### MOLECULAR DYNAMICS STUDY OF WATER-HBN NANOFLUID

by

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"If we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that all things are made of atoms, and that everything that living things do can be understood in terms of the jigglings and wigglings of atoms."

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Richard Feynman, 1963.

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### ABSTRACT

# MOLECULAR DYNAMICS STUDY OF WATER-HBN NANOFLUID

This study considers the molecular simulations of nanofluids and the goal is to investigate the thermomechanical mechanisms in nanoscale thermal transport. The enhanced thermal conductivity and limited shear viscosity increase is the fundamental phenomena that makes nanofluids as a hot research topic of the recent thermal-fluid and nanoscience literature, and a potential novel complex liquids for variety of applications. The nanofluid problem has been studied from the nanomechanical point of view and molecular dynamics simulations are used to investigate the physical aspects. A water-copper system has been modelled as a benchmark study to understand the nanocolloid concept and the capacity of existing methodologies. Green-Kubo formalism, pure water system, thermal enhancement and viscosity increase of water-copper nanofluids and Brownian motion effect has been studied and compared with the experimental results. Potential function improvement has been aimed for a water-hexagonal boron nitride system to obtain a robust mathematical foundation for the molecular dynamics simulations. Therefore, interlayer interactions of hexagonal boron nitride and interface interactions at the water-hexagonal boron nitride interface have been formulated using recent quantum simulation results and experimental data. Thermomechanical properties of hexagonal boron nitride have been accurately estimated using simulations with derived potentials, and water-hexagonal boron nitride interfacial dynamics have been discussed for the interfacial thermal transport. A new temperature calculation algorithm for non-equilibrium simulations has been introduced and tested for rigid and flexible water model. A new approach has been preliminarily developed to study the agglomeration in nanofluids with orthotropic nanoparticles using simulations and experimental images.

### ÖZET

# SU-HBN NANOAKISKANLARIN MOLEKULER DINAMIK SIMULASYONU

Bu çalışmada nanoakışkanların moleküler dinamik simülasyonu yapılmış ve nanoboyutlardaki termomekanik mekanizmaların ortaya çıkarılması amaçlanmıştır. Yüksek ısıl iletkenlik ve sınırlı vizkozite artışı, bu yeni nesil nanomalzemelerin ısı-akışkan ve nanobilim literatürünün son yıllardaki popüler araştırma konularından biri olmasını saglamış ve birçok uygulamada kullanılması için potansiyel yaratmıştır. Nanoakışkan problemi nanomekanik bir perspektiften ele alınmış ve ilgili fiziksel olguları belirlemek ve ölçmek için moleküler dinamik simülasyonları kullanılmıştır. Nanoakışkan konseptini ve literatürdeki metotların yeterliliklerini anlayabilmek için ilk olarak bir subakır nanoakışkan sistemi modellenmiştir. Bu sistem ve saf su sisteminde Green-Kubo formalizmi, nanoakışkandaki ısıl iletkenlik ve vizkozite artışları ve nanoparçacıkların Brownian hareketinin ısıl iletkenlige etkisi nümerik olarak çalışılmış ve deneysel verilerle karşılaştırılmıştır. Ayrıca su-hegzagonal bor nitrat nanoakışkan sistemi de çalışılmış, fakat modellere daha isabetli bir matematiksel altyapı oluşturmak için potansiyel fonksiyon geliştirilmesi hedeflenmiştir. Bu amaçla hegzagonal bor nitrat katmanları arası etkileşimler ve su ile hegzagonal bor nitrat yüzey etkileşimleri güncel kuantum simülasyon sonuçları ve deney verilerinden yararlanılarak matematiksel olarak tanımlanmıştır. Hegzagonal bor nitratın termomekanik özellikleri bu potansiyeller kullanılarak isabetli bir şekilde hesaplanmıştır. Su-hegzagonal bor nitrat arayüzey dinamikeri yüzeydeki ısı iletimi açısından tartışılmıştır. Ayrıca dengede olmayan moleküler dinamik analizleri için yeni bir sıcaklık hesaplama prosedürü literatüre tanıtılmış ve rijit ve esnek su modelleri ile test edilmiştir. Ortotropik nanoparçacıklardaki topaklanma mekanizmalarını simülasyonlar ile incelemek için yeni bir metot onerilmiş ve yöntem nano-akışkanların mikroskop görüntülerine dayandırılmıştır.

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## LIST OF SYMBOLS

A	Area
$C_i$	Number of distance constraints of atom i
C <sub>33</sub>	Elastic constant in z-direction
$c_{44}$	Elastic constant in xy-direction
d	Interlayer distance
e	Total energy of an atom
E	Interlayer interaction energy
$E_a$	Angle energy
$E_b$	Binding energy
$E_{bo}$	Bond energy
$f_i$	force acting on an atom i
$ec{g}$	Reciprocal lattice vectors
Ι	Internal energy
$I_i$	Moment of inertia fraction for atom i
J	Heat flux vector
k	Thermal conductivity
$k_{nf}$	Nanofluid thermal conductivity
$k_{bf}$	Base fluid thermal conductivity
$\vec{k_{MD}}$	Thermal conductivity results as a vector
$\vec{k_p}$	Thermal conductivity results in principal directions
$K_a$	Harmonic angle constant
$K_{bo}$	Harmonic bond constant
$k_B$	Boltzmann's constant
$K_c$	Coulombic constant
$KE_i$	Kinetic energy of atom i
$m_i$	mass of atom i
N	Number of atoms
$M_i$	Number of degree of freedom of atom i

Р	Stress tensor
Р	Reference frame attached to the top layer of the nanoparticle
$ec{p_i}$	Vector components of frame ${\bf P}$
$a_i, b_i, c_i$	Scalar components of vector $\vec{p}$
Q	Fixed reference frame of the simulation box
q	Partial charge
$q^{\prime\prime}$	Heat flux
$r_{ij}$	Interatomic position between atoms i and j
R	Thermal resistivity
R	Transformation matrix between frame ${\bf Q}$ and frame ${\bf P}$
S	Entropy
T	Temperature
u	Potential energy of an atom
$\vec{u}$	lateral shift vector of the layer
V	Volume
$V_N$	Brownian velocity
$\alpha$	Attractive energy coefficient
eta	Repulsive energy coefficient
eta $\epsilon$	Repulsive energy coefficient Lennard-Jones energy parameter
eta $\epsilon$ $\gamma_s$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum
eta $\epsilon$ $\gamma_s$ $\gamma_l$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum surface energy of the liquid with vacuum
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum surface energy of the liquid with vacuum interfacial energy of the solid and liquid
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$ $ heta_C$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum surface energy of the liquid with vacuum interfacial energy of the solid and liquid Contact angle
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$ $ heta_C$ $\mu$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum surface energy of the liquid with vacuum interfacial energy of the solid and liquid Contact angle Shear viscosity
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$ $ heta_C$ $\mu$ $\Phi$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum surface energy of the liquid with vacuum interfacial energy of the solid and liquid Contact angle Shear viscosity Potential energy
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$ $ heta_C$ $\mu$ $\Phi$ $\phi$	Repulsive energy coefficient Lennard-Jones energy parameter surface energy of solid with vacuum surface energy of the liquid with vacuum interfacial energy of the solid and liquid Contact angle Shear viscosity Potential energy Volume fraction for nanofluids
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$ $ heta_C$ $\mu$ $\Phi$ $\phi$ $\sigma$	Repulsive energy coefficientLennard-Jones energy parametersurface energy of solid with vacuumsurface energy of the liquid with vacuuminterfacial energy of the solid and liquidContact angleShear viscosityPotential energyVolume fraction for nanofluidsLennard-Jones length parameter
eta $\epsilon$ $\gamma_s$ $\gamma_l$ $\gamma_{sl}$ $\theta_C$ $\mu$ $\Phi$ $\phi$ $\sigma$ $\sigma_{zz}$	Repulsive energy coefficientLennard-Jones energy parametersurface energy of solid with vacuumsurface energy of the liquid with vacuuminterfacial energy of the solid and liquidContact angleShear viscosityPotential energyVolume fraction for nanofluidsLennard-Jones length parameterStress along z-direction

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# LIST OF ACRONYMS/ABBREVIATIONS

2D	Two dimensional
ACF	Auto Correlation Function
AR	Aspect Ratio
CFD	Computational Fluid Dynamics
CNT	Carbon Nanotube
COMPASS	Condensed-Phase Optimised Molecular Potentials for Atom-
DEM	istic Simulation Studies Discrete Element Method
DFT	Density Functional Theory
DMC	Diffusion Monte Carlo
DOF	Degree of Freedom
DPD	Dissipative Particle Dynamics
EG	Ethylene glycol
EMD	Equilibrium Molecular Dynamics
GK	Green-Kubo
HACF	Heat Auto Correlation Function
hBN	Hexagonal Boron Nitride
ITC	Interfacial Thermal Conductivity
ITR	Interfacial Thermal Resistivity
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LB	Lorentz-Berthelot
LJ	Lennard-Jones
MD	Molecular Dynamics
MLhBN	Multi-layer Hexagonal Boron Nitride
NEMD	Non-equilibrium Molecular Dynamics
NVE	Micro-canonical ensemble
NVT	Macro-canonical ensemble
OTC	Overall Thermal Conductivity
PBC	Periodic Boundary Conditions

RPA	Random Phase Approximation
SACF	Stress Auto Correlation Function
SEM	Scanning Electron Microscopy
SPC/E	Extended Simple Point Charge
SV	Shear Viscosity
TC	Thermal Conductivity
TEM	Transmission Electron Microscopy
TIP3P	Transferable Intermolecular Potential with 3 Points
TIP4P	Transferable Intermolecular Potential with 4 Points
TIP5P	Transferable Intermolecular Potential with 5 Points
VMD	Visual Molecular Dynamics

### 1. INTRODUCTION

### 1.1. Motivation

Improved heat transfer is sought in many engineering applications, either to improve system efficiency or for the safe or reliable operation. Many researchers have been working on heat transfer enhancement in wide range of applications, from energy systems to vehicles or from space vehicles to opto/electronic thermal management etc. One means of enhancing heat transfer is through the use of engineered materials such as heat transfer fluids specifically designed to improve the thermal efficiency. Colloidal suspensions can be produced by dispersing small particles with high conductivity within a base fluid and then used as heat transfer fluid. This idea was first introduced experimentally by Ahuja [1]. However, stability and clogging problems have been observed when particles with micrometer size are used. Choi [2] suggested using nanometer sized particles for improved stability, and referred these as *nanofluid* which triggered the development of a new research topic of thermal nanoscience. He suggested that nanoparticles are small enough to behave like liquid molecules and do not clog the flow channel. Since then, nanofluids have often been considered as the next generation heat transfer fluids due to their enhanced thermal properties and there has been an increasing number of studies about nanofluids.

Nanoscience is a new emerging field, which is triggered with the synthesis of new nanostructures in recent years. Therefore, there is an increasing amount of research interest for these new concepts, and nanofluids have also been gaining attention of researchers from different backgrounds in that context. Although much progress have been made to understand the fluids, colloids and associated flow properties, there are still open questions when nanoparticles are introduced to a typical fluid, such as how transport properties change and why.

