text{eff}} \text{ as a function of temperature for a single } n\text{-eicosane/graphite interface as estimated from RNEMD simulations shows a decrease in } R_{\text{eff}} \text{ at 325 K due to solid-to-liquid phase transformation of } n\text{-eicosane. The error bars are estimated by computing } R_{\text{eff}} \text{ over different time windows during the simulation. (d) Steady state temperature profile (equilibrated at 250 K) and } n\text{-eicosane mass density profile (at 300 K) of the simulated system along the x-direction. } \Delta T \text{ used in calculating } R_{\text{eff}} \text{ is the mean of } \Delta T_1 \text{ and } \Delta T_2. \text{ Mass density peaks are characteristic of the layering behavior of } n\text{-eicosane on graphite surfaces. The fluctuations in the peaks decay away from the interface as } n\text{-eicosane approaches the bulk density.} \]
4.4.3 Applicability of effective medium theory (EMT) model

We now use the $R_{\text{eff}}$ calculated from MD in an EMT based model to predict the effective $k$ of the mixture at different filler concentrations. From the EMT model [1, 7]

$$k_{\text{eff}} = k_m \frac{3 + f_{\text{vol}}[2\beta_{xx}(1 - L_{xx}) + \beta_{zz}(1 - L_{zz})]}{3 - f_{\text{vol}}(2\beta_{xx}L_{xx} + \beta_{zz}L_{zz})}$$

where

$$L_{xx} = \frac{a^2}{2(a^2 - 1)} + \frac{a}{2(1 - a^2)3/2 \cos^{-1}a}$$

$$L_{zz} = 1 - 2L_{xx}$$

$$\beta_{xx} = \frac{k_{f,xx} - k_m}{k_m + L_{11}(k_{f,xx} - k_m)}$$

$$\beta_{zz} = \frac{k_{f,zz} - k_m}{k_m + L_{zz}(k_{f,zz} - k_m)}$$

$$k_{f,xx} = \frac{d}{2R_{\text{eff}} + d/k_{f,\text{in-plane}}}$$

$k_{\text{eff}}$ is the effective thermal conductivity of the mixture, $k_m$ is the thermal conductivity of the matrix ($n$-eicosane), $f_{\text{vol}}$ is the volume fraction of GP, $a$ is the aspect ratio of GP (assumed to be 5/2000)[1], $k_{f,zz}$ is the out-of-plane thermal conductivity of GP, $d$ is the diameter of GP (~ 0.8 µm), $k_{f,\text{in-plane}}$ is the in-plane thermal conductivity of GP, $k_{f,xx}$ is the modified in-plane thermal conductivity which takes into account the effective interfacial thermal resistance $R_{\text{eff}}$. The $R_{\text{eff}}$ predicted from the NEMD simulation at 300 K is $2.9 \times 10^{-7}$ m$^2$K/W which is larger than $R_{\text{eff}}$ calculated for graphene/polyethylene ($1.785 \times 10^{-8}$ m$^2$K/W; NEMD),[24] graphene/epoxy ($3.500 \times 10^{-9}$ m$^2$K/W; experimental),[25] graphene laminates ($1.886 \times 10^{-8}$ m$^2$K/W; multi-scale
model),[26] graphene/Si (1.754 × 10⁻⁸ m²K/W),[27] and graphene/n-octane (0.561 × 10⁻⁷ m²K/W – 1.388 × 10⁻⁷ m²K/W).[28] Nevertheless, we still observe a significant enhancement in \( k \) with increase in filler concentration owing to the remarkable \( k \) of graphite. The experimental measurements shown in Figure 3(a) suggest an increase in \( k \) with concentration, contrary to the predictions of the EMT model (black line). We assume a constant \( R_{\text{eff}} \) as predicted by MD, and note that the model hugely underestimates the \( k \) enhancement.

Now, we consider \( R_{\text{eff}} \) to be a function of filler concentration and derive its values using a curve fit between the EMT model and the experimental \( k \) measurements. At very low volume fraction of GP, \( R_{\text{eff}} \) is the least (\( \approx 0.30 \times 10^{-8} \) m²K/W) since the number of interfaces are less. As the volume fraction of GP increases, the number of interfaces are more and hence \( R_{\text{eff}} \) increases to 1.85 \( \times \) 10⁻⁸ m²K/W. However, at a suitably high volume fraction (~0.035% vol.) the GP form a percolating network,[25] causing a significant decrease in the \( R_{\text{eff}} \) (\( \approx 0.72 \times 10^{-8} \) m²K/W).

Although, the numerical value of \( R_{\text{eff}} \) is sensitive to aspect ratio, the above discussed variation of \( R_{\text{eff}} \) with concentration stays the same for any assumed value of \( a \). Thus, \( R_{\text{eff}} \) is a strong function of filler concentration and this dependence has to be accounted for when modeling \( k_{\text{eff}} \) of mixtures containing additives with high thermal conductivities.

Figure 4-4 shows the ratio of \( \mu \) of graphite-eicosane mixture and pure eicosane as a function of different GP concentrations. The addition of GP increases the \( \mu \) of the mixture. For instance, at 318 K the enhancement in \( \mu \) is 12.5 times that of pure \( n \)-eicosane for 3.5% vol. GP dispersion. The increase in viscosity can be attributed to the layering of the fluid molecules on the graphite surfaces, which reduces the effective number of mobile fluid molecules especially in the vicinity of the GP.[9] Additionally, with increasing concentration, particles tend to agglomerate into clusters that causes a reduction in \( \mu \), as has been shown earlier for nanofluids.[8]
Figure 4.4: Enhancement in $\mu$ as a function of temperature for different concentrations of GP fillers. $\mu$ increases with GP concentration due to the agglomeration of the particles and layering of the fluid molecules on the surface of the GP, both of which impede mobility.

4.5 Conclusions

In summary, we characterize $k$ and $\mu$ of PCM $n$-eicosane as a function of temperature, and examine the effects of adding graphite particle (GP) fillers. Our experimental results and corresponding atomistic simulations show that the temperature dependence of $k$ of pure $n$-eicosane is negligible, while $\mu$ decreases monotonically with temperature. The addition of graphite particles (3.5% vol.) results in an enhancement of $k$ (450%) due to the high thermal conductivity of GP and reduced interfacial thermal resistance $R_{\text{eff}}$ with increasing filler concentration. $R_{\text{eff}}$ across a single $n$-eicosane/graphite interface, computed using MD simulations, increases with temperature until $n$-eicosane undergoes melting. The density profile of liquid $n$-eicosane adjacent to the graphite surfaces shows fluid layering, which is responsible for the drop in interfacial resistance in liquid phase. The enhancement in $\mu$ (1200%) is attributed to the ordering of liquid $n$-eicosane at the interface and the agglomeration of GP at higher concentrations. Our results aid in
understanding the transport phenomena in a mixture of simple organic hydrocarbons impregnated with graphitic particles, and the roles of interfacial thermal resistance and molecular ordering. We also note that the current models based on effective medium theory are insufficient to describe the property variations since they do not account for changes in interfacial resistance with filler particle concentration.

4.6 References


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CHAPTER 5. EFFECT OF FLAKE ORIENTATION AND KAPITZA RESISTANCE ON THE EVAPORATION RATES OF WATER OVER GRAPHENE

Modified version of this chapter will be submitted for publication in *Applied Surface Science*.

5.1 Abstract

The role of Kapitza resistance on the evaporation rates of water over the graphene surface is investigated for using molecular dynamics simulation. The Kapitza resistance between graphene and water, when the graphene flakes are parallel ($\phi = 0^\circ$) and perpendicular to the interface ($\phi = 90^\circ$), are calculated using non-equilibrium molecular dynamics simulations (NEMD). The hydrophilicity of graphene when $\phi = 0^\circ$ leads to enhanced liquid layering adjacent to the surface resulting in a lower Kapitza resistance compared to the $\phi = 90^\circ$ case. We also calculate the evaporation rates of water thin film for the two interfaces. The evaporation rates on $\phi = 0^\circ$ surface are higher than $\phi = 90^\circ$ surface due to the efficient heat transfer between the substrate and water thin film. The predictions of our simulations matches with the collaborative experimental observations on inkjet printed graphene (IPG) via direct pulsed laser writing (DPLW). Our findings suggests a possibility of tuning the evaporation rates on graphene surfaces using DPLW.