Nanofluids have been a popular research topic of the thermal-fluid science in the last decade, and the current literature suggests that there are still more to discover to accelerate the translation of this technology from laboratories to the applications. There has been a recent significant attempt to improve this process, and one of the main objectives is to clarify the physical mechanisms involved. These mechanisms were introduced in the literature 16 years ago [3] and have been accepted and studied by the majority of the researchers, but the full picture of the involving physics has not been clarified yet. The hypothesis for these mechanisms are enhanced ballistic heat transfer in the nanoparticles, nanolayering around the nanoparticle, Brownian motion of the nanoparticle, and the aggregation of nanoparticles. They are constructed based on the governing physics associated with the nanoparticles, interaction between nanoparticles and the base fluid, and the interaction between nanoparticles, which are different than the case of colloids with large particles.

Nanofluids may lead to significant improvements in different applications such as enhancing critical heat flux in nuclear reactors [4], controlling spacecraft thermal systems [5], or oil and gas production [6]. It was shown that 100 MW solar thermal power tower in Tucson, AZ can save about \$3.5 million per year [7], or over \$2 million tons of  $CO_2$  emission can be avoided in solar hot water technologies in Phoenix, AZ [8] by using nanofluids to increase the efficiency. As a result, there have been increasing number of studies on nanofluids from variety of different aspects such as feasibility, economics, application, engineering and scientific points of views. One of the most important components of these attempts is the material selection for nanofluids.

Hexagonal boron nitride (hBN) nanoparticles are recently synthesized and there is a growing scientific focus to characterize hBN since it has several unique properties. Hexagonal boron nitride has a very high thermal conductivity and is used as an industrial lubricator [9]; therefore, it has a potential to enhance the heat transfer while limiting the shear viscosity increase for nanofluids, which is supported by experiments. Recently it was shown that the enhancement in thermal conductivity exceeds the increase of shear viscosity [10]. However, there are other limitations associated with the experimentation when the nanoparticles are considered and this is the basic motivation for computational and theoretical studies. While Ilhan *et al.* [10] proposed that the enhancement is due to percolation qualitatively, no quantification data was presented to support this hypothesis,

As in the case of all science and engineering problems, the nanofluid studies can be classified as experimental, theoretical, and numerical. Experimentation has a major role in every science and engineering problem; however, this has several limitations when the characteristic lengths are on the order of nanometers since it is very difficult to observe and quantify the dynamics in molecular level with devices. Therefore, theoretical and numerical models are also common approaches. It is difficult to derive a theoretical model, where all the physical effects associated with nanoparticles are considered, due to limited knowledge of the mathematical definition of interatomic interactions. However, numerical modelling is becoming a common practice for the design and improvement of the nanofluids, which can also be categorized as macro and micro models. Macroscale numerical studies assume continuum fields similar to classical Computational Fluid Dynamics schemes and are important for the application of nanofluids. They require the use of proper properties to solve heat and momentum equations, and the governing physical mechanism must be introduced through predefined constitutive relations. As a consequence, simulations that are valid in nanoscale characteristic lengths are required to observe the molecular behavior in and around the suspended nanoparticles in nanofluids, and Molecular Dynamics simulations are one of the well established methods for the proposed purpose, as shown by numerous researchers for the few decades.

Computational nanoscience can be considered as an emerging branch of computational physics, where nanoscale length scales in nanosecond timescales are considered to analyse the behavior in the molecular level. One such approach is the molecular dynamics (MD), where molecular interactions are defined in terms of Newtonian mechanics and potential function. Therefore, MD is one of the most popular simulation techniques in computational nanoscience since the method fundamentally consider the interatomic forces and the resulting dynamics of the system, and it has been widely used in numerous computational studies [11]. Molecular Dynamics approach has several advantages including the detailed description of interatomic dynamics; the energy flow in different mediums or interfaces, interaction between any type of substance or the trajectory of any particular group of atoms can be estimated. However, there are major limitations as well, such as the lack of potential functions for different materials. These mathematical formulations are describing a constitutive equation for a system of atoms, and they are crucial for the simulations, but potential functions are well defined only for small number of material types and their validity in more complex structures are highly questionable. Another disadvantage of the MD simulations are their computational expense that limits simulations with nanometer length and microsecond times at most (using supercomputers). Considering these specifications, MD is a feasible and promising tool for studying colloidal systems having nanoparticles.

Several simulation results of nanofluids are presented in this dissertation, and they mainly focus on nanoscale mechanisms and modelling methods from a scientific point of view. It is believed that these theoretical and numerical approaches are necessary for further nanofluid studies, and this cumulative knowledge will not only allow us to develop this technology and to achieve commercial products in the future, but also to understand the physics in smaller scales extending our vision about the nature. As in the case of most of the nanoscience projects, understanding the full picture of the nanofluids also requires different types of approaches in terms of computational modelling and experimentation. Multiscale studies are feasible and may be even necessary to understand the physical aspects, where considerations start from the electron cloud and goes beyond the macro scale applications. This can be observed in the nanofluid literature; quantum, Molecular Dynamics or Monte Carlo simulations, mesoscale and Computational Fluid Dynamics simulations along with the experiments are parts of a chain of information flow from the smallest to the largest scales. These methods may have advantageous and disadvantageous depending on the problem as in the case of all numerical modelling techniques. There is a significant effort in the current literature to overcome the modelling limitations, aiming to make use of these tools to understand the complete physical behavior of different systems.

#### 1.2. Objective

The main objective of this dissertation is to study water based nanofluids with hexagonal boron nitride (hBN) nanoparticles using MD simulations. hBN is selected considering its unique thermal, mechanical and tribological properties, and promising behavior observed in experiments as will be discussed in detail in the upcoming chapters. Water and water-Cu nanofluid were also studied for validation and improvement purposes. MD simulations have been used and tested for several different cases to make investigations beyond the state of the art. Both Equilibrium and non-Equilibrium MD methods have been extensively studied to clarify the physical aspects of the nanofluid problem and improve the capabilities of the existing well established methods.

A water-Cu nanocolloidal system has been studied to estimate the transport properties first, which is motivated by the observation that the method has not been validated extensively for more common nanofluids such as water based metallic nanoparticles. A water-hBN system has also been considered; however, the simulation of hBN nanoparticles requires improved MD potentials since the available ones in the literature are observed to have lower accuracy with respect to experiments. Therefore, it is aimed to develop a new interlayer potential for hBN layers. Besides, interfaces are important in thermal transport between different phases, which must be considered for the water-hBN system. The interfacial thermal resistance of the water-hBN interface has been studied to investigate the effect of solid-liquid interactions on the thermal behavior of nanofluids. Water is the majority part of the nanofluid systems, and there is not many robust water models in the literature for MD simulations. The existing studies differ for both methodological details and resulted values. A new temperature formulation has been studied for non-equilibrium MD (NEMD) to obtain an accurate model for the thermal conductivity and avoid any suppressing effect of potential function errors (high thermal conductivity for water) for the heat transfer enhancement of nanofluids. With these studies done, significant amount of knowledge has been gained for the three different components of a nanofluid; that are the nanoparticle, interface and base fluid. Aggregation is believed to be a major effect in nanoscale heat transfer mechanism in nanofluids, and this phenomena has been considered using the outcomes

of the previous sections to estimate the effect of agglomeration of nanoparticles on the heat transfer using the experimental images and simulation results.

#### 1.3. Organization and Contributions

This thesis comprises of 7 Chapters, and the studies addressing the objectives listed in the previous section are presented in individual chapters that is followed by conclusions and recommendations for future work. Chapter 2 of the thesis presents the estimation of the thermal conductivity enhancement and shear viscosity increase of water-Cu nanofluid using MD simulations, discusses the related physical mechanisms, and taken from Ref. [12]. Then a water-hBN nanofluid has been considered in Chapter 3, a new interlayer potential has been parametrized for the interlayer interactions of hBN, and this chapter includes findings published in Ref. [13]. A water-hBN system has been considered in Chapter 4 based on Ref. [14], where water-hBN interface potential and the interfacial thermal resistance have been focussed particularly. Investigation of different potentials using different MD techniques for the thermal conductivity is presented in Chapter 5 based on Ref. [15]. Finally, the effect of orthotropic hBN nanoparticles and Brownian rotation on the effective properties of hBN nanofluids are presented in Chapter 6 using the results presented in the previous chapters. The conclusion of the dissertation and future work recommendations are given in Chapter 7.

# 2. PREDICTION OF THERMAL CONDUCTIVITY AND SHEAR VISCOSITY OF WATER-CU NANOFLUIDS USING EQUILIBRIUM MOLECULAR DYNAMICS

#### 2.1. Introduction

Many nanofluid studies are experimental investigations of the thermal and rheological behavior of nanofluids [16, 17]. Others perform on macroscopic modelling of the heat and fluid flow as is required to investigate various nanofluid applications. Effective properties of thermal conductivity and viscosity, are used in these models, and the accuracy of these properties is essential to correctly predict the thermal and flow behavior of nanofluids. The active transport mechanisms must be known in order to develop theoretical models that are capable of accurately predicting the effective nanofluid properties though.

Four physical mechanisms have been suggested to explain the increase in the effective transport properties of nanofluids by Keblinski *et al.* [3]; heat transfer due to ballistic phonon transfer through the nanoparticle, dense liquid layering at the liquid-solid interface, enhanced energy transfer due to Brownian motion of nanoparticles, and clustering of highly conductive nanoparticles. These have been assumed to be the fundamental basis for the physics of nanofluids and have been subject of investigation for more than a decade.

• Energy transfer becomes ballistic rather than diffusive when the length scales are smaller than the mean free path of phonons. Keblinski *et al.* [3] estimated Al<sub>2</sub>0<sub>3</sub> nanoparticles' phonon mean free path as 35 nm, and that heat is transported ballistically for particles with smaller diameters. They also noted that ballistic phonon transfer is possible only if the nanoparticles are very close to each other, i.e. ballistic heat transfer becomes significant in nanofluids with aggregates. Nie *et al.* [18] studied ballistic heat transfer for the base fluid using density functional

theory (DFT), and concluded that the mean free path of the fluid molecules does not change significantly due to presence of nanoparticles. Since fluid is the majority of the volume in a typical nanofluid, they contended that ballistic phonon transfer instead has an insignificant effect on the heat transfer enhancement of nanofluids.

- When a liquid is in contact with a solid, an interface layer forms due to solidliquid interactions based on tribological properties and surface topography. The "nanolayer" that forms around the nanoparticles can affect the thermal enhancement of nanofluids [17]. Xue *et al.* [19] studied the effect of liquid layering at the liquid-solid interface of the nanoparticle using molecular dynamics (MD), and concluded that the nanolayer around the particle has a negligible effect on thermal transport enhancement for mono-atomic liquids. However, they also reported that complex liquids might behave differently. Similarly, Doroodchi *et al.* [20] found that nanolayering could not explain the thermal conductivity enhancement observed in nanofluids. Conflicting evidence is given by Zhou and Gaou [21], who showed a significant nanolayer effect theoretically, using a differential effective dipole approximation and multiple image methods.
- Brownian motion is the random motion of suspended small particles in a liquid, and is believed to enhance the energy transfer by creating a nano-convection effect around the particle. Bhattarcharya *et al.* [22] performed a Brownian dynamics simulation and found a significant Brownian motion effect and thermal enhancement results that agreed with the experimental data. Prasher *et al.* [23] also studied the convection induced by Brownian motion and found a significant effect on the thermal conductivity enhancement. However, Evans *et al.* [24] used a kinetic theory based analysis and found a smaller effect. Gupta and Kumar [25] also performed a Brownian dynamics simulation and found that only 6% of the thermal conductivity enhancement was based on the Brownian motion. Keblinski *et al.* [26] studied experimental data, and concluded that the Brownian motion and nanolayer formation are not the major causes of thermal conductivity enhancement, and suggested that effective medium theories be extended to include the effect of clustering.

• In a nanofluid, the suspended particles can collide with each other and agglomerate from attractive forces [27]. This is important because agglomeration is a design parameter for nanofluids, can cause clogging and increase the pumping power, and it is also considered as the most important of the four mechanisms of in the current literature. Prasher *et al.* [28] showed that the nanoparticles form clusters, and since heat can be conducted more efficiently through solids than liquids, clustering enhances phonon transport through agglomerated particles. Evans et al. [29] used Monte Carlo simulations to determine the effective thermal conductivity of the nanofluid and found that thermal conductivity increases with increasing cluster size. However, the viscosity also increases with cluster size. Keblinski et al. [26] show how effective medium theories can be modified for nanofluids using agglomeration mechanisms, and suggested further research considering the thermal enhancement and viscosity increase simultaneously. This was studied by Prasher et al. [30] where the viscosity increase and thermal enhancement were mathematically coupled. He showed that the relative increase in the viscosity had to be less than four times the relative enhancement of the thermal conductivity to be beneficial. Kang et al. [31] studied an argon copper system with multiple nanoparticles using MD simulations, and achieved a 71%thermal enhancement and 26% viscosity increase with a specific cluster geometry.

Those studies show that a nanofluid with agglomerated particles can improve efficiency; however, agglomeration can also degrade the stability. In addition to clogging and pumping power problems, the heat transfer properties could change over time with the presence of precipitates. Therefore, long term stability is sought for engineering applications and is achieved using techniques including ultrasonic mixing, pH control and surfactant additives [32].

There is no consensus in the literature on a single mechanism that completely explains the enhancement in thermal conductivity, and as a result there is no general model capable of accurately predicting nanofluid properties. Effective medium theories such as Maxwell theory [33] or Hamilton-Crosser theory [34] assume that the nanofluid is a well dispersed mixture with small particles, do not consider any of the mechanisms above and underpredict the enhancement with respect to experimental data [35, 36]. The Einstein relation [37], can be used to predict effective nanofluid viscosity for particle volume fractions less than 2% and Batchelor [38] derived a relation for higher volume fractions. However, both of these shear viscosity models consider only the Brownian effect, and neither the Einstein nor the Batchelor relations accurately predict the effective viscosity.

Another means of predicting the nanofluid conductivity and viscosity is to use correlations based on experimental data. Xiang and Mujumdar [16] gave a detailed review of experimental studies, including those studying different measurement methods, nanofluids with different materials and the effects of particle volume fraction, mean nanoparticle diameter, temperature, etc. These studies showed that enhancements up to a reported 125% is possible depending on the choice of nanoparticle and base fluid material. The most commonly used nanoparticles in these studies are Cu.  $Al_2O_3$  and CuO due to their availability. Eastman *et al.* [39] presented thermal conductivities of water based nanofluids, and reported up to a 60% increase in thermal conductivity for a 5% particle volume concentration. A similar study conducted by Li and Peterson [40] reported the effect of temperature and particle volume fraction on the thermal conductivity of water based nanofluids with  $Al_2O_3$  and CuO. They concluded that the nanoparticle material, nanoparticle size, volume fraction and base fluid temperature have all significant effects on the thermal conductivity enhancement of nanofluids, and derived correlations for the thermal conductivity. Xuan and Li [41] studied metallic and ceramic nanoparticles in both water and oil, and compared their results with those of Eastman et al. [39]. They reported a 78% increase in thermal conductivity for Cu-water, and a 45% increase for Cu-oil nanofluids with 8% particle concentration.

Mahbubul *et al.* [42] reviewed viscosity measurement studies and concluded that particle size, shape, temperature and volume concentration have significant effects on the viscosity of nanofluids. They observed that the viscosity increases with particle volume fraction, and that nanofluids show Newtonian behavior in low concentrations. They provided temperature dependent empirical correlations indicating that viscosity is inversely proportional to the temperature. Balasubramanian *et al.* [43] performed experiments on silica nanoparticles dispersed in water and also found that the shear viscosity of the nanofluid increases with particle volume fraction. They also developed an empirical correlation in terms of particle size, shape and volume fraction.

Experimental studies provide reliable information about the increase in thermal conductivity and viscosity. However, these procedures are not capable of deriving generalized relations, and focus on specific cases due to the high cost and limitations at the nanoscale. The physical mechanisms relevant to the nanofluids are mostly governed by atomic interactions that are not directly observable in experiments. Therefore, these procedures are mostly limited to property measurements rather than investigation of the physical aspects of the problem, quantification of the effect of atomic interactions, and iterative design of the nanoparticles can all be done more easily with numerical techniques.

Molecular dynamics (MD) is a well established method for estimating liquid properties that has recently been extended to nanofluids. MD is believed to be one of the most powerful tools when the challenges associated with understanding the governing physical mechanisms for the nanofluids are considered. The two main approaches to estimate fluid properties are equilibrium molecular dynamics (EMD) using the Green-Kubo method, and non-equilibrium molecular dynamics (NEMD) using the Muller-Plathe algorithm. Sarkar and Selvam [35] used equilibrium MD simulations with Lennard-Jones (LJ) potential to predict the thermal conductivity of liquid Ar-Cu nanofluids, and reported up to a 52% increase with respect to that of liquid argon. Kang et al. [31] extended that study using the Embedded Atom Method (EAM) to describe the Cu inter-atomic forces. They showed that the thermal conductivity was roughly a linear function of the nanoparticle volume fraction, and found conductivities higher than those predicted by conventional effective medium theories. Sankar et al. [36] considered a water-Pt nanofluid using the Extended Simple Point Charge (SPC/E) water model, Spohr-Heinzinger, Morse and finitely Extendable Nonlinear Elastic (FENE) potentials for the nanoparticles. They also reported an approximately linear relation

between particle concentration and thermal conductivity, and that Maxwell theory significantly underpredicts the enhancement for more than 2% particle loading. Balasubramanian *et al.* [43] simulated a SiO<sub>2</sub>-water nanofluid using MD with the TIP3P water model and a Tersoff potential for silica, and found that the nanofluid shear viscosity increased with particle volume fraction. They attributed the increase to nanolayering around the particle. Wang *et al.* [44] studied Poiseuille flow using a non-equilibrium molecular dynamics simulation and observed local viscosity and wall-fluid interaction effects on the flow characteristics. They found large viscosity values for nanofluids with a 5% particle volume fraction.

Modelling Ar based nanofluids are more straightforward when compared to the commonly used base fluids such as oil and water, and used in MD simulations to investigate the different mechanisms; however, use of real fluids is necessary for comparison with experiments. Sankar et al. [36] considered a water-Pt nanofluid using the Extended Simple Point Charge (SPC/E) water model and Spohr-Heinzinger, Morse and finitely Extendable Nonlinear Elastic (FENE) potentials for the nanoparticle interactions. They reported an approximately linear relation between particle concentration and thermal conductivity, and concluded that Maxwell theory significantly underpredicted the thermal conductivity for more than 2% particle loadings. Lee et al. [45] simulated Carbon Nanotube (CNT) nanoparticles in water, compared their thermal conductivity results with experiments and discussed the difference of nanoparticle dimensions in MD simulations and experiments. Another MD simulation of water based nanofluids can be found in the work of Milanese et al. [46] where Cu and CuO nanoparticles are used. They studied nanolayering around the nanoparticle and the effect of oxide layer which can be also observed in some experiments. Shear viscosity has been studied for water- $Al_2O_3$  [47] and water- $SiO_2$  [43] nanofluids, and it has been shown that the shear viscosity increase with particle volume fraction is due to the solid-liquid interface interactions and resulting nanolayering around the particle. There are variety of different MD results of nanofluids in these studies mentioned; however, thermal conductivity and shear viscosity increases in a same nanofluid model with complete validation and feasibility analysis is missing in the literature to our knowledge.
Considering these MD studies, a basic requirement of a nanofluid model is an accurate and robust base fluid model. Since water is the most widely used heat transfer fluid, several MD studies have investigated the thermophysical properties of various water models. Berendsen et al. [48] developed an extended version of the simple point charge water model (SPC/E) and stated that the model properties are in good agreement with experiments. Maruyama [49] also supported this conclusion. Sirk et al. [50] conducted a comprehensive study of different water models to estimate thermal conductivity using both EMD and NEMD. They reported similar thermophysical properties for rigid SPC, SPC/E and TIP3P-Ew models, whereas flexible models show difference with respect to the rigid models. English and Tse [51] also investigated different flexible and rigid water models including TIP4P, TIP4P/2005 and TIP5P, and estimated the thermal conductivity of supercooled water using the GK method. Their results are in relative agreement with experiments for all three models. Mao et al. [52] studied the thermal conductivity, shear viscosity and specific heat values of eight different rigid water models using NEMD. Kumar et al. [53] also used NEMD and the TIP5P model to analyse liquid water behavior at low temperatures.

The literature suggests that MD simulations can be used to predict effective thermal conductivity and shear viscosity of nanofluids. However, many MD results have not been sufficiently validated by comparison with the more common experimental data in the literature such as that for water-Cu nanofluids. This chapter considers the thermal conductivity and shear viscosity of a water-Cu nanofluid and investigates the effect of Brownian motion using molecular dynamics simulations. Equilibrium molecular dynamics simulations of pure water are carried out to assess the water model, since the accuracy of the nanofluid model depends on the performance of the base fluid. The thermal conductivity enhancement and shear viscosity increase with suspended Cu nanoparticles are measured and discussed. Finally, Brownian motion is studied using equilibrium molecular dynamics.

### 2.2. Methodology

#### 2.2.1. Molecular Dynamics

Molecular Dynamics is a microscopic modelling technique relevant to the length and time scales shown in Figure 2.1. A system comprising a finite number of molecules is simulated using intermolecular forces based on Newtonian mechanics [11]. The intermolecular forces acting within the system are defined through potential functions and include various effects such as Pauli repulsion, Van der Waals attraction, and Coulumbic forces. Since it is possible to use MD to simulate the physical behavior of systems containing any type of molecules (as long as the potential function is given), it is widely used in different disciplines of science and engineering including material science, chemistry, biochemistry or biophysics.



Figure 2.1: Simulation techniques for different time and length scales. Figure taken from [54].

MD is limited to certain length and time scales to maintain reasonable simulation times. Previous MD studies could simulate systems with approximately 100 atoms for 200 ps [55], but recently computers are able to handle more than  $10^6$  atoms [56] or milliseconds production runs [57]. Same studies show promising results with graphics

processing unit (GPU) acceleration of MD simulations and report speed-up factors up to 70 (depending on the problem) when compared to central processing units (CPU) [58].