5.2 Introduction

The advancements in materials science, nanotechnology and device fabrication techniques have led a drastic reduction of sizes of various electronic devices in the last few decades. The continuous miniaturization of electronic devices is however limited by the engineering bottlenecks of thermal management at micro and nanoscale[1]. The need for an efficient heat removal

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**Note:** In this chapter, the MD study is my contribution.
mechanism is ever so important to sustain the technological advancement and to design efficient electronic devices. Solutions based on highly conductive graphene structures have been proposed to be a viable way forward [2-10]. With this regard, suspensions of graphene structures in a liquid are of particular interest due to the contrasting thermal transport properties of graphene and liquid medium [10-12]. Understanding the nanoscale interactions of graphene with the surrounding liquid and the heat transport at the interface is critical for its integration into existing cooling systems based on micro- and nano-fluidics[13, 14]. Furthermore, the understanding the effect of interfacial thermal resistance on the evaporation rate of the liquid on graphene surfaces is of fundamental importance. Theoretical predictions of effective thermal conductivity of nanofluids differ by an order of magnitude compared to the experimental measurements[15]. Moreover, there have been very few studies[16] on the effect of interfacial thermal resistance on the heated evaporation rates of the surrounding liquid. In this study, we use molecular dynamics (MD) simulations to investigate the effect of the graphene flake orientation on the Kapitza resistance between water and graphene. We show that the Kapitza resistance of graphene is lower when the flakes are parallel to the interface compared to the graphene structures with flakes perpendicular to the interface (graphene edges). In addition, we also compute the evaporation rates for the two interfaces. The evaporation on parallel graphene surface is faster than the perpendicular graphene interface due to the efficient heat transfer between graphene and water, particularly at higher temperatures.

5.3 Computational Methods

5.3.1 Kapitza resistance

The Kapitza resistance ($R_K$) between water and the graphene substrate, when the graphene flakes are parallel ($\varphi = 0^\circ$, Figure 5-1(a)) and perpendicular ($\varphi = 90^\circ$, Figure 5-1(b)) to the
interfaces are computed using non-equilibrium molecular dynamics (NEMD) simulations. A block of 4000 water molecules are sandwiched between the substrates (Figure 5-1(a) and 5-1(b)). The initial dimensions of the simulation domain for the $\varphi = 0^\circ$ and $\varphi = 90^\circ$ along $-x$, $-y$ and $-z$ directions are $7.76 \text{ nm} \times 4.48 \text{ nm} \times 12.7 \text{ nm}$ and $8.16 \text{ nm} \times 4.74 \text{ nm} \times 10.02 \text{ nm}$ respectively. Periodic boundary conditions are employed in all the directions. The interatomic interactions between the carbon atoms in the substrate are modeled using the optimized Tersoff potential which captures the correct phonon dispersion of graphene and suitable to study thermal transport phenomena. The interaction between the water molecules are modeled using the extended rigid simple point charge (SPC/E) model which includes the long-range columbic interaction between the O ($-0.8476e$) and the H ($+0.4238e$) atoms in addition to the short-ranged 12-6 Lennard Jones potential between the O atoms. In the SPC/E model, O-H bonds and the H-O-H angle are made rigid. The van der Waals interaction between the substrate and the water molecules are modeled using 12-6 Lennard Jones potential between the C and O atoms. The parameters of the LJ potentials are the same as in Table 7-1 and 7-2.

The Columbic interactions between pair of atoms within 0.1 nm are treated explicitly, while a particle-particle particle mesh [19-21] long range solver with a tolerance of $10^{-6}$ is used to compute the columbic interactions beyond 0.1 nm. The system is initially equilibrated for 1 ns under an NPT ensemble at 300 K and 1 bar using a Nosé-Hoover thermostat and barostat respectively. Subsequently, the atoms within 3.4 nm from the top and bottom edge of the simulation box are held fixed. NEMD simulations are performed by placing a Langevin thermostats at 325 K and 275 K on a region of 6.8 nm thickness adjacent to the fixed layer at the top and bottom respectively. After the system attains steady state, the Kapitza resistance is calculated as $R_K = \frac{\Delta T}{J}$ where $\Delta T$ is the temperature difference at the interface and $J$ is the heat flux
passing through the interface. Unless otherwise specified, the time step of integration used in all our simulations is 1 fs.

Figure 5-1: Schematic representation of the NEMD simulation setup for (a) $\varphi = 0^\circ$ and (b) $\varphi = 90^\circ$, (c) Temperature profile of across the $-z$ direction simulation domain after steady state. The $R_K$ when the heat transfer is from water to graphene and graphene to water is calculated using $\Delta T_1$ and $\Delta T_2$ respectively, (d) Mass density profile of water along the $-z$ direction. The peaks are due to the liquid layering next to the solid substrate. The larger peak density for $\varphi = 0^\circ$ compared to $\varphi = 90^\circ$ case indicates that former is more hydrophilic

5.3.2 Evaporation rates

The initial configuration consists of 4000 water molecules placed on top of the substrate in a cubic lattice (Figure 5-2(a) and 5-2(c)). The dimensions of the simulation domain for $\varphi = 0^\circ$ and $\varphi = 90^\circ$ case along the $-x$ and $-y$ directions are 7.75 nm $\times$ 4.48 nm and 8.16 nm $\times$ 3.83 nm, respectively. The length of the simulation box along the $-z$ direction is 20 nm. Periodic boundary conditions are used along the $-x$ and $-y$ directions, while a fixed boundary condition was used in
the \(-z\) direction. The carbon atoms within the bottom 3.4 nm of the simulation box are held fixed throughout the simulation. Equilibration is performed under NVT ensemble using a Nosé-Hoover thermostat at 300 K for 2 ns. During the equilibration step, a reflective wall is placed on the top of the simulation box to avoid the water molecules crossing the \(-z\) boundary. After 2 ns, the water molecules form a thin film adjacent to the substrate with a thickness of about 4 nm (Figure 5-2(b) and 5-2(d)). The reflective wall is subsequently removed and the substrate is suddenly heated to the desired temperature to simulate substrate heating during evaporation. Any water molecules crossing an imaginary wall placed at a distance of 8 nm from the top of the interface are deleted to simulate the evaporation process. The evaporation simulations are performed for 3 ns and the evaporation rates are calculated by recording the number of water molecules crossing the imaginary wall per ns. All simulations are performed using the LAMMPS simulation package[22] and OVITO is used for visualization[23].

5.4 Results and Discussion

It has already been shown in Chapter 6 that graphene petal orientation has a direct relationship between the water contact angles since it changes the net attractive energies \(U_{H_2O}\) and the liquid density peak adjacent to the surface[24]. Since the absolute value of \(U_{H_2O}\) for \(\phi = 0^\circ\) is more, the peak value of liquid density adjacent to the surface is larger than the \(\phi = 90^\circ\) at the hot and cold interface (Figure 5-1(d)). Correspondingly, the Kapitza resistance is smaller than the \(\phi = 90^\circ\) case at hot and cold interfaces (Table 5-1). The peak density due to characteristic liquid layering next to the solid atoms is indicative of liquid ordering[10]. The larger liquid density peak indicates that it is more hydrophilic[24] which results in higher acoustic phonon matching, lower phonon scattering at the interface and reduced Kapitza resistance. In fact, an inverse proportionality relationship between the Kapitza resistance and density peak for graphene/water interfaces have
been previously reported [25] by using reverse non-equilibrium molecular dynamics (RNEMD) simulations.

Figure 5-2: (a), (c) Schematic representation of the initial configuration for evaporation rate simulations. (b), (d) Schematic representation of the system after equilibration, (e) Mass density profile of water along –z direction for the two surfaces at 300 K and 400 K.

We also compute the $R_K$ values using a flexible water model (SPC/Fw)[26] to capture the effects of high frequency phonons due to hydrogen atoms. The time step of integration used with the SPC/Fw is 0.2 fs. The difference between the results from simulations using SPC/E and SPC/Fw water models is negligible and does not change the conclusions (see supporting
information). Hence, the contribution due to the high frequency phonons in water can be neglected and we use the rigid SPC/E model for the rest of the study for computational efficiency. It is worth noting the small thermal rectification we observe in our simulations. The $R_K$ for the heat transfer from water to graphene (cold interface) is larger than graphene to water (hot interface) consistent with the results from Ref [25].

Table 5-1: Kapitza resistance ($R_K$) for graphene flakes parallel and perpendicular to the interface computed using NEMD simulations.

<table>
<thead>
<tr>
<th>Graphene flake orientation</th>
<th>Direction of heat transfer</th>
<th>Kapitza resistance ($R_K \times 10^{-8} m^2/W.K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varphi = 0^\circ$</td>
<td>Graphene to water</td>
<td>0.48 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>Water to graphene</td>
<td>1.08 ± 0.04</td>
</tr>
<tr>
<td>$\varphi = 90^\circ$</td>
<td>Graphene to water</td>
<td>1.30 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>Water to graphene</td>
<td>2.25 ± 0.02</td>
</tr>
</tbody>
</table>

Figure 5-3: Evaporation rates computed using MD for $\varphi = 0^\circ$ and $\varphi = 90^\circ$ case. The inset shows the Arrhenius plot (ln R vs 1/T).
Next, we investigate the evaporation rates for $\varphi = 0^\circ$, $\varphi = 90^\circ$, and the role of Kapitza resistance during heated evaporation. The evaporation rates computed for $\varphi = 0^\circ$ in our simulations are larger than $\varphi = 90^\circ$ case for all the temperatures considered (Figure 5-3). At 300 K, the dominant driving force for the evaporation is the diffusion of water molecules since the water thin film (see Figure 5-2) and the underlying substrate were initially at thermal equilibrium. However, at temperatures above 300 K, there is an effective heat transfer between the substrate and water during the initial stage of evaporation. Hence, the evaporation rates are determined by diffusion of water molecules as well as the efficiency of heat transfer from graphene to water. In general, evaporation due to diffusion increases exponentially with temperature. This is confirmed by the typical Arrhenius behavior that we observe (inset Figure 5-3). Hence, the difference between $\varphi = 0^\circ$ and $\varphi = 90^\circ$ is due to the dissimilar heat transfer rates with water. The heat transfer in the case of $\varphi = 0^\circ$ is more effective due to the smaller $R_K$ values resulting in faster evaporation rates. The small difference in the evaporation rates at 300 K can be attributed to the heat transfer from graphene to water due to the evaporative cooling of water film. The water molecules that evaporate possess excess kinetic energy to overcome the barrier due to the surface tension of thin film. During evaporation, energy is removed from the water thin film in the form of latent heat by those water molecules that evaporate.