#### 2.2.2. Potential Functions

One of the most crucial parts of a MD simulation is the selection of a potential function. The potential function governs all the interactions within the system, and is often selected from the ones available in the literature. This is delicate though, since the validity of some functions is limited to particular situations. Developing a potential function is an alternative, but requires additional data from experiments or electronic structure calculations.

Potentials frequently found in the literature include Lennard-Jones, Sutherland, Tersoff, Buckingham, and Buckingham-Corner [59]. The LJ 6-12 potential is one of the most widely accepted, and is often used as the intermolecular potential for non-polar molecules.

$$\phi(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$
(2.1)

where  $\epsilon_{ij}$  is an energy scale,  $\sigma_{ij}$  is a characteristic length,  $r_{ij}$  is the scalar distance between atoms *i* and *j*. This potential function and its derivatives are used extensively throughout the dissertation.

Modelling water is more cumbersome than mono-atomic fluids due to the internal structure and the existence of Coulombic forces. There are many studies on simulating water since this is common in engineering applications. Guillot [60] reviewed 46 water models, including TIP3P, TIP4P, TIP5P, SPC and others. Berendsen's [48] and Alejandre *et al.*'s [61] results showed that the (SPC/E) model is in good agreement with experimental values for density, energy, radial distribution function and surface tension. Mao and Zhang [52] measured TC and SV for the commonly used potentials by NEMD, and they reported TC and SV results higher than experiments for the TIP3P, TIP4P, SPC, and SPC/E potentials. They did find excellent agreement with TIP5P potential of Rick [62]; but their method is considered further in Chapter 5. The SPC/E potential is used in this chapter with a cutoff distance of 0.9 nm.

Water models usually include the electrostatic contribution to the LJ potential as:

$$\phi(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{K_c q_i q_j}{r_{ij}}$$
(2.2)

where,  $q_i$  is the charge of atom *i*, and  $K_c$  is Coulomb's constant. There is a cut-off distance  $r_c$  for the short range interactions  $(r_{ij}^{-6} \text{ and } r_{ij}^{-12})$  to reduce the computation expense. However, the Coulombic term  $r_{ij}^{-1}$  can be conditionally convergent, and must be handled delicately. This can be resolved by summing the particle interactions in reciprocal space, or by a particle-particle-particle-mesh (PPPM) solver which aggregates atom charge on a three dimensional mesh and uses a fast Fourier transform to interpolate electric fields on the mesh points [63].

The effective energy of the bonds in a water molecule is usually separated into angular and radial components:

$$E_{bo} = K_{bo}(r - r_0)^2 \tag{2.3}$$

$$E_a = K_a (\theta - \theta_0)^2 \tag{2.4}$$

where  $E_b$  is the energy of the radial component,  $E_a$  is the energy of the angular component,  $K_b$  and  $K_a$  is are the constants with units of energy,  $r_0$  is the equilibrium distance for the bond, and  $\theta_0$  is the equilibrium angle. The potential parameters for some of the models are presented in Table 2.1. The SPC/E water model is employed neglecting all LJ interactions of H-H and O-H for intramolecular pairs and the rigid bonds and angles were implemented using the SHAKE algorithm [64].

	TIP3P [65]	TIP3P [66]	SPC [48]	SPC/E [48]
$\epsilon_{OO}$ (kcal/mole)	0.152	0.102	0.155	0.155
$\sigma_{OO}$ (Å)	3.151	3.188	3.166	3.166
$r_0$ (Å)	0.957	0.957	1	1
$ heta_0~(^o)$	104.52	104.52	109.47	109.47
$K_b$ (kcal/mole)	450	450	Rigid	Rigid
$K_a$ (kcal/mole)	55	55	Rigid	Rigid
$q_O(\mathbf{e})$	-0.834	-0.83	-0.82	-0.848
$q_H(e)$	0.471	0.415	0.41	0.424

Table 2.1: Potential parameters of different water models.

Cu atoms have metallic bonding which ideally requires something other than a LJ type function, such as the embedded-atom method (EAM) potential of Mei *et al.* [67]. However, multibody potentials are computationally expensive and there are several studies that approximate the interatomic Cu interactions in nanofluids with a LJ 6-12 potential [36,68]. We also used a LJ 6-12 function for the Cu interactions with  $\epsilon = 9.4353$ , and  $\sigma = 2.3387$  [69], and a cut-off distance of 0.63 nm. There are several combination rules to determine the Lennard-Jones potential coefficients between the atoms. One of the most commonly used is the Lorentz-Berthelot (LB) rule that uses arithmetic and geometric averaging:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{2.5}$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \tag{2.6}$$

This mixing rule has no physical justification, but gives similar results to the alternative sixth power rule [70] for nanofluid properties [12]. Chapter 4 discusses the surface interactions for a water-hBN in more detail.

## 2.2.3. Ensembles

MD simulations require a choice of which thermodynamic variables to control and which to let vary, i.e., a choice of ensembles. The macro-canonical ensemble (NVT) and micro-canonical ensemble (NVE) specify the system's volume, number of molecules, and temperature for NVT or total energy for NVE. The system is brought to an equilibrium state in the NVT ensemble using a Nose-Hoover thermostat, which adds an extra kinetic energy term to keep the Helmholtz free energy constant and stabilize the system at the target temperature. Once the system reaches equilibrium, the NVE ensemble is used for the GK formalism since this method is sensitive to small variations in the overall atomic energy. The equations of motion used by Shinoda et al. [71], which combine the hydrostatic equations of Martyna et al. [72] with the strain energy proposed by Parrinello and Rahman [73] are followed in this study. The time integration schemes uses Verlet and rRESPA integrators derived by Tuckerman et al. [74].

## 2.2.4. Green-Kubo

Thermal conductivity and shear viscosity of a fluid can be estimated with molecular dynamics using two options. In equilibrium molecular dynamics (EMD), the transport properties are expressed in terms of integrals of the corresponding time autocorrelations functions [75] in the equilibrium state. This is known as the Green-Kubo method. Alternatively, in nonequilibrium molecular dynamics (NEMD), a heat flux or stress is imposed on the system and the thermal conductivity or viscosity is directly calculated based on the resulting temperature or velocity gradient [76,77]. It can be difficult to stabilize the temperature in NEMD due to the external disturbance, and finite size effects are more severe in NEMD because of the magnitude of the resulting temperature gradients [78]. The selection of the equilibrium or non-equilibrium method should be done considering the problem conditions. As an example, EMD does require more computational power but it does not suffer from the high unstable thermal fluxes. On the other hand, NEMD can be applied to larger systems as long as the applied heat fluxes are precisely tuned. The Green-Kubo formalism is used in this chapter and all MD simulations and visualizations are done with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [79] software and Visual Molecular Dynamics (VMD) [80] in this dissertation. Water and water-Cu systems are first studied using EMD approach since there are accurate thermal conductivity results with respect to experiments using this technique [50, 51].

The Green-Kubo method relies on the fluctuation-dissipation theorem and linearresponse theory [81] and describes the dynamics of the system using time correlation functions. It has been shown to give consistent results with experiments and NEMD simulations if the system considered has decaying auto-correlation functions [82]. The thermal conductivity is defined by the integral:

$$k = \frac{1}{3k_B V T^2} \int_0^\infty \left\langle \bar{J}(0) \cdot \bar{J}(t) \right\rangle dt \tag{2.7}$$

where  $k_B$  is Boltzmann's constant, T is the temperature in Kelvin, V is the volume of the system,  $\overline{J}$  is the heat current vector, and the integrand is the heat autocorrelation function (HACF) defined as an ensemble average. The HACF relates the thermal conductivity to the heat current in an equilibrated system. Auto-correlation functions (ACF) involve integrals in the continuous case, but since time is discrete in MD simulations, integral is replaced by a sum. The heat current vector is calculated as:

$$\bar{J} = \frac{1}{V} \left[ \sum_{i} e_i \bar{v}_i + \frac{1}{2} \sum_{i < j} \left( \bar{f}_{ij} \cdot (\bar{v}_i + \bar{v}_j) \right) \bar{r}_{ij} \right]$$
(2.8)

where  $\bar{v}_i$  is the velocity of atom *i*, and  $\bar{r}_{ij}$  and  $\bar{f}_{ij}$  are distance and force vectors between atoms *i* and *j*. The total energy  $e_i$  is the sum of the atom's kinetic and potential energy and can be expressed as

$$e_i = \frac{1}{2}m_i\bar{v}_i^2 + \frac{1}{2}\sum_j \Phi(r_{ij})$$
(2.9)

The shear viscosity calculations follow a similar procedure where the heat current vector is found from the stress tensor. The Green-Kubo integral form for the shear viscosity is:

$$\mu = \frac{V}{3k_BT} \int_0^\infty \sum_{p < q} \left\langle P_{pq}(0) P_{pq}(t) \right\rangle dt \tag{2.10}$$

where the integrand is the stress auto-correlation function (SACF).  $P_{pq}$  denotes the non-diagonal terms of the stress tensor which can be along the planes xy, xz and yz and has the form:

$$\bar{\bar{P}} = \frac{1}{V} \left[ \sum_{i} m_i \bar{v}_i \otimes \bar{v}_i + \sum_{i \neq j} \bar{r}_{ij} \otimes \bar{f}_{ij} \right]$$
(2.11)

#### 2.2.5. Models

2.2.5.1. Liquid Water. Cubical simulation cells ranging from 1.855 to 5.49 nm in one dimension, and containing 125 to 6590 water molecules are used to study the effect of number of molecules. No significant size effect is observed for models having more than 1400 water molecules. For the initial configuration, the water molecules are spaced on a uniform grid with edge length 0.32 nm to satisfy the liquid density; the oxygen atoms are placed first and then the hydrogen atoms are placed to satisfy the O-H bond length and bond angle constraints as shown in Figures 2.2 and 2.3. The density is kept constant by applying the NVT and NVE ensembles, and the initial velocities of the water molecules are randomly sampled from a uniform Gaussian distribution to satisfy the specified temperature. Periodic boundary conditions are applied in all directions [83].

<u>2.2.5.2. Water-Cu Nanofluid.</u> A spherical region is created in the center of the simulation box and the water molecules in this region are replaced with Cu atoms spaced 0.363 nm apart, on a face centered cubic (FCC) lattice. One of the objectives of



Figure 2.2: Initial configuration for water molecules, side view.



Figure 2.3: Initial configuration for water molecules, isometric view.

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this chapter is to identify the effect of changing particle volume fraction on the thermal conductivity and viscosity. Nanofluids with different particle volume fractions are modelled by changing the number of water molecules, while the nanoparticle diameter is kept constant at approximately 2 nm. Another objective of the study is to investigate the contribution of Brownian motion to the thermal transport. For this portion of the study, the particle diameter is changed from 1 to 2 nm and the simulation cell size is increased from 2.305 to 4.355 nm to keep the volume concentration constant. A snapshot of a 4.3% volume fraction water-Cu nanofluid with 2615 water molecules and 228 Cu atoms is shown in Figures 2.4 and 2.5. The initial velocities for the Cu atoms are randomly sampled from a Gaussian distribution, the same as for the water molecules.



Figure 2.4: Snapshot of a water-Cu nanofluid with 4.3% particle volume fraction, frontal view of initial geometry.