To confirm the findings of our simulations, the evaporation rates on inkjet printed graphene (IPG) via direct pulsed laser writing were measured through collaborative experimental efforts (Experiments performed by collaborators at Kansas State University - P.P. Chakraborty, S. R. Das, M. M. Derby). The wetting and orientation of the graphene flakes of the IPG can be tuned at the nanoscale using the power density of the laser used during DPLW[24]. Figure 5-4 and 5-5 shows the evolution of the droplet during evaporation on hydrophilic ($\varphi = 0^\circ$) and hydrophobic ($\varphi =$
90°) substrates respectively. The substrates are made using direct pulsed laser writing inkjet printing technique which is discussed in more detail in Ref. [24].

Figure 5-4: Experiments performed by collaborators at Kansas State University (P.P. Chakraborty, S. R. Das, M. M. Derby). Evaporation from the hydrophilic graphene surface: (a)-(c) 1-μL water droplet (average evaporation time: 16 min) and (d)-(f) 4-μL water droplet (average evaporation time: 35 min)

Figure 5-5 Experiments performed by collaborators at Kansas State University (P.P. Chakraborty, S. R. Das, M. M. Derby). Evaporation from the hydrophobic graphene surface: (a)-(c) 1-μL water droplet (average evaporation time: 21 min) and (d)-(f) 4-μL water droplet (average evaporation time: 38 min)

As predicted by our simulations, the evaporation on hydrophilic substrate is faster than that on hydrophobic substrate, even at room temperature.
5.5 Conclusions

In conclusion, we have used MD simulations to investigate the effect of graphene flake orientation on the Kapitza resistance between water and the evaporation rates. Our results, show that the Kapitza resistance between graphene flakes and water depend on the extent of liquid layering adjacent to the substrate. The Kapitza resistance of the interface with perpendicular graphene flake is higher than parallel graphene flakes. Consequently, the evaporation rates on the perpendicular graphene flakes are lower than parallel graphene flakes. The results from our simulations matches with collaborative experimental observations of evaporation on inkjet printed graphene. Our results help in understanding the role of Kapitza resistance on the evaporation rates and suggests a possibility of engineering interfaces with tunable evaporation rates using direct pulsed laser writing.

5.6 References


CHAPTER 6. CONCLUSIONS FROM THERMAL TRANSPORT ACROSS STRUCTURALLY AND DEFECT-ENGINEERED GRAPHENE-BASED MATERIALS

The primary objective of this thesis is to highlight some of the possible mechanisms by which graphene can be structurally engineered to achieve the desired thermal properties targeted for particular applications, such as photovoltaics, electronic displays, sensors, batteries, catalyst, photodetectors, thin-film transistor and other energy conversion devices[1-7]. In general, thermal transport in any material is facilitated by phonons (lattice vibrations) and electron-phonon interactions[8]. In the case of graphene, the electronic contribution can be neglected since the phononic specific heat ($C_{ph}$) is much greater than the electronic specific heat ($C_e$) at room temperature [9, 10], and thermal conductivity is proportional to ($C_{ph} + C_e$) from kinetic theory[11]. Thus, impeding motion of phonons holds the key to limiting thermal transport in graphene-based nanomaterials.

The intrinsic thermal conductivity of monolayer suspended graphene is highest among known materials with reported values ranging from 2000 to 4000 W/mK [12-14]. This huge spread in the reported values is due to the difference in the quality of graphene sheets synthesized and measured. Samples with smaller grain size, vacancy defects, isotope impurities lead to a reduction in thermal conductivity [13, 14]. The presence of a substrate to support graphene monolayer in devices further leads to a reduction in thermal conductivity [15-17]. Although these reductions in thermal conductivity are established, the exact phonon mechanisms causing the reduction is not conclusive. In this thesis, I have attempted to explain the variations in heat transport through engineered graphene nanomaterials by studying the phonon properties with the introduction of vacancy and isotope defects, and changing the surrounding interactions with graphene, using molecular dynamics simulations.
The discussions in the second chapter relate to the effects of vacancy defects and isotope impurities on the thermal transport within a graphene monolayer. With the addition of a small amount of isotope impurity and vacancy defects, the short ranged longitudinal and transverse modes get scattered at the mass disorder sites leading to reduced thermal conductivity. However, at higher fractions of isotope (lower mass disorder) the original thermal conductivity is recovered. On the contrary, with increasing vacancy defect density the reduction in thermal conductivity saturates. While short ranged mass disorder strongly affect the population of in-plane longitudinal and transverse modes, the intensities of out-of-plane flexural modes are largely unaffected due to their delocalized nature. In addition to the point defects (like vacancy and isotope impurities commonly present in monolayer graphene), the presence of substrates also affects the thermal transport. Hence, the next step is to understand the effect of surface and interfacial interactions on the phonon modes.

In chapter three I show that the contribution of out-of-plane acoustic modes can be reduced by stacking graphene on monolayer MoS$_2$. The van der Waals interaction with the adjacent monolayer leads to additional scattering events resulting in a reduced phonon lifetimes of the delocalized low frequency out-of-plane modes. The findings from chapter two and three demonstrates the potential to structurally engineer graphene to modify the phonon properties of in-plane modes by controllably introducing mass disorder in the lattice, or, the out-of-plane modes by stacking graphene on other solid materials.

With the understanding of the effects of stacking graphene on a lattice with well-defined phonon modes (solid-solid interface), I next look at thermal transport across solid-soft matter interface and its influences on the overall heat conduction in a graphene embedded composite material. In chapter four, it is shown that interfacial thermal transport can be enhanced by
engineering the structural arrangement of surrounding medium at the interface. A more ordered atomic packing at the interface leads to a reduction in interfacial thermal resistance. Despite the remarkably high thermal conductivity of suspended graphene, its usage in practical applications as a heat dissipation material is often limited by the resistance at interconnects and the interfacial thermal resistance between the substrate, usually insulating and amorphous SiO$_2$. The findings presented in chapter four suggests possibilities to improve the thermal packaging in practical devices by using a phase change material with the right transition temperature as the insulating medium to minimize the formation of local hot spots at the interconnects and other interfaces in the circuit. When the temperature exceeds the melting point, the molecules of the surrounding medium rearrange to form ordered atomic packing at the interface resulting in efficient thermal transport. Furthermore, it is interesting to see the influence of such ordering on the interfacial thermal transport across a solid-fluid interface. Specifically, I look at the dependence of interfacial thermal conductance on the graphene flake orientation in a graphene-water interface.

The discussions in chapter five show that density of water at the interface is strongly related to the Kapitza resistance between water and graphene. A higher density peak indicates more efficient atomic packing and heat transport across the interface. When the graphene flakes are oriented parallel to the interface ($\varphi=0^\circ$), the water density at the interface is higher compared to perpendicular graphene flakes ($\varphi=90^\circ$). This also suggests that the parallel graphene flakes are more hydrophilic compared to perpendicular flakes. Next, the role of Kapitza resistance on the evaporation rates of water on graphene surfaces is investigated. Water droplets formation on surface are ubiquitous and common, especially in humid conditions. It is important to understand the evaporation phenomena of water on these surfaces to design efficient graphene-based devices that can operate in humid environment. The results presented in chapter five also shows that heated
evaporation on hydrophilic surfaces ($\varphi=0^\circ$) are faster compared to hydrophobic surfaces ($\varphi=90^\circ$), due to the efficient heat transfer from the substrate to the water molecules. The change in hydrophilicity with the orientation of graphene flakes are investigated in more detail in the subsequent chapters where the static contact angle of water are estimated as a function of flake orientation ($\varphi$) using MD simulations.

In summary, the key findings of the work presented here are the following:

1. While the in-plane phonon modes are strongly scattered by mass disorder in the lattice, the out-of-plane phonon modes can be suppressed by stacking graphene on other 2D materials or on a substrate.
2. The in-plane longitudinal and transverse phonon modes are the dominant contributors to the effective thermal conductivity of graphene.
3. Similar to monolayer MoS$_2$ and graphene, the graphene/MoS$_2$/graphene heterostructure has negligible anisotropic heat conduction and the effect of twist angle between the layers can also be neglected. In addition, the thermal conductance across the graphene/MoS$_2$ heterostructure also shows negligible rectification.
4. The interfacial thermal conductance between graphene and $n$-eicosane drops beyond the melting temperature due to the molecular rearrangement of $n$-eicosane at the interface resulting in the formation of ordered atomic layers.
5. The dependence of interfacial thermal conductance on the molecular ordering is also displayed by other disordered surrounding medium, for example, water.

The primary focus of this thesis has been to investigate the changes in thermal transport properties with structurally engineered graphene nanomaterials and the interfaces formed by them. Using atomistic modeling, we explain the variation in thermal conductivity due to controlled
structural manipulations. It will be interesting to study the changes in the electrical conductivity as well as Seebeck co-efficient and optimize the structural configuration to have an enhanced thermoelectric figure of merit. Such exploration will answer whether graphene will aid the search for efficient thermoelectric devices. A more sound understanding of role of defects in energy transport within the material from an atomistic standpoint will enable the fabrication of energy conversion devices using a bottom-up approach instead of a top-down approach.

6.1 References


CHAPTER 7. SUPERHYDROPHOBIC INKJET PRINTED FLEXIBLE GRAPHENE CIRCUITS VIA DIRECT-PULSED LASER WRITING

Modified version of this chapter is published in *Nanoscale* 6

7.1 Abstract

Solution-phase printing of exfoliated graphene flakes is emerging as a low-cost means to create flexible electronics for numerous applications. The electrical conductivity and electrochemical reactivity of printed graphene has been shown to improve with post-print processing methods such as thermal, photonic, and laser annealing. However, to date no reports have shown the manipulation of surface wettability via post-print processing of printed graphene. Herein, we demonstrate how the energy density of a direct-pulsed laser writing (DPLW) technique can be varied to tune the hydrophobicity of inkjet-printed graphene (IPG). Experimental results demonstrate that the DPLW process can convert the IPG surface from one that is initially hydrophilic (contact angle ~ 47.7°) to one that is superhydrophobic (CA ~157.2°). Molecular dynamic (MD) simulations reveal that both the nanoscale graphene flake orientation and surface chemistry of the IPG after DPLW processing induce these changes in surface wettability. Moreover, the DPLW processed IPG is electrically conductive, mechanically flexible, and non-destructive to fragile materials (e.g., paper) and hence could be useful for a wide range of applications such as self-cleaning, wearable/washable electronics.

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**Note:** In this work, my contribution is the MD study and interpretation of experimental trends using simulation results.
7.2 Introduction

Large-area, solution-phase printing of nanomaterials has facilitated the fabrication of low-cost, high-throughput flexible electronics for diverse applications including thin-film transistors, photovoltaics, batteries/capacitors, electronic displays, and strain/pressure sensors [1-5]. Solution-phase printing of graphene-based inks has shown promise in improving the performance of printed electronics due to graphene’s favorable electrical and thermal conductivity, chemical and thermal stability, biocompatibility, and the material’s abundance [6, 7]. High-throughput printing of graphene including inkjet, gravure, flexographic, and screen printing typically requires the use of post-print annealing processes such as thermal, photonic, or laser annealing to make the graphene sufficiently electrically conductive [8-13]. However, these post-print annealing processes have not focused on tuning the surface wettability or hydrophobicity of the printed graphene. The formation of superhydrophobic IPG that is also flexible and electrically conductivity would lend enormous value to self-cleaning wearable/washable electronics that are resistant to stains, or ice and biofilm formation for example.[14, 15]

Recent research on the hexagonal honeycomb carbon lattice in single/few layer graphene have shown that these surfaces display hydrophilic or hydrophobic properties depending on the material composition of the underlying substrate or adsorption of hydrocarbons and epoxide groups to graphene.[16, 17] For example, single layer graphene creates a surface that can display ‘wetting transparency’ in some cases, where water molecules do not effectively ‘see’ graphene and instead behave in accordance with the contact angle of the underlying substrate.[16, 18, 19] In contrast, multilayer graphene, at least four atomic layers thick, impedes wetting transparency and graphene hydrophobicity depends primarily upon superficial hydrocarbon and epoxide groups.[17, 20, 21] No reports have been conducted on manipulating the hydrophobicity of IPG.
Here we report the creation of IPG that is electrically conductive, mechanically robust, and superhydrophobic \([\text{contact angle (CA)} > 150^\circ]\) after UV-pulsed laser irradiation. Experimental results including static CA measurements and scanning electron microscopy (SEM) micrographs confirm that the wettability of the IPG transforms from one that is hydrophilic \((\text{CA} \sim 47.7^\circ)\) to one that is superhydrophobic \((157.2^\circ)\) by manipulating the energy density of laser irradiation via DPLW. Micrographs obtained from an SEM operating in environmental mode demonstrate the formation of water droplets on hydrophilic (untreated laser regions) and not on hydrophobic (laser treated) regions. Molecular Dynamic (MD) simulations help elucidate the physiochemical underpinnings of the surface wettability and show that both the graphene flake orientation (nanopatterning) and surface chemistry induced by the DPLW process play an important role in changing the surface wettability of the IPG.

### 7.3 Computational Methods

Due to the intrinsic size limitation of MD, simulating a water droplet sufficiently large for the line tension force at the contact line to be negligible is not practical. Hence, the value of the contact angle (CA) calculated from MD, in general, has some size dependence. We therefore adopt a semi-infinite cylindrical slab of water droplet in which the simulation box is narrow in the \(y\)-direction compared to the \(x\) and \(z\) direction\([16, 22]\). Size dependence of the contact angle thus calculated using this approach has been shown to be negligible\([22]\). The size of our simulation box is a \(25.84 \times 3.83 \times 20\) nm\(^3\) with 4,000 water molecules arranged in a periodic-cube placed on top of a graphitic substrate. The simulation box is periodic in \(x\) and \(y\) direction while it has a fixed boundary along the \(z\)-direction. Figure 7-1 shows an example of the starting configuration where the substrate is horizontally oriented for few layer graphene. The equilibrated system is shown in Figure 7-2, where the contact line is straight and hence the line tension contribution is zero due to
the infinite curvature. We use the rigid simple extended point charge (SPC/E) model,[23] for the interactions between water molecules. In the SPC/E model, the O-H bonds and the H-O-H angles are considered rigid. The water molecules interact with each other via Coulombic interactions and 12-6 Lennard Jones (LJ) interaction between the oxygen atoms. The parameters used for the SPC/E model is listed in Table 6-1.

**Figure 7-1** *(Left)* Side view of the initial configuration of the simulation box and *(Right)* top view of the initial configuration of the simulation box

**Figure 7-2** *(Left)* Side view of a snap shot of the equilibrated system and *(Right)* top view of the snap shot of the equilibrated system
Table 7-1: Parameters for SPC/E water model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge on Oxygen, $Q_o$</td>
<td>-0.8476</td>
</tr>
<tr>
<td>Charge on hydrogen, $Q_H$</td>
<td>0.4238</td>
</tr>
<tr>
<td>$\varepsilon_{O-O}$</td>
<td>0.650 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{O-O}$</td>
<td>3.166 Å</td>
</tr>
</tbody>
</table>

The cut-off for the LJ interactions and the short range Coulombic interactions between the water molecules is 10 Å. The long range Coulombic interactions were computed in k-space using the particle-particle particle-mesh (PPPM) solver[24]. Since the simulation box is non-periodic in the z-direction we introduce an artificial reflecting wall on top edge of the simulation box to prevent water molecules from escaping the simulation box. For the purpose of computing the long range Coulombic interactions, the PPPM solver treats the system as if it was periodic in z direction while inserting an empty volume between the periodic images and turning off the interactions between the periodic images in the z direction[25]. The ratio of the extended z dimension to the initial z dimension was set as 3.

The interaction between the water molecule and the underlying substrate is also modeled as a 12-6 LJ potential between the oxygen atoms and the substrate atoms. We use two sets of LJ parameters: a) derived by Werder et. al, [26] and, b) parameters derived from the All Atom Optimized potential for Liquid Simulations (OPLS-AA) [27]. The appropriate parameters for the different models used are listed in Table 6-2. In the case of epoxy terminated graphene, the terminal oxygen and carbon attached to the epoxy oxygen carry partial charge of $Q_{OT} = -0.28e$ and $Q_{CT} = +0.14e$ due to the polar nature of the C-O bonds.
It has been shown that the total water-substrate interaction energy \( U_{H2O-C} \) directly affects the computed contact angle values in MD[21]. Hence, it is important to calculate \( U_{H2O-C} \) accurately. For the same reason we set the cut-off for the water-substrate interaction as 20 Å. Accordingly, the thickness of the substrates used in our simulations were always between 20 Å and 25 Å since atoms deeper than 25 Å from the surface of the substrate do not contribute.