## 2.3. Results and Discussion

## 2.3.1. Simulation Details and Equilibration

The simulation size, timestep, and interatomic potential can all affect the accuracy of MD simulations. A 1 fs timestep was found to give the optimal balance of accuracy and required computational time, and consistent with the literature [43,51,84].



Figure 2.5: Snapshot of a water-Cu nanofluid with 4.3% particle volume fraction, isometric view during equilibration.

Next, a pure water system was equilibrated in the NVT ensemble at 300 K for 200 ps with a timestep size of 1 fs. The temperature and energy equilibrated after approximately 20 ps as shown in Figure 2.6. After equilibration, the GK calculations require significant computational time as the ACF decays and the desired properties converge. Eqns. (2.7) and (2.10) are integrated for 1 ps intervals using heat flux or stress tensor data. 1 ps integration interval for GK is used following the analysis in next section. The thermal conductivity and shear viscosity are calculated at 3 ns, significantly after both properties converge at about 2 ns as shown in Figure 2.7.

#### 2.3.2. Green-Kubo Accuracy

EMD calculations involve various parameters, such as the time step and integration time which can affect the accuracy. Most EMD studies do not justify the selection of time scales for the transport property calculations; however, the literature discusses the significant effect of the Green Kubo parameters on the thermal conductivity results. Chen *et al.* [85] proposed a statistical approach to improve the accuracy of EMD simulations. They stated that random fluctuations can have a significant effect on the accuracy of Green-Kubo results, and proposed a cut-off time for each ACF integration.



Figure 2.6: Temperature and energy stabilization for water using the SPC/E potential.



Figure 2.7: Thermal conductivity and shear viscosity results for water using the SPC/E potential.

English and Tse [51] calculated thermal conductivities of different water models using a 20 ps integration time, and stated that longer integration periods are required to capture the physical processes involved in thermal conductivity. However, they did not provide any supporting statistical or physical evidence. Recently, Oliveira and Greaney [86] proposed a statistical approach where they modelled the slower decay of ACFs as random walks and calculated uncertainty envelopes to assess the statistical accuracy of EMD results. Their results show that the convergence of the ACF and the corresponding integration schemes should be considered.

The effect of integration time on the ACFs and the resulting statistical behavior is considered in Figures 2.8 to 2.11. The normalized HACF and SACF converge to 0 as shown in Figures 2.8 and 2.9, but a relatively small overshoot in the tail of the SACF is observed. This manifests in Figures 2.10 and 2.11, as the shear viscosity almost converging after integrating the SACF up to 2 ps; longer than that is used in the literature [43]. Unless otherwise indicated, an integration time of 2 ps and a timestep of 1 fs is used throughout this chapter.

## 2.3.3. Validation

The equilibrium MD results for the SPC/E water model are validated by comparing the thermal conductivity and shear viscosity with experimental and reverse NEMD (RNEMD) results in Figures 2.12 and 2.13. The thermal conductivity measurements of EMD agree with the RNEMD of Mao and Zhang [52], and both simulation results follow the same trend as the experimental data [87]. The 40% relative error with respect to experiments can be attributed to limitations of the SPC/E potential. The shear viscosity values agree with the experimental data in Ref. [87] at the higher temperatures investigated. The average relative error is only 20% with respect to experiments, and less than that of the RNEMD predictions of Mao and Zhang [52]. However, relatively large absolute errors for water properties is neglected for now, since the focus of this study is to investigate the thermal conductivity enhancement and shear viscosity increase.



Figure 2.8: Convergence of normalized HACF of SPC/E water model for ACF and simulation time.

## 2.3.4. Nanofluid Properties

An ideally dispersed water-Cu suspension is assumed with the configuration explained in Section 2.2.5.2 using simulation parameters described in Section 2.3.1. Nanofluids with different concentrations are instantiated by changing the number of water molecules and the dimensions of the cell while keeping the particle diameter fixed. The system is equilibrated in the NVT ensemble for 200 ps before being switched to the NVE ensemble for production run, the same for pure water case. The nanofluid thermal conductivity and shear viscosity values are divided by the corresponding ones for pure water to obtain enhancement values for both properties. The same cell dimensions are used for both the nanofluid and pure water to eliminate any size effect. These enhancement values are then compared to the Maxwell [33] equation for thermal conductivity and Batchelor [38] for shear viscosity, and with experimental data from the literature [41].



Figure 2.9: Convergence of normalized SACF of SPC/E water model for ACF and simulation time.

The particle diameter in the experimental work of Xuan and Li [41] that is used for comparisons is reported as 100 nm. However, simulations of nanofluids with 100 nm diameter particles are computationally prohibitive. Instead, the simulations are carried out with 2 nm diameter particles. This not only introduces a higher surface area to volume ratio, but also increases the Brownian effect, both of which may increase the thermal conductivity relative to experiments. On the other hand, the model assumes that the nanofluid is well dispersed, and agglomeration effects are not considered. The relative magnitudes of these counteracting effects are not yet well established.

The thermal conductivity enhancement is measured for three different particle volume concentrations (2, 4.3 and 7%) at 300 K and 1 atm. The change in the nanofluid to basefluid thermal conductivity ratio,  $k_{nf}/k_{bf}$ , as a function of the particle volume fraction,  $\phi$ , is presented in Figure 2.14. The EMD values agree well with the experimental data of Xuan and Li [41] despite the sources of error described above. Since there are slight differences in the particle volume fraction values for the model and the



Figure 2.10: Convergence of thermal conductivity of SPC/E water model for ACF and simulation time.

experiments, the relative error is calculated at the same simulated concentration by using a second order polynomial curve fitted to the experimental values. The EMD errors for volume fractions 2, 4.3 and 7% are 19, 18 and 2%, respectively. The Maxwell equation under predicts the nanofluid thermal conductivity, as expected. Based on these results, we conclude that EMD with the SPC/E water model and a Lennard-Jones potential for Cu is capable of predicting the thermal conductivity enhancements of water-Cu nanofluids.

Nanoparticle sizes in MD simulations are generally much smaller than in experiments due to the computational expense. The only experimental study considering smaller nanoparticles is by Jiang *et al.* [89], who synthesized water-Cu nanofluid with particle diameters ranging from 2.9 to 6.4 nm. They used a water based nanofluid with dispersed 6 nm Cu nanoparticles without surfactant, and reported decreasing thermal conductivity with increasing volume fraction. However, our simulations showed significant enhancement with 2 nm well-dispersed Cu nanoparticles. The main difference



Figure 2.11: Convergence of shear viscosity of SPC/E water model for ACF and simulation time.



Figure 2.12: Simulated thermal conductivity values of Mao and Zhang [52], experimental values of Lemmon *et al.* [88], and EMD results.



Figure 2.13: Simulated shear viscosity values of Mao and Zhang [52], experimental values of Lemmon *et al.* [88], and EMD results.

between their experiment and our simulations is the volume fraction; they only consider volume concentrations up to 0.5% whereas we were not able to simulate such low volume fractions due to their computational demand. Figure 2.15 shows that our thermal conductivity enhancement could also be negligible for 0.5% volume fraction. Combined with statistical uncertainty, this could lead to the decrease observed by Jiang *et al.*.

The accuracy of the shear viscosity is evaluated only with the Batchelor model [38], as there is no experimental data available in the volume fraction range of 2 to 7%. The literature generally considers very dilute suspensions, and simulating nanofluids with such low particle volume concentrations is not feasible due to the required computational time. The effective shear viscosity  $\mu_{nf}/\mu_{bf}$  is presented in Figure 2.14. Note that the simulation includes the Brownian effect that is the basis of Batchelor's derivation [38]. As a result of this, the EMD predictions are in agreement with the analytical expression, with relative errors of 7, 9 and 9% for increasing volume concentration, but it should be noted that Batchelor's relation is known to under predict the shear



Figure 2.14: EMD thermal conductivity enhancements for different volume concentrations compared to theoretical [33] and experimental results [41].



Figure 2.15: EMD shear viscosity increase for water-copper nanofluids as compared to the Batchelor relation [38].

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viscosity increase of nanofluids [44] due to the ignoring of percolation and the existence of particle-particle interactions.

Most MD studies of nanofluids report either thermal conductivity or shear viscosity, but not both. However, considering these two parameters together is important to quantify the feasibility of nanofluid design. This can be done using the formulation of Prasher *et al.* [30] where the balance between thermal enhancement and pumping power increase is considered for nanofluids in terms of the thermal conductivity and shear viscosity. They showed that the expression  $(\mu_{nf}/\mu_{bf}-1)/(k_{nf}/k_{bf}-1)$  should be less than 4 for a nanofluid to be an effective heat transfer fluid. The results of Figures 2.14 and 2.15 for this calculation lead to 0.064, 0.272 and 0.37 for volume fractions 2, 4.3 and 7%, respectively. These results show superior nanofluid performance in terms of transport properties; however, the effect of particle aggregation on these findings should be clarified.

#### 2.3.5. Brownian Motion Effect

Brownian effect is one of the thermal conductivity enhancement mechanisms proposed by Keblinski *et al.* [3] and Prasher *et al.* [23]. Some subsequent studies, such as Babaei *et al.* [90], contend that the effect of Brownian motion on the thermal conductivity enhancement is negligible. In order to investigate the effect of Brownian motion on thermal conductivity of water-Cu nanofluids, the simulated particle behavior is first validated. The Brownian velocity is given as [91]:

$$V_N = \frac{1}{d_N} \sqrt{\frac{18k_B T}{\pi \rho_N d_N}} \tag{2.12}$$

where  $d_N$  is the particle diameter and  $\rho_N$  is the material density (8960 kg/m<sup>3</sup> for Cu). The velocity of the center of mass of the Cu nanoparticle is calculated for a 4.3% volume concentration. Three different nanoparticle diameters of 1, 1.6 and 2 nm are considered at 300 K, and the results are compared with the analytical formula in Figure 2.16. The simulations are observed to be in good agreement with the theory, and the maximum and average errors are 14 and 8%, respectively. We therefore conclude that MD is capable of successfully capturing the Brownian motion of the nanoparticles, and can be used to further investigate the importance of Brownian motion as a thermal enhancement mechanism.



Figure 2.16: Brownian velocity of copper nanoparticles with different particle diameters.

Prasher *et al.* [28] suggested a nano-convection effect that increases the kinetic energy of the fluid molecules around the nanoparticle. This was investigated by Babaei *et al.* [90] using EMD in a methane-Cu nanofluid. Their analysis relied on the decomposition of the heat flux into kinetic energy, potential energy and virial terms which are shown in Equations (2.8) and (2.9). They found that the effect of the kinetic energy term on the thermal conductivity was negligible, and that the virial term was the most significant [90]. This implies that the nano-convection effect due to particle movement is insignificant to the heat transfer enhancement. In order to investigate if their conclusion is also valid for a water-Cu nanofluid, the average directional heat flux is calculated by neglecting the kinetic energy term, and the heat flux results are compared for varying volume fractions. Figure 2.17 shows that the heat flux does not significantly change when the kinetic energy term is neglected, but that it differs by a considerable amount when the virial term is not taken into account. We conclude that the nano-convection does not significantly enhance the heat transfer, confirming the conclusions presented by Babaei *et al.* [90].



Figure 2.17: Heat flux with kinetic energy term and without kinetic energy term for different volume concentrations.