Table 7-2: LJ parameters from Werder et. al and OPLS-AA force field. The subscripts ‘O’, ‘CG’, ‘CH’, ‘CT’ and ‘OT’ refer to oxygen atom in water molecules, graphitic carbon, hydrogen termination at the graphene edges, carbon attached to an epoxy group at the graphene edges and oxygen in the epoxy group respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Werder et. al</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_{O-CG} )</td>
<td>0.392 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{O-CG} )</td>
<td>3.190 Å</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_{O-CH} )</td>
<td>0.436 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_{O-CT} )</td>
<td>0.285 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_{O-OT} )</td>
<td>0.423 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{O-CG} )</td>
<td>0.617 kJ mol(^{-1})</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{O-CH} )</td>
<td>3.352 Å</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{O-CT} )</td>
<td>2.768 Å</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{O-OT} )</td>
<td>3.329 Å</td>
<td></td>
</tr>
</tbody>
</table>

The initial configuration (Figure 7-1) is equilibrated under an NVT ensemble at 300 K using the Nosé–Hoover thermostat with a coupling constant of 10 fs. The time step of integration used in all our simulations is 1 fs. Ma et. al [28], showed that water nanodroplets on graphene sheet has a high diffusion co-efficient due to the thermal ripples in graphene. Here, we keep the
substrate atoms frozen and integrate the positions of only the water molecules. Such a simplification has been shown not to affect the resulting contact angle[26]. We still observe a non-negligible diffusion on the graphene sheets. Hence to compare against the experimental static contact angles, the linear momentum of the center of mass of the water droplet was reset to zero every 1 ps. All the data for the calculation of contact angle was sampled after the $U_{\text{H2O-C}}$ and temperature converges to a constant value, i.e., after equilibration. Figure 7-3 shows the convergence of $U_{\text{H2O-C}}$ and temperature with time.

![Figure 7-3 (Left) Evolution of the interaction energy between the water droplet and substrate with time. Convergence was achieved within 2.5 ns in all the cases. (Right) Temperature fluctuations are minimum and the system is well equilibrated under the thermostat.](image)

The mass density profile of the water droplet was obtained by dividing the simulation box into bins in the shape of pencils of uniform cross-section running parallel to the y-direction of the simulation box (Figure 7-4a). The mass density of water in each bin was averaged over a span of 1 ns to generate the mass-density profile (Figure 7-4b). The mass density profile of the water-droplet is further divided into slabs along the z direction.
**Figure 7-4:** (a) The simulation box is divided into bins, along the x-z plane, in the shape of pencils running parallel to the y-axis. (b) The mass density in each bin is averaged over a span of 1 ns to generate the density map. The cross section of the bins is used to generate this density map.

Figure 7-5 shows the mass-density at the center of the water droplet along the z direction. The peaks at the first few bins agree with the typical ordering behavior of a fluid near a solid surface. In experiments, the macroscopic contact angle measured are at least a few tens of atomic
layers away from the surface. We thus eliminate the data before the first two peaks for calculating contact angle.

![Mass density profile](image)

**Figure 7-5**: Mass density profile at the center of the droplet along the direction.

The following sigmoidal function is curve fitted over the mass density of each slab.

$$
\rho(r) = \frac{1}{2} \left( \rho_\beta(dr) + \rho_\beta(g) \right) - \frac{1}{2} \left( \rho_\beta(dr) - \rho_\beta(g) \right) \tanh \left( \frac{2(r-r_\beta)}{d_\beta} \right)
$$

(1)

where $r$ is the distance from the center of the water droplet, $\rho$ is the mass-density, $\rho_\beta(dr)$ is the mass density in sheet $\beta$ near the center of the water droplet, $\rho_\beta(g)$ is mass density of surrounding gas (assumed to be zero), $r_\beta$ is the radius of the droplet in slab $\beta$, $d_\beta$ is the thickness of the interface and $\Delta z$ is the thickness of each slab. The contact angle is calculated as[29]:

$$
\theta = \lim_{\Delta z \to 0} \tan^{-1} \left( \frac{\Delta z}{r_2 - r_1} \right)
$$

(2)

where $r_1$ and $r_2$ are the radius of the water-droplet in the first two sheets considered.
7.4 Collaborative Experiments

Printable graphene ink, formulated following our previous recipes,[8] is loaded into the printer cartridge (10 pL nominal drop volume nozzle) of a Fujifilm Dmatix materials inkjet printer (DMP2800). Graphene writing parameters (such as waveform, temperature, viscosity of ink, drop spacing etc.) are used as optimized before,[8] on silicon as well as the polyimide substrates. The thermal annealing is performed (on graphene on silicon/oxide substrates) using a furnace with forming gas flow. Samples were annealed for 1 hour at 700°C, 800°C, 900°C, and 1000°C. The laser irradiation was performed on graphene printed on polyimide surface (25µm thick) using a Nd:YAG pulsed laser (3rd harmonic at 355 nm and 15 ns pulse width) and the sample is exposed to the laser beam using an x-y translator.

Further details on capturing scanning electron microscope (SEM) images, environmental scanning electron microscopy (ESEM), measurement of sheet resistance and contact angle can be found in Ref. [30]

7.5 Results and Discussion

IPG films were developed on a silicon substrate with a thickness of ~7 µm and post-processed via both DPLW and conventional thermal annealing (Figure 7-6a and 7-6b). DPLW processing was conducted with increasing laser energy density (40, 70, 85, 100, and 120 mJ cm\(^{-2}\) respectively). Thermal annealing was conducted with annealing temperatures between 700-1000°C within a forming gas ambient. Results indicate that DPLW processing of IPG generates 3D nanostructures with features of two characteristic length scales: a local fin-like nanoscale structure (Fig. 6-6f), as well as a micron-scale rose-petal structure (Fig. 6-6d). In contrast, thermal annealing revealed a comparatively smooth surface (Fig. 6-6e & 6-6g).
Figure 7-6 Experiments performed by collaborators at Iowa State University (S.R. Das, L.R. Stromberg, Q. He, N. Garland, W.E. Straszheim, J.C. Claussen). (a) Schematic diagram and field emission scanning electron microscopy (FESEM) images showing the inkjet printing of reduced graphene oxide and (b) the subsequent DPLW or thermal annealing processing. (c) The IPG on polyimide withstands mechanical bending and twisting with a ~ 2-3% and 24% resistance change. (d) Top view of the printed graphene surface after DPLW processing at an energy density of 100 mJ cm\(^{-2}\). (e) Top view of graphene after thermal annealing at a temperature of 900°C. (f) Cross-sectional view of the DPLW processed graphene. (g) Cross-sectional view of thermally annealed graphene. All scale bars are 2 µm.

The hydrophobicity and electrical conductivity of the IPG was significantly altered/improved by DPLW and thermal annealing processes. Droplets of deionized water (3-6 µL, resistivity ~18.3 MΩ-cm) were dispensed in several locations onto the surface, and the static CA of both DPLW and thermally treated graphene were measured via contact goniometry (Supplementary Information, S1). DPLW treated graphene displayed a sharp increase in the CA with the lowest fluence setting (125.2°, 40 mJ cm\(^{-2}\)) as compared to the control samples, Si/SiO\(_2\) with a ~300 nm oxide layer and IPG without any annealing which yielded CAs of approximately 44.5° and 47.7° respectively. The control value was found to be consistent with that previously reported for graphene oxide (GO).[31] Note that, the IPG films created herein are accompanied
with oxygen functional groups.[8] DPLW operated at a laser energy density within the range of 85-100 mJ cm$^{-2}$ transformed the surface into one that was superhydrophobic (i.e., CA > 150°). However, the IPG CA decreased (~138°) when laser fluence was increased to 120 mJ cm$^{-2}$, which is most likely attributed to electrode degradation.[8] The thermal annealing of IPG did not induce superhydrophobicity (maximum measured CA was 70.8°) across annealing temperatures of 800 - 1000°C (Fig. 6-7b). Moreover, the CAs for the thermally annealed IPG were approximately 20° smaller than those obtained for multilayer (>6 layers) and flat graphene[16], but similar in magnitude to those reported for chemically synthesized reduced GO films.[32] The CA of thermally annealed graphene begin to diminish at higher temperatures where CA values were 51.1° and 41.4° at respective annealing temperatures of 900°C and 1000°C. This decrease in CA at high annealing temperatures is most likely due to the smoothening of the graphene surface at higher temperatures.[10] In a similar fashion, the electrical conductivity of the distinctly annealed IPG samples changed with increasing laser energy density or annealing temperature (Fig. 6-7e & 6-7f). The electrical sheet resistance of the IPG samples decreased by more than three orders of magnitude from 21 MΩ/□ to 1.1 kΩ/□ as DPLW energy density was increased to 100 mJ cm$^{-2}$ (Figure 7-7e). It is interesting to note that 100 mJ × cm$^{-2}$ is the same laser energy density that maximizes both the superhydrophobicity and the electrical conductivity of the IPG, ensuring the scalability of laser annealed IPG for electronics and self-cleaning applications for example. Similarly, the electrical sheet resistance of the IPG samples decreased by more than three orders of magnitude from 21 MΩ/□ to 0.3 kΩ/□ as the thermal annealing temperature was increased to 1000°C (Fig. 6-7f).