## 2.4. Conclusion

Nanofluids are considered as the next generation of heat transfer fluids due to their enhanced thermal properties. Predictions of their effective transport properties as required for macroscopic modelling are not sufficiently accurate. Molecular dynamics simulations provide an alternative, and have been used in several studies of nanofluid systems. Although there are many equilibrium molecular dynamics studies of nanofluids such as Ar-Cu available in the literature, there are just a few of nanofluids composed of realistic materials such as water. The objective of this chapter is to predict the thermal conductivity and shear viscosity of water-Cu nanofluids using equilibrium molecular dynamics simulations with the Green-Kubo formalism, and to validate the method by comparing the results with experimental data from the literature. A statistical assessment of the Green-Kubo method is presented for the calculation of transport properties.

The nanofluid is modeled as having well dispersed smaller particles (1-2 nm) in the simulations due to computational limitations of the method. The predicted effective thermal conductivity is agreement with the literature and experiments for different particle volume concentrations [41]. Similarly, the shear viscosity results are consistent with the analytical expression of Batchelor [38] with the absence of the agglomeration effect and using smaller particle diameter; these are believed to be the reason for the experimentally observed higher viscosity values.

The Brownian motion of the nanoparticles and the related nano-convection effect induced by Brownian motion are considered to be the potential heat transfer enhancement mechanisms. We find though that the heat current does not change appreciably when the kinetic energy is neglected. Considering the heat current as the measure of nano-convection, we conclude that nano-convection has an insignificant contribution to the heat transfer enhancement of water-Cu nanofluids, consistent with the findings of other researchers in the literature. Based on the results, we also conclude that other nanofluids with more complex atomic structures could be analysed with the proposed method as well. However, the method would need to be further developed to include other effects like percolation to improve the accuracy of the measured effective transport properties.

# 3. A NEW INTERLAYER POTENTIAL FOR HEXAGONAL BORON NITRIDE

#### 3.1. Introduction

The properties of low dimensional materials often differ significantly from those of their bulk counterparts, and offer promising opportunities for novel devices and applications. Current advanced materials research aims to develop new material components or designs that benefit from the improved properties of low dimensional materials. For hexagonal boron nitride (hBN), improved properties include superior stability, high chemical resistance, hardness, mechanical strength and thermal conductivity [92,93]. Moreover, hBN is distinguished as an electrical insulator, and has been used as a high temperature lubricant, a substrate or heat sink for electronic devices, and in ceramic production and coatings [94]. Structurally, hBN is a low dimensional material with a honeycomb lattice of alternating boron and nitrogen atoms in plane (Figure 3.1), and with layers stacked with an AB stacking arrangement out of plane (Figure 3.2). The figures are created using the VMD software [80].

Studies concerning hBN are more limited than those on similar materials such as graphene, and further characterization of hBN is required. Moreover, there are inconsistencies in the available data. For example, experiments show that the measured thermal conductivity depends on the synthesis method, measurement technique, and sample size. In-plane measured thermal conductivities of 11.7 nm and 13.3 nm thick samples were reported to be 150 W/mK and 225 W/mK at 300 K, respectively [95], whereas the measured thermal conductivities of 5-layer and 11-layer samples were reported to be 250 W/mK and 360 W/mK at 300 K, respectively [96].

Molecular dynamics simulations offer the ability to investigate material properties in the absence of experimental complications. However, the accurate representation of the system requires suitable interatomic potentials. These has been extensively



Figure 3.1: The in-plane atomic structure of hBN, a is the lattice parameter.



Figure 3.2: The out-of-plane atomic structure of hBN.

developed for materials such as graphene [97–99], but the number of studies for hBN is limited. While mechanical and thermal properties such as the bending and tensile rigidity, Poisson's ratio, heat capacity, and thermal expansion coefficient have been considered [100, 101], many of these properties have not been characterized accurately or precisely. Notably, the thermal conductivity of hBN in MD simulations is reported to be anywhere from 80 W/mK to 1000 W/mK [102, 103].

The existing MD simulations only examine the in-plane properties of hBN, and most consider just a single hBN sheet even though hBN is usually multi-layered in practice [92, 95, 96]. This is significant because multi-layered hBN (MLhBN) has thermal and mechanical properties that differ by orders of magnitude along the in-plane and out-of-plane directions. Experiments on 50-120  $\mu$ m thick hBN samples found the in-plane elastic constant  $c_{11}$  and out-of-plane elastic constant  $c_{33}$  to be 811 GPa and 27 GPa, respectively [104]. Similarly, experiments found the thermal conductivity at 300 K to be 250 W/mK and 2 W/mK in the in-plane and out-of-plane directions, respectively [105].

Since the accuracy of MD simulations is limited by the interatomic potentials used, the interatomic potential should be able to accurately reproduce relevant behaviors at the nano-scales. In the case of thermal properties, this includes collective motions such as phonon transport [106, 107]. There are just a few studies in the literature with interatomic potentials which are capable of characterizing the anisotropic behavior accurately, and the objective of this chapter is to improve on them.

The structure of hBN naturally suggests that the in-plane and out-of-plane atomic bonding be handled differently. The Tersoff potential [108] is commonly used for the covalent in-plane interactions between adjacent borons and nitrogens. Originally developed for Si-Ge and C-Si systems, the potential was eventually extended to hBN [109] and is now used extensively in the literature [102, 103, 110]. The out-of-plane interactions appear to be mainly governed by Coulombic forces, dispersion forces and Pauli repulsion, meaning that it would not be appropriate to use the Tersoff potential for interlayer bonding and a different potential should be used. Lindsay and Broido [110] neglected Coulombic forces and assumed same Lennard-Jones 6-12 parameters for all of the B-B, N-N and B-N interactions in a recent study, but this contradicts (DFT) calculations that showed that the Coulombic forces play a critical part in stabilizing the stacking mode and regulating interlayer sliding corrugation [111]. Leven et al. [112] developed a potential for the interlayer interactions based on extensive DFT simulations. However, this function is computationally expensive for sizable MD simulations, and potentials calibrated to DFT results do not necessarily give physically reasonable behavior at finite temperatures [113]. Green et al. [114] proposed a LJ 6-12 potential with a Coulombic term, with the potential parameters and resulting elastic constants are calculated theoretically. Since there were few experiments available at that time, they were able to compare their results only for  $c_{33}$  and did not test the potential performance for other properties. Kuzuba et al. [115] adopted a similar approach using the same functional form, but derived the potential parameters from the experimental structure and elastic constants of MLhBN. However, the derivations of these potentials included some questionable assumptions such as the same parameters for different types of atomic interactions, and used only the limited experimental data that was available at that time.

The objective of this study is to derive a computationally efficient and easy to implement interlayer potential that is capable of reproducing the thermo-physical properties of hBN accurately, using MD simulations. More recent experimental data is used to improve the accuracy of existing potentials and a comparison of the potential with other potentials in the literature is presented.

## 3.2. Methodology

### 3.2.1. Potential Function Parameters: Derivation

The calculation follows a similar procedure to that of Kuzuba *et al.* [115]. Let  $\Phi_{ij}(r_{ij})$  be the interaction energy between the *i*-th and *j*-th atoms in two distinct layers

separated by a distance

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$
(3.1)

where the layers are parallel to the x-y plane. The interlayer interaction energy of the infinite crystal is then

$$E = \frac{1}{2} \sum_{m} \sum_{n \neq m} \sum_{i \in L_m} \sum_{j \in L_n} \Phi_{ij}(r_{ij})$$
(3.2)

where m and n are integer labels for the layers and  $L_m$  and  $L_n$  are the set of integer labels for the atoms in layer m and n, respectively. The contribution to the interaction energy of a single pair of B and N atoms in layer zero (the reference layer) is then

$$E = \frac{1}{2} \sum_{n \neq 0} \sum_{j \in L_n} \Phi_{Bj}(r_{Bj}) + \Phi_{Nj}(r_{Nj})$$
(3.3)

where  $\Phi_{Bj}$  and  $\Phi_{Nj}$  are the potentials between the pair of atoms in the reference layer and atom j. The function defined by Equation (3.3) has attractive, repulsive and electrostatic components. The repulsive and attractive terms are assumed to be of the LJ 6-12 type, and Coulomb's law is used for the electrostatic interactions. This yields

$$\Phi_N = -\alpha_{Bj} r_{Bj}^{-6} + \beta_{Bj} r_{Bj}^{-12} + K_c q_B q_j r_{Bj}^{-1}$$
(3.4)

$$\Phi_B = -\alpha_{Nj} r_{Nj}^{-6} + \beta_{Nj} r_{Nj}^{-12} + K_c q_N q_j r_{Nj}^{-1}$$
(3.5)

where the coefficients  $\alpha_{Bj}$ ,  $\alpha_{Nj}$  and  $\beta_{Bj}$ ,  $\beta_{Nj}$  are assumed to be positive and control the strength of the attractive and repulsive interactions, q is the atomic partial charge in units of the elementary charge, and  $K_c$  is the Coulombic constant. Since charge balance requires that the partial charges of the B and N atoms have same magnitude, the three different interactions (B-B, N-N, B-N) lead to the seven unknowns;  $\alpha_{NN}$ ,  $\alpha_{BB}$ ,  $\alpha_{BN}$ ,  $\beta_{NN}$ ,  $\beta_{BB}$ ,  $\beta_{BN}$  and q. This implies that at least seven constraint equations are required to solve for the parameters of the interlayer potential of MLhBN. The Van der Waals radius for B is 192 pm [116], much smaller than the 330 pm between hBN layers. Neglecting the short range B-B interactions, as is often done for ionic materials [117], reduces the number of unknowns to five. Since N has a nonbonding electron orbital that extends above and below the layer [118], the N-N and B-N interactions cannot similarly be neglected. If Eqns. (3.4) and (3.5) are inserted into Equation (3.3) with this simplification, the interlayer contribution of the reference pair becomes:

$$E = -\frac{1}{2} \alpha_{Bj} \sum_{n \neq 0} \sum_{j \in L_n} r_{Bj}^{-6} + \frac{1}{2} \beta_{Bj} \sum_{n \neq 0} \sum_{j \in L_n} r_{Bj}^{-12} + \frac{K_C}{2} q_B q_j \sum_{n \neq 0} \sum_{j \in L_n} r_{Bj}^{-1} - \frac{1}{2} \alpha_{Nj} \sum_{n \neq 0} \sum_{j \in L_n} r_{Nj}^{-6} + \frac{1}{2} \beta_{Nj} \sum_{n \neq 0} \sum_{j \in L_n} r_{Nj}^{-12} + \frac{K_C}{2} q_N q_j \sum_{n \neq 0} \sum_{j \in L_n} r_{Nj}^{-1}$$
(3.6)

The attractive and repulsive lattice summations in Equation (3.6) can be evaluated term-by-term since the atomic positions in the ground state structure are known. It is observed that these summations converge with 400 atoms in each layer, and the calculations are done for 900 atoms in a layer.