The surface wettability of the superhydrophobic DPLW treated (100 mJ cm$^{-2}$) and hydrophilic thermally annealed (800°C) IPG were characterized via environmental scanning
electron microscopy (ESEM) (Fig. 6-7c & 6-7d). Distinctly shaped, spherical water beads (dia. < 5-50 µm) formed on the DPLW treated IPG during ESEM imaging (Fig. 6-7c). These water droplets appeared as the environmental vapor pressure, relative humidity temperature and vapor pressure were altered within the ESEM (see Fig. 6-10 discussion). Beaded water droplet formation was noticeably absent from the thermally annealed IPG during ESEM experiments (Fig. 6-7d)—thus further corroborating the hydrophobic and hydrophilic nature of the DPLW and thermally

![Figure 7-7 Experiments performed by collaborators at Iowa State University (S.R. Das, L.R. Stromberg, Q. He, N. Garland, W.E. Straszheim, J.C. Claussen). Comparison of CA, condensation, and electrical sheet resistance of IPG that was DPLW annealed (a, c, e) or thermally annealed (b, d, f). (a) CAs for IPG electrodes treated with DPLW at distinct laser energy densities. Inset shows the CA of a control Si/SiO2 surface without IPG. (b) CAs measured on IPG that were thermally annealed at distinct temperatures. Water condensation experiments performed on (c) laser annealed (100 mJ/cm2) and (d) thermally annealed (800°C) IPG inside an environmental SEM chamber. Scale bars correspond to 50 µm. (e) Larger spherical droplets indicate water condensation and small bright spots (red arrows) indicate initial water droplet formation. Electrical conductivity experiments display sheet resistance vs. (e) laser energy density and (f) temperature for laser and thermally annealed IPG respectively.](image-url)
annealed IPG samples. It should be noted that the induced superhydrophobicity is not due to wetting transparency as GO and multi-layer graphene with thicknesses of 30 nm or greater are generally optically opaque[16]. Furthermore, subsequent MD simulations demonstrate that the nanoscale patterning of the graphene, via the laser, and subsequent contamination of the graphene with airborne hydrocarbon or epoxide adsorption help facilitate the superhydrophobic nature of the DPLW treated graphene.[17, 33].

To further investigate the geometric microscale origins of superhydrophobicity[34], MD simulations were used to understand the mechanism for hydrophilic-to-hydrophobic conversion of DPLW-treated IPG. The superficial graphene CA was predicted as a function of the graphene petal orientation by modeling the molecular interactions between graphene and water. Droplet-graphene interaction energy ($U_{H2O-C}$) was computed for different graphene petal orientations. The results demonstrate CA values change with the orientation of graphene flakes. However, these simulations (i) only capture the nanoscale phenomena and (ii) are performed on ordered structures, not accounting for the disorder in interlayer spacing and the petal orientation observed in the experiment. In all the simulations, the distance between the graphene layers was set to 3.4 Å based on the experimentally observed interplanar spacing in graphite[35]. We note that the spacing between graphene flakes in IPG is subject to change after DPLW-treatment and there is a randomness associated with the petal orientation. Nevertheless, our idealized simulations help in isolating the role of petal orientation from other morphological changes due to laser treatment, and elucidates its effect on CA. The simulation domain was a 25.84 × 3.83 × 20 nm$^3$ box with 4,000 water molecules arranged over a graphitic substrate, and equilibrated at 26.85°C. The intermolecular interactions between the water molecules are described by the rigid extended simple point charge model (SPC/E)[36] and the graphene-water interactions are modeled with a 12-6 Lennard Jones potential using parameters ($\epsilon_{CO}$ and $\sigma_{CO}$) proposed by Werder et. al.[37] The
CA of the water droplet was determined by curve fitting a sigmoidal function over the mass density profile of the water droplet divided into sheets along the z-direction.[19, 38-40]

Results from the atomistic simulations corroborate the change in CA due to local changes in the graphene petal orientation. The CAs for intermediate orientations between the horizontal and vertical positions of multi-layer graphene flakes, denoted by \( \phi \) (angle between the plane of the graphene sheet and the positive x-axis in the horizontal direction), are calculated to further support the trend. Differences in the predicted absolute values of the CAs from the experiments are due to: (i) the system size limitation that constraints the MD analyses to only nanoscale features without including effects of microstructures observed on the samples, and (ii) notable disparity in the water droplet size between experiments and simulations, (iii) randomness in the petal orientation, spacing and functionalization in DPLW-treated IPG, which are not included in our model. Hence a computational scheme which can address the shortcomings of the MD model is necessary to understand the role of factors other than petal orientation.

Figures 7-8(a)-(c) show the change in CA due to change in orientations of graphene and the evolution of \( U_{H2O-C} \) with time. The CA (\( \theta_c \)) of water droplet on horizontally oriented graphene, \( \theta_c = 76.87^\circ \), is in agreement with earlier theoretical calculations [16, 19, 41] and experimental measurement of CAs on exposed graphene sheets.[16, 17, 42] For the vertically oriented graphene sheets only arm-chair configurations of graphene edge states are considered. \( U_{H2O-C} \) measures the interaction strength between the droplet and the substrate. \( U_{H2O-C} \) converges \( \cong -0.2 \) Mcal/mol for vertically oriented graphene, while horizontally oriented graphene petals with \( U_{H2O-C} \cong -0.6 \) Mcal/mol (Figure 7-8c) reflect a relatively stronger attraction between the droplet and the substrate. When the adhesive interaction due to the attractive van der Waals forces between the droplet and substrate molecules overcomes the cohesive interaction between the water molecules,
the surface becomes hydrophilic. Alternately, a stronger intermolecular interaction between droplet molecules relative to the adhesive forces renders the surface hydrophobic.

Figure 7-8 MD simulations of water contact angle of printed graphene with horizontally and vertically aligned flakes. (a & b) Average mass density profile projected over the y-z plane of the equilibrated water droplet on horizontally and vertically oriented graphene respectively using Werder parameters. (c) Transient evolution and convergence of the water-graphene interaction energy using Werder parameters. (d & e) Average mass density profile projected over the y-z plane of an equilibrated water droplet on horizontally and vertically oriented graphene respectively using OPLS parameters. (f) Transient evolution and convergence of the water-graphene interaction energy using OPLS parameters. (g) Calculated contact angle of the droplet on the graphitic substrate for different graphene petal orientations (φ). Black squares are Werder potential parameters without any functional groups attached. Red circles are OPLS potential parameters without any functional groups attached. Blue triangles are OPLS potential parameters with hydrogen (-H) terminated edge atoms. Pink triangles are OPLS potential parameters with epoxy terminated graphene edge atoms.

The horizontal configuration of few layer graphene exerts strong van der Waals attraction to the water molecules placed above given the continuous spread of carbon atoms beneath. This interaction results in a small CA and a hydrophilic surface. As the graphene layers are oriented away from horizontal and towards a vertical ordering, the nanoscale spaces developed underneath the droplet due to the interlayer spacing weakens the net attraction, i.e., adhesive forces, resulting in a hydrophobic surface. Since the cohesive interactions between water molecules remain
invariant for different petal orientations, the wettability of the surface is driven by the net attractive energies \( U_{H2O-C} \) due to adhesive forces between the droplet and substrate for the horizontal, vertical and intermediate configurations. Correspondingly, we observe a shift in \( \theta_c \) from 76.87° to 118.5° when \( \phi \) increases from 0° to 90° as illustrated in Figure 7-8 (g) (data shown with solid black squares).

CA values for water on graphene and graphite surfaces in the literature are inconclusive. For a given pair of liquid and solid substrate, several values of CAs can be obtained due to the intrinsic chemical heterogeneity and roughness of the solid substrate.[41, 43] Furthermore, it was recently shown by Li et.al[17] that adsorption of airborne contaminants like hydrocarbons directly influences the wetting CA, while uncontaminated graphene is more hydrophilic than previously thought. Since the Werder.[37] parameters were optimized to reproduce the macroscopic CA of water droplet on a contaminated graphite sample \( (\theta = 86^\circ) \), it implicitly includes some of the effects of contaminants. In order to eliminate the effects of adsorbed contaminants, we performed additional simulations with the water-graphene interaction parameters derived from Optimized Potential for Liquid Simulations-All Atoms (OPLS-AA) force field.[44] Figures 7-8(d)-(f) reveal the changes in CA due to horizontal and vertical orientations of graphene petals and the corresponding convergence of water-graphene interaction energy. Similar to earlier predictions, \( U_{H2O-C} \) for horizontally oriented graphene assumes a value \( (\approx -1.1 \text{ Mcal/mol}) \) significantly more negative compared to the vertically oriented configuration \( (\approx -0.35 \text{ Mcal/mol}) \). Correspondingly, as \( \phi \) increases from 0° to 90° for bare graphene surfaces, \( \theta_c \) also increases from 38.36° to 91.12° (Figure 7-8(g)). This result confirms that the orientation of the graphene flakes has a direct influence on the \( U_{H2O-C} \), thus impacting CA and wettability. It is worth noting that the stacking sequence of the graphene sheet in our model has negligible effect on the CA. All the simulations in our work were done with energetically favored AB stacking sequence of graphene. In order to
investigate the effect of stacking sequence, we estimate the contact angle of AA stacked vertically oriented graphene with Werder parameters. The results are compared against AB stacking in Table 6-3.

**Table 7-3:** Estimated CA’s for graphene with AB and AA stacking respectively.

<table>
<thead>
<tr>
<th>Stacking</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB stacking</td>
<td>$\theta_c = 118.50$</td>
</tr>
<tr>
<td>AA stacking</td>
<td>$\theta_c = 118.79$</td>
</tr>
</tbody>
</table>

The dangling bonds on the edges of the vertically oriented graphene in our model are highly reactive, and experimental evidence (heat loss and mass loss shown in Figure 7-9) confirms the presence of functional groups. The experimental details on heat loss and mass loss measurement are given in Ref. [30]

To understand the role of these functional groups, we performed additional simulations of two idealized cases: (i) all edge atoms of the graphene are hydrogen (−H) terminated, (ii) all the edge atoms of the graphene are epoxy terminated, each at 5 different graphene petal orientations ($\phi = 0^\circ, 30^\circ, 45^\circ, 60^\circ$, and $90^\circ$). The epoxy terminated graphene sheets are more hydrophilic compared to the −H terminated sheets due to polar nature of the C-O bonds (Figure 7-8(g)). This interaction increases the negative interaction energy ($U_{H2O-C}$), due to stronger adhesive forces that enable surface wetting characteristics.

Although there exist quantitative differences between the experimental and computational predictions of $\theta_c$, we can clearly see that $\theta_c$ increases with $\phi$ in all of the cases considered. We attribute the mismatch in $\theta_c$ to the microscopic patterns (Figure 7-6 (d),(f)) resulting from laser processing, which were absent in idealized simulations. Nevertheless, these results provide strong
evidence that merely changing the orientation of the underlying graphene flakes induces hydrophobicity.

Figure 7-9 Experiments performed by collaborators at Iowa State University (S.R. Das, L.R. Stromberg, Q. He, N. Garland, W.E. Straszheim, J.C. Claussen). The heat loss and mass loss, caused by airborne hydrocarbon contamination, were studied on unannealed and laser annealed (at 100 mJ/cm$^2$) IPG that was printed on silicon/silicon dioxide substrates.

Finally, we present the simplicity and versatility of using DPLW to selectively pattern distinct superhydrophobic regions on IPG on an arbitrary surface to form distinct hydrophilic and hydrophobic regions on the same surface. The hydrophilic IPG regions were not treated with the laser while the hydrophobic regions were treated with the laser set with an energy density of 100 mJ cm$^2$ (Figure 7-10). The wetting properties of these regions were analyzed within a FEI FESEM where the chamber pressure, humidity, and temperature were altered in a controlled fashion (Fig.
6-10 (b – (e)). Initial water droplet formation could be noticeable observed on the hydrophilic regions when the chamber humidity was set to ~100%, the pressure at 640 Pa, and the temperature to 1.1°C (Fig. 6-4(b)). Large water droplet formation gradually occurred as the chamber temperature was reduced from 1.1°C to 0.8°C, 0.4°C, and 0.1°C (Fig. 6-4(c)-(e)).

![Hydrophobic boundaries](image)

**Figure 7-10** Experiments performed by collaborators at Iowa State University (S.R. Das, L.R. Stromberg, Q. He, N. Garland, W.E. Straszheim, J.C. Claussen). FESEM images of a graphene hydrophilic/super-hydrophobic region formed using laser patterning and water droplet manipulation in the design. (a) Overall view of the distinctly treated IPG showing a hydrophilic region (darker region with width of ~ 1.5 mm) without laser processing confined by two superhydrophobic regions (lighter regions) treated with laser at an energy density of 100 mJ cm⁻². (b-e) Water condensation experiments conducted within the FESEM operated in environmental mode display micrographs that capture the boundary (dotted red line) between the hydrophilic region (area the left of the red line) and the laser treated or hydrophobic region (region to the right of the dotted red line). As noted on the micrographs the humidity (H) and pressure (P) were held constant at approximately 100% and 640 Pa while the temperature (T) was varied from 1.1°C to 0.1°C. Water droplet formation begins to appear on the surface of the hydrophilic region of the IPG as the temperature is decreased to 0.8°C and increases in magnitude as the temperature is dropped further to 0.4°C and 0.1°C.

### 7.6 Conclusions

In summary, we have demonstrated a simple and scalable manufacturing method to produce large-scale 3D nanostructured graphene surface features that enable multifunctional properties:
hydrophobic-superhydrophobic surface tunability, high electrical conductivity, and mechanical flexibility. In particular, this report demonstrates that the wettability of inkjet-printed graphene can be tuned via UV-laser irradiation. Molecular dynamics simulations confirm that the nanoscale vertical arrangement of the IPG after laser processing facilitates the induced superhydrophobicity. This modeling elucidates the relationship between nanoscale patterning and hydrophobicity—as most hydrophobicity studies focus on the relationship between microscale patterning and hydrophobicity. Moreover, the ability to selectively pattern superhydrophobic areas of hydrophilic IPG presents a material platform that could enable a wide range of emerging technologies such as self-cleaning chemical/biological sensors, flexible electronics, open microfluidics, and drag reduction and/or de-icing surfaces.[45-47] Also, the ability to selectively pattern superhydrophobic areas of hydrophilic IPG presents a potential scalable process that does not require the use of costly vacuum or cleanroom associated equipment such as lithographic patterning, metal evaporation, plasma treatment, and chemical vapor deposition.[48].

7.7 References


CHAPTER 8. FRICTION IN GRAPHENE WRAPPED NANODIAMOND AND GRAPHTITIZED NANODIAMOND

Modified version of this chapter will be submitted for publication in *Applied Physics Letters*.

8.1 Abstract

Macroscale superlubricity have been demonstrated between diamond like carbon (DLC) and nanodiamond (ND) in the presence of graphene flakes[1]. Atomistic simulations show that graphene flakes wrap around the ND at the sliding interface leading to superlubric behavior. While the graphene wrapped ND has low contact area and results in an incommensurate contact, a ND with similar template synthesized by graphitizing the outer surface of the ND results in a diamond core and graphitized shell. Here, we elucidate the mechanism of energy dissipation by comparing the frictional forces between the DLC/graphene wrapped-ND interface and DLC/graphitized-ND interface using atomistic simulations. Our results indicate that graphene wrapped ND exhibits lower friction compared to graphitized ND. The weak interactions between wrapped graphene and ND allows easy rotation of ND. On the other hand, in case of graphitized ND, chemical bonding between graphitized carbon and core ND prevent such rotation resulting in increased work and thus higher friction. The results from our simulations matches with experimental observations.

8.2 Introduction

Superlubricity is the phenomena in which two sliding bodies at incommensurate contact experience almost zero mechanical energy dissipation due to the absence of collective stick slip.

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5 Srilok Srinivasan, Diana Berman, Ganesh Balasubramanian, Subramanian Sankaranarayanan, Ali Erdemir, Anirudha V. Sumant, *Effect of graphene wrapped nanodiamond vs graphitized nanodiamond on superlubricity*, under preparation

Note: In this chapter, the MD study is my contribution. This work was done during my internship at Argonne National Laboratory, Lemont, IL, USA.
motion at the nanoscale [2-5]. Several works in the past focused on understanding the origin of superlubricity at the atomic scale either by modeling[3-5] or using frictional force microscopy [2, 6-10]. Translating the nanoscale superlubricity to macroscale is non-trivial and has tremendous implications in the real life applications ranging from MEMS devices to energy saving and increasing the lifetime of mechanical assemblies used in industries. Diana et.al[1] reported the formation of nanoscrolls when graphene flakes are dispersed with nanodiamonds (ND) leading to macroscopic superlubricity in dry N\textsubscript{2} environment. However, the formation of nanoscrolls at ambient condition is inhibited due to the humidity[1]. Although there are few other works demonstrating superlubricity in the absence of humidity [11-13], achieving superlubricity at ambient conditions still remains an engineering challenge. Here we explore the possibility of using other ND based nanoparticle and their effect on superlubricity.

A ND particle with a graphitized outer shell and a diamond core is structurally very similar to the wrapped ND scrolls. Collaborative experimental results show that while wrapped ND leads to superlubric behavior in dry conditions, graphitized ND does not. We use atomistic modeling to explain the high friction in the case of graphitized ND and compare with the frictional characteristics of graphene wrapped ND.