The Coulombic contribution to the interaction energy is only conditionally convergent, preventing similar evaluation of these sums. The Ewald summation method is used, following a procedure described elsewhere [114, 115], to replace those with exponentially decaying sums over the in-plane reciprocal lattice vectors  $\vec{g}$ . The mathematical derivation of the method is given in Appendix A.1. This yields the energy due to electrostatic interactions as

$$E_c = K_C q^2 \frac{2\pi}{A} \sum_{\vec{g}} \cos(\vec{g} \cdot \vec{u}) \exp(-|\vec{g}|d)$$
(3.7)

where A is the area of the real-space unit cell (0.0543 nm<sup>2</sup>),  $\vec{u}$  is the lateral shift of the layer relative to the reference layer, and d is the distance between neighboring layers. Equation (3.7) replaces the summations over  $r^{-1}$  in Equation (3.6). As a result, the interlayer potential E can be defined as a function of five fitting parameters, together with  $\vec{u}$  and d as determined by the structure. Constraints on this function include the DFT equilibrium layer separation, experimental  $c_{33}$  and  $c_{44}$  values, and the binding energy at equilibrium. This yields 4 constraints and 5 unknowns, leaving an undetermined system of equations. This is resolved by assuming that the potential function for rhombohedral boron nitride (rBN) is identical to hBN, differing only in the registration of neighbouring layers; the stacking of rBN shifts the third layer by one B-N bond length in the in-plane direction as shown in Figure 3.3. The experimental equilibrium layer separation,  $c_{33}$  and  $c_{44}$  values, and binding energy at equilibrium for rBN provide four additional constraints.



Figure 3.3: Schematic for hBN and bond shifted structure of rBN.

The experimental lattice parameters are reported as a = 0.2506 nm and c = 0.6657 nm (Figure 3.1) for hBN [104], and a = 0.2504 nm and c = 0.6667 nm for rBN [119]. Since the derivation procedure effectively calibrates the potential for the 0 K structure, the experimental room temperature lattice constants are larger than the ideal because of thermal expansion. Therefore the interlayer distance, d, is taken to be 0.320 nm for hBN and 0.319 nm for rBN as predicted by DFT calculations at 0 K [120]. The requirement that the potential be at a minimum at the equilibrium layer

spacing yields two constraint equations, one for hBN and one for rBN:

$$\frac{\partial E}{\partial z} = \sum_{n \neq 0} \sum_{j \in L_n} \frac{\partial \phi(r_{ij})}{\partial z_{ij}} \bigg|_{z_{ij} = nd} = 0$$
(3.8)

where  $z_{ij}$  is the z-component of the atomic separation. The following four constraint equations are obtained by relating the experimental elastic constants to the second derivatives of Equation (3.3).

$$\frac{\partial^2 E}{\partial z^2} = \sum_{n \neq 0} \sum_{j \in L_n} \frac{\partial^2 \phi(r_{ij})}{\partial z_{ij}^2} \bigg|_{z_{ij} = nd} = \frac{c_{33}A}{d}$$
(3.9)

$$\frac{\partial^2 E}{\partial x^2} = \sum_{n \neq 0} \sum_{j \in L_n} \frac{\partial^2 \phi(r_{ij})}{\partial x_{ij}^2} \bigg|_{z_{ij} = nd} = \frac{c_{44}A}{d}$$
(3.10)

Equations (3.9) and (3.10) are evaluated with the atoms in the 0 K equilibrium positions. Experimental elastic constants for hBN [104] and rBN [119] are evaluated for the room temperature equilibrium interlayer spacing in an attempt to handle thermal softening. The last two constraint equations simply equate Equation (3.3) to an overall binding energy. The values of the elastic constants and theoretical binding energy per pair of atoms are taken from the literature, and are shown in Table 3.1. The resulting overdetermined system is solved by least squares minimization to find the parameters reported in Table 3.2 [121]. These are presented for the following type of LJ 6-12 function.

$$\phi(r_{ij})_{LJ} = 4\epsilon_{ij} \left[ -\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{-6} + \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{-12} \right] + K_C q_i q_j r_{ij}^{-1}$$
(3.11)

where  $K_c$  is Coulombic constant,  $\sigma$ ,  $\epsilon$ , and q are the potential parameters.

	MD	Fitted	Target		
$\frac{\partial E}{\partial z}$ (kcal/moleÅ)	-	0	0		
$\frac{\partial E}{\partial z}$ (kcal/moleÅ)	-	0.3299	0		
$c_{33}^{hBN}$ (GPa)	29.9086	26.876	27 [104]		
$c_{33}^{rBN}$ (GPa)	-	28.5822	28.5 [119]		
$c_{44}^{hBN}$ (GPa)	5.1873	7.5855	$7.7 \ [104]$		
$c_{44}^{rBN}$ (GPa)	-	2.166	$2.052 \ [119]$		
$\mathbf{E}_{b}^{hBN}$ (kcal/mole)	-3.5949	-1.9332	-1.9063 [114]		
$\mathbf{E}_{b}^{rBN}$ (kcal/mole)	-	-1.8204	-1.8516 [114]		
$E_b^{\prime DV}$ (kcal/mole)	-	-1.8204	-1.8516 [114]		

Table 3.1: Target constraint equation values, the 0 K least square solution, and 300 K MD results.

Table 3.2: Fitting parameters of the proposed study and others from the literature.

	This work	Ref. [114]	Ref. [115]
$\epsilon_{BN}(kcal/mole)$	0.007	0.0476	0.0872
$\epsilon_{NN}(kcal/mole)$	0.2496	0.0544	0.027
$\sigma_{BN}(nm)$	0.375	0.34256	0.3137
$\sigma_{NN}(nm)$	0.31461	0.33106	0.38013
q(e)	1.1378	1.15	1.05

## 3.2.2. Performance of Potential Function: MD Simulation Details

MD simulations were used to evaluate the performance of the LJ 6-12 potential derived in Section 3.2. An hBN model with 12 layers (shown in Figure 3.1) ensured sufficient length in the z direction to allow the application of small strains without periodic boundary effects. The model was  $5 \times 4.7$  nm<sup>2</sup> in plane, and included 10560 atoms spaced according to the equilibrium spacing of hBN with periodic boundary conditions in all directions. The timestep was set to 1 fs, orders of magnitude smaller than the estimated phonon lifetime in transverse mode for hBN [110]. A standard Tersoff potential [109] was employed for the intralayer interactions, and the proposed LJ 6-12 potential from Section 3.2.1 and two potentials from the literature [114, 115] (shown in Table 3.2) were used for the interlayer interactions. Cutoff distances were set to 0.8 nm for the attractive and repulsive terms. The energy of the system was first minimized, then the temperature and pressure were equilibrated using the isothermalisobaric ensemble (NPT) at specified temperature. All components of the stress tensor were independently set to 0 atm for 20 ps, at which point the system was observed to be in equilibrium. All MD calculations were carried out in LAMMPS [79].

<u>3.2.2.1. Elastic Constant Calculations.</u> After stabilization, the system was switched to the canonical ensemble (NVT) and the stress tensor was measured for 100 ps. The simulation box was then deformed, the system energy was minimized, and the stress tensor was averaged over 100 fs intervals in the deformed condition for an additional 100 ps. Note that the individual stress components must be controlled separately due to the orthotropy of MLhBN. Strain was applied in tension or compression in the z direction, or as a shear in the x direction on the z face. For sufficiently small strains, the elastic constants can be calculated as follows:

$$c_{33} = \frac{\sigma_{zz}^d - \sigma_{zz}^i}{\epsilon_{zz}} \tag{3.12}$$

$$c_{44} = \frac{\sigma_{xz}^d - \sigma_{xz}^i}{\gamma_{xz}} \tag{3.13}$$

where  $\epsilon_{zz}$  and  $\gamma_{xz}$  are the imposed normal and shear strains, and the superscripts dand i respectively denote the deformed and initial stages for the stress component  $\sigma$ , respectively.

3.2.2.2. Thermal Conductivity Calculations. The same initial simulation conditions and equilibration procedure were used as for the elastic constant calculation, and the thermal conductivity of MLhBN in the out-of-plane direction was estimated using RNEMD with the Muller-Plathe algorithm [76]. The simulation box was divided into 12 slabs along the out-of-plane direction with each slab containing one hBN sheet, and a heat flux was applied in this direction by exchanging the velocities of atoms in different slabs. Velocity swapping occurred every 100 fs, with the two atoms with the highest velocities in one slab and the lowest velocities in the other being swapped. After NPT equilibration, the ensemble was switched to the NVE, a heat flux was applied to the system for 50 ps, and the temperature difference between the hot and cold slabs was measured for another 500 ps. The temperature of a slab was calculated with the formula

$$T = \frac{\sum m_i v_i^2}{3Nk_B} \tag{3.14}$$

where  $m_i$  is the mass, and  $v_i$  is the velocity of the *i*th atom, N is the number of atoms, and  $k_B$  is Boltzmann's constant. The temperature gradient was averaged over 100 fs intervals. We observed that the heat flux and temperature gradient had converged for the last 400 ps, meaning that the system had reached steady state. Once the heat flux and the temperature gradient were calculated, the thermal conductivity was estimated using Fourier's law:

$$k = \frac{q''}{\partial T / \partial z} \tag{3.15}$$

where q'' is heat flux per unit area and  $\partial T/\partial z$  is the temperature gradient along the out-of-plane direction.

## 3.3. Results and Discussion

#### 3.3.1. Potential Functions

The interatomic distance vs. potential energy is shown for the derived potential and the potential offered by Green *et al.* [114] in Figure 3.4. The proposed potential has a noticeably higher binding energy for the N-N interaction.



Figure 3.4: Potential energy vs. interatomic distance for proposed LJ 6-12 potential (in the form of (3.11)) and Green *et al.* [114].

#### 3.3.2. Stability of the Structure

The equilibrium interlayer spacing is calculated from MD simulations by averaging the distance between layers, and is presented for the derived potential and those of Green *et al.* [114] and Kuzuba *et al.* [115] in Figure 3.5. Our potential deviates 2.25% from the experimental value of 0.33 nm, while the other potentials deviate by 3% and 6%, respectively. A corresponding trend is also observed for the density of MLhBN in Figure 3.6, where the other potentials underestimate the density as compared to the proposed potential. It can be observed that the potentials in the literature overestimate the interlayer spacing while the derived potential slightly underestimates it.



Figure 3.5: Layer spacing for MLhBN calculated by MD simulations.



Figure 3.6: Density for MLhBN calculated by MD simulations.
# 3.3.3. Elastic Constants

The temperature and pressure responses of the model with the proposed potential are shown in Figures 3.7 and 3.8. The system is equilibrated for 100 ps and the components of the stress tensor are averaged over 100 fs intervals. Then the system is deformed and evolved for 200 ps, with 100 ps for the system to converge and 100 ps to average the stress components.



Figure 3.7: Temperature equilibrium of MD simulations for 12 layers hBN model at 300 K.



Figure 3.8: Stress equilibrium of MD simulations for 12 layers hBN model at 300 K.