### 8.3 Computational Methods

In this work, the frictional characteristics of nanodiamond (ND) wrapped with graphene nanoribbon is compared against a graphitized ND system using molecular dynamics simulations. Graphene spontaneously wraps around the ND as can be seen from our MD simulations (Figure 5-1(a)-(d)). The outer shell of the ND can be graphitized by heating to 2500 K and cooling it to room temperature [14-16] while fixing the core atoms. The graphitization of the surface atoms of the ND in our simulations can be seen from Figure 8-1(e)-(h). The diameter of ND is 4 nm and the
Figure 8-1: (a)–(d) Spontaneous wrapping of graphene over ND; (e)-(h) graphitization of the outer shell of ND during annealing; (i) cut-section of the graphitized ND showing graphitized shell with diamond core.

size of the nanoribbon that wraps around it is 19 nm × 3 nm. We study the frictional forces between DLC/graphitized ND and DLC/wrapped ND by encapsulating the ND particle between DLC and few layer graphene as shown in Figure 8-2(a) and 8-2(b). The size of the graphene substrate is 7.2 nm × 8.1 nm and the DLC contains 15092 atoms. The bottom most graphene layer is held fixed and an external load of 10 nN is applied on top of DLC. DLC is connected to a slider, moving at
a constant velocity of 10 ms\(^{-1}\), with a spring of stiffness \(k = 16.02\) Nm\(^{-1}\). The equilibrium distance of the spring is the initial distance between the slider and the center of mass of DLC.

The interactions between the carbon atoms in DLC, wrapped ND and graphitized ND are modeled using AIREBO potential [17]. The cross-interaction between DLC, wrapped ND, graphitized ND and graphene are modeled using a 12-6 Lennard Jones potential with \(\epsilon = 2.39\) meV and \(\sigma = 3.41\) Å. The graphene – graphene interactions are modeled using a registry dependent Kolmogorov-Crespi potential [18]. The simulations are performed at 300 K under NVT ensemble using Nosé-Hoover thermostat. All simulations are done using LAMMPS simulation package[19].

### 8.4 Results and Discussion

The spring force required to maintain the constant velocity of the slider increases during the first 1 ns (Figure 8-2(c)) for both the graphitized ND and wrapped ND which indicates the onset of the DLC sliding against the test particle. However, after 2 ns the spring pulling force saturates and a steady state sliding is attained. The steady state pulling force for the graphitized ND is about 6 nN more than the wrapped ND. After the system attains steady state, the work done by the spring is equal to the energy dissipation due to friction. Correspondingly the accumulated work done by the spring to slide the graphitized ND is more than the wrapped ND (Figure 8-2(d)). The weak van der Waals forces between the graphene and ND is not strong enough to prevent the rotation of ND within the wrapped graphene. On the contrary, the presence of chemical bonds between the graphitic shell and ND core in the case of graphitized ND does not allow for rotation of the core relative to the shell contributing to higher friction. In order to confirm this hypothesis we performed the sliding simulations after freezing the internal degrees of freedom in the nanoparticles by making them rigid. While the results for graphitized ND remains unchanged, there is a noticeable increase in the pulling force and energy dissipation in the case of wrapped ND
(Figure 8-2(c) and 8-2(d)). The energy dissipation in graphitized ND is still larger than rigid wrapped ND due to the dangling bonds on the surface of the graphitized ND. When the nanoparticles are rigid the two sliding interface in the system are nanoparticle/graphene and nanoparticle/DLC.

**Figure 8-2 (a), (b):** Schematic of simulation setup used for studying frictional properties. The DLC is pulled using a spring connected to slider moving at a constant velocity of 1 ms⁻¹. The stiffness of the spring is 16.02 Nm⁻¹ (c) spring pulling force with respect to time, (d) accumulated work of pulling

In order to estimate the effects of dangling bonds we repeat the simulation by adding a no-slip constrain between the graphene and the rigid nanoparticle. The frictional resistance is a result of sliding at nanoparticle/DLC interface only. The larger pulling force and energy dissipation in the case of graphitized ND (Figure 8-3) indicates that the presence of dangling bonds contributes
to higher friction at the sliding interface. In addition, the frictional force between the nanoparticle and DLC is directly calculated by averaging the force along the direction of sliding solely due to the interaction with the nanoparticle. The average frictional force in the case of graphitized ND is 0.88 nN, and 0.30 nN in the case of wrapped ND.

Although the difference in the pulling force in our MD simulations are only in the order of few nN, it translates to a significant difference at the experimental scale where there is an ensemble of nanoparticles forming multi-nano-asperity contact which undergoes sliding simultaneously.

![Figure 8-3](image)

**Figure 8-3** Spring pulling force (a) and accumulated work (b) with respect to time when the sliding is only at DLC/nanoparticle interface.

Our results matches qualitatively with the experimentally measured co-efficient of friction (COF) (Figure 8-4(c) and 8-4(d)). The experiments were performed by Anirudha V. Sumant and Diana Berman at the Center for Nanoscale Materials, Argonne National Lab, Lemont, IL. While the COF of graphitized nanodiamond is below 0.05, it is still higher than graphene wrapped nanodiamond which is superlubric[1] (< 0.01).
Figure 8-4: Experiments performed by collaborators (Anirudha V. Sumant and Diana Berman) at Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL. TEM images of the wear track showing the presence of (a) graphene wrapped ND and (b) graphitized ND, COF measured by for (c) graphene wrapped ND and (d) graphitized ND

8.5 Conclusions

We adopted atomistic modeling using molecular dynamics to investigate the influence of graphene wrapped ND and graphitized ND. Our results indicates that the rotational degree of freedom between the ND core and wrapped graphene flake leads to lower friction while the chemical bonds prevent any relative rotation between the ND core ad the graphitic shell in graphitized ND. Additionally, by adding a no-slip constrain at the graphene/nanoparticle interface we can estimate the friction only due to sliding of DLC over the nanoparticle. The dangling bonds on the surface of the graphitized ND contributes to higher friction. Our results also suggests that a
reduction of few nN in frictional forces at the nanoscale can help us to get close to achieving macroscopic superlubricity.

8.6 References


CHAPTER 9. CONCLUSIONS

The thermal transport characteristics in graphene with vacancy defects, isotope impurities, graphene in 2D heterostructures and graphene in composite materials were studied computationally using atomistic molecular dynamics. The effect of various defects and the influence of the surrounding interactions with graphene on its thermal transport properties were investigated. Additionally, the chemical interactions that enable graphene’s potential as a solid lubricants, additive in phase change material and a candidate for tunable surface wettability were explored using computational techniques.

The overall conclusions of the previous chapters in this dissertation can be summarized as follows:

1. The presence of mass disorder in the form of isotope impurities and vacancy defects results in a reduction in the overall thermal conductivity of graphene due to the perturbation of the phonon modes. As the defect density increases the reduction in thermal conductivity saturates.

2. Graphene encapsulated MoS$_2$ van der Waals heterostructure (graphene/MoS$_2$/graphene) has negligible anisotropy along the zigzag and armchair directions, while the thermal sheet conductance of the heterostructure is an order of magnitude larger than that for monolayer MoS$_2$. Thus, encapsulating MoS$_2$ within graphene provides a way to efficiently manage thermal energy in MoS$_2$ based photoelectronic devices. Additionally, $k$ of the graphene and MoS$_2$ in heterostructure is reduced compared to that of their monolayer counterparts due to the suppression of the out-of-plane ZA modes, an overall blue shift in phonon power spectra, and reduced phonon lifetime and mean free path.
3. The addition of graphite particles (3.5% vol.) in \( n \)-eicosane phase change material results in an enhancement of \( k \) (450 \%) due to the high thermal conductivity of GP and reduced interfacial thermal resistance (\( R_{\text{eff}} \)). The enhancement in \( \mu \) (1200 \%) is attributed to the ordering of liquid \( n \)-eicosane at the interface and the agglomeration of GP at higher concentrations.

4. The frictional characteristics of between graphene wrapped nanodiamond (ND) graphitized ND were compared. The rotational degree of freedom between the ND core and wrapped graphene flake leads to lower friction while the chemical bonds prevent any relative rotation between the ND core and the graphitic shell in graphitized ND.

5. The effect of orientation of graphene sheets on the wettability of the surface were studied. The hydrophobicity of graphene surfaces increases as the sheets are oriented towards the surface. The increase in hydrophobicity is due to the reduction in the net attractive energies between the surface and water droplet.

6. The Kapitza resistance between graphene surface and water increases with hydrophobicity. Consequentially, the evaporation rates are slower on the hydrophobic graphene surfaces.

The contents of this dissertation includes valuable knowledge necessary to design energy efficient graphene based devices which can operate at different conditions. While carbon nanotubes and hydrophobic graphene nano-channels have been found to enhance the fluid flow[1-3], the contents in this dissertation provides useful insights to designing nanoscale heat exchangers and nano-fluidic cooling systems based on graphitic flow enhanced nano-channels. In the future, scaling up the modeling approaches presented here to device scale, may help in understanding the performance of such cooling systems.
9.1 References