Stress-strain plots for simulations and experiment [104] are presented in Figures 3.9, 3.10 and 3.11. The elastic constants  $c_{33}$  (in compression and tension), and  $c_{44}$  for three different strain values for each of the three interlayer potentials are also evaluated from stress-strain plots and compared with the experimental values in Table 3.3. Figure

3.9 shows that the proposed LJ 6-12 potential parameters slightly overestimates the experimental  $c_{33}$  in compression, whereas the others slightly underestimate. However, MD results of the proposed LJ 6-12 potential is much closer to the experimental  $c_{33}$  in tension than the others as seen in Figure 3.10. More precisely, a relative error of 11.5%, while those of Green *et al.* [114] and Kuzuba *et al.* [115] have relative errors of 28.6% and 41.4% as seen in Table 3.3. The reason that  $c_{33}$  is higher in compression than tension is the asymmetry of the potential. The improved accuracy of the proposed LJ 6-12 potential, when compared to the other potentials can also be observed for  $c_{44}$  in Figure 3.11.



Figure 3.9: MD results of  $c_{33}$  in compression using three different interlayer potentials.



Figure 3.10: MD results of  $c_{33}$  in tension using three different interlayer potentials.

The more accurate elastic constants suggest that the proposed LJ 6-12 will model transverse phonon modes more accurately, compared to the other potentials. Note that the experimental value of  $c_{44}$  may be artificially high. This can be attributed to the



Figure 3.11: MD results of  $c_{44}$  using three different interlayer potentials.

use of pyrolytic samples [105], which generally have some covalent bonding between layers. These covalent bonds stiffen the structure, whereas our model assumes a perfect crystal.

Table 3.3: Elastic constants in GPa, and the percentage errors are presented in parenthesis.

	$c_{33}$ (tension)	$c_{33}$ (compression)	C44
This work	23.9(11.5%)	31.2(15.6%)	5.25(31.9%)
Green $et al.$ [114]	19.3(28.6%)	24.98(7.5%)	2.73(64.6%)
Kuzuba et al. [115]	15.83(41.4%)	21.56(20.1%)	2.67(65.4%)
Experiment [104]	27	27	7.7

## 3.3.4. Thermal Conductivity

The thermal conductivity is calculated in the out-of-plane direction for the three different potentials at five different temperatures in the interval from 200 K to 400 K. Temperature is plotted vs. non-dimensional length ( $z^* = z/L$ ) in the out-of-plane direction in Figure 3.12 for the proposed LJ 6-12 potential at an average temperature of 200 K, 250 K, 300 K, 350 K and 400 K. Only half of the simulation box is considered since the system is symmetric in the z dimension due to the nature of the Muller-Plathe algorithm. Linear temperature profiles are obtained for all five different cases, allowing Fourier's law to be applied.



Figure 3.12: Temperature profile along out-of-plane direction of MLhBN.

The thermal conductivity calculation is repeated for different numbers of layers to determine if there is any size effect. Results for all three potentials are presented for 6, 8, 10, 12, 14, and 16 layers in Figure 3.13. The absence of information about the number of layers in experiments precludes us from making a detailed comparison of thermal conductivity for each number of layers; however, the thermal conductivity in MD tends to increase with number of layers up to 14 layers. This is attributed to increased phonon boundary scattering for small models. Since there appear to be no significant changes in thermal conductivity from 12 layers to 16 layers, apart from fluctuations, the thermal conductivity of the 12 layer model is considered to be sufficient for the further analysis.

The thermal conductivity of MD simulations as a function of temperature for the different potentials is also considered, with the results presented in Figure 3.14. The proposed LJ 6-12 potential has the same (fluctuating) decreasing trend in thermal conductivity as the experimental studies [105]. The potentials of Green *et al.* [114] and Kuzuba *et al.* [115] fluctuate more and do not follow the experimental trend as well as the proposed potential. Moreover, the proposed potential predicts higher conductivities than the others, and its predictions are closer to experiments. More accurate representation of the transverse phonon modes may lead to this slight improvement



Figure 3.13: Out-of-plane thermal conductivity results for different potentials for different number of layers.

of the thermal conductivity. All MD results are lower than the reported value of 2 W/mK, [105] though. This is reasonable because the experimental samples were pyrolytic with covalent bonds that could enhance the phonon transport along the out-of-plane direction. Hence, this difference in thermal conductivity is attributed to the ideal structure assumption in our models. The average errors with respect to the experimental thermal conductivity results in Figure 3.13 and Figure 3.14 are also presented in Table 3.4.



Figure 3.14: Out-of-plane thermal conductivity results of different potentials for different temperatures.

Figure	This work	Ref. [114]	Ref. [115]
3.14	30.2	41.5	53
3.13	16	23.4	43

Table 3.4: Average thermal conductivity percentage errors with respect to the experiments (for the results of Figure 3.14 and Figure 3.13) for different potentials.

#### 3.4. Conclusion

A new interlayer potential composed of Lennard-Jones 6-12 terms and a Coulombic term is developed for multi-layer hexagonal boron nitride. The derivation follows a similar fitting procedure to Kuzuba *et al.* [115], but is calibrated with more recent experimental data for the hexagonal boron nitride and the rhombohedral boron nitride structures. The calibration is performed by a least squares minimization, and molecular dynamics simulations allow the performance of the proposed potential to be compared with two others with regard to interlayer spacing, elastic constants, and thermal conductivity. The proposed potential is found to predict the interlayer spacing more accurately, while errors for  $c_{33}$  predictions in compression are similar for all three potentials. The proposed potential again leads to the smallest error for  $c_{33}$  predictions in tension and for  $c_{44}$  predictions. More accurate elastic constants suggest that the proposed potential better reproduces phonon modes in the out-of-plane direction.

The thermal conductivity is evaluated for the three potentials using the Muller-Plathe algorithm and the RNEMD method [76] as a function of temperature and the number of layers. The size effect is found not to be significant for systems with more than 10 layers. The thermal conductivity of the 12 layer model with the proposed potential decreases with increasing temperature, consistent with the increased phonon scattering that occurs in experiments. Overall, the proposed potential is found to more accurately predict properties such as density, elastic constants and thermal conductivity, and it is believed that this improvement will lead more accurate MD simulations of multi layer hexagonal boron nitride.

# 4. NANOLAYERING AROUND AND THERMAL RESISTIVITY OF THE WATER-HEXAGONAL BORON NITRIDE INTERFACE

### 4.1. Introduction

Solid-liquid interfaces have been extensively studied due to their critical importance in a variety of physical phenomena, including electrochemical deposition [122], adsorption of proteins [123], solid-melt systems [124], etc. However, there are still open questions regarding the dynamics and wetting properties of solid-liquid interfaces [125]. In colloidal suspensions of nanoparticles (nanofluids), the interfaces are believed to be one of the main heat transfer enhancement mechanisms [3]. This has encouraged the development of a literature on interfaces in nanofluids, mainly concerned with clarifying and understanding the physical phenomena involved. These studies use experimental, numerical modelling, and theoretical approaches.

The nanolayer is a dense liquid layer that forms around the nanoparticle, and its effect on the heat transfer enhancement of nanofluids is unclear. Most theoretical approaches to the interfacial properties of nanofluids introduce nanolayering in effective medium theories by modifying the Maxwell [33] or Hamilton-Crosser [34] equations. The Hamilton-Crosser equation for the thermal conductivity enhancement in nanofluids was developed for non-spherical particles [126], though other similar mathematical relations can be found in the literature [127, 128]. However, effective medium theories rely on empirical parameters that depend on the material type and shape, limiting the generality of the model. These calculations also assume a continuous medium even though the nanolayer has a thickness in the order of nanometers.

Molecular dynamics can be used to study a variety of interfaces and interfacial properties [129–131], provided that suitable interatomic potentials have been found. For example, a NEMD simulation was performed of a Cu-ethylene glycol nanofluid, and the thermal conductivities of the nanofluid and nanolayer were calculated [132]. The results did not agree with experimental thermal conductivity data. These studies mostly rely on the Lorentz-Berthelot rule to define the interatomic potential at the interface; this simply averages the LJ 6-12 parameters of the solid and the liquid phases, and does not have a rigorous justification. The interatomic potential at the interface should ideally be derived from experimental data or more fundamental numerical results, and should be validated to ensure that it adequately captures the thermo-physical behavior at the interface.

Eapen *et al.* [133] studied the effect of the interatomic potential between the solid and liquid phases for LJ fluids by changing the energy parameter of the LJ 6-12 function. They showed that the nanolayering and thermal conductivity enhancement of the nanofluid both increase with the energy parameter. Sikkenk *et al.* [134] used MD simulations to find the potential parameters between solid and liquid phases using the wetting and drying transitions. They suggested further investigation of van der Waals forces at different interfaces. Maruyama *et al.* [131] studied the contact angle of a liquid droplet on a solid surface using MD simulations, and showed that the interfacial properties depend strongly on the interatomic potential between atoms in the solid and liquid phases. They also reported that changing the energy parameters of the LJ 6-12 potential between the two phases changed the liquid density in the vicinity of the surface, but not the thermal conductivity. The effect of interfacial thermal resistance was not considered in this study.

A similar approach was followed by Leroy and Muller-Plathe [135], who found the surface free energy and contact angle for different LJ interaction parameters. The work of adhesion of the water-graphene interface was calculated by Leroy *et al.* [136] as a function of the energy parameters of the LJ612 potential. Coulombic interactions were neglected and relegated to the future work. Geysermans *et al.* [137] used the experimental cohesive energy to define the interatomic potential between liquid Ar and solid Cu and investigated the liquid layering on metal surfaces by means of the density profile, interfacial atomic vacancies, and adsorption of the liquid. Vanzo *et al.* [138] showed that the energy of the solid-liquid interface changes dramatically when Coulombic interactions are included and the partial charges of the surface atoms are varied in a graphene and water system. Bratko *et al.* [139] came to a similar conclusion by studying electrowetting in a nanopore geometry. Giovambattista *et al.* [140] showed that the hydrophobicity of a silica-water interface could be controlled by scaling the surface charges of the atoms. They found a significant variation in the contact angle for different surface dipole moments, showing that the effect of surface charges on the interface interactions can be substantial. Considering the limited knowledge about interfacial interactions and the validity of LB mixing for the LJ 6-12 parameters in the literature, our conclusion is that there is still much work to be done in understanding solid-liquid interactions and interfacial properties in MD simulations.

In particular, the Kapitza resistance is the interfacial thermal resistance at solidliquid interfaces, and likely has a strong effect on the thermal conductivity enhancement in nanofluids. One study of a pump-probe setup involving a nanoparticle considered the cooling rate of the nanoparticle as a function of the attractive part of the LJ612 function [141]. No thermal conductivity enhancement was observed, and the researchers attributed this to the presence of a Kapitza resistance at the nanoparticle-liquid interface. This resistance was observed in a NEMD study [142] as well, where the temperature jump at the interface was found to depend on the attractive parameters of the LJ interaction between the solid and liquid. The Kapitza length at Ar-graphite and Ar-Ag interfaces was calculated using many body potentials for graphite and Ag [130]. This study considered the temperature effect on the Kapitza length, and the investigation of more complex surfaces and the effect of electrical charges and polar fluids were suggested as future work. All of these studies used LB mixing for the LJ 6-12 parameters that define the solid-liquid interactions.

Most of the studies mentioned above show some nanolayering at the interface for simple monoatomic substances. However, the materials of interest for nanofluids typically involve more than pairwise potentials and require more complex dynamical analysis. Wei *et al.* [143] studied a solid-liquid problem where they explored the wetting properties of graphene oxide with water, combining MD simulations and theoretical analysis. One of their major findings was that the contact angle can change depending on the surface roughness in experimental samples, whereas most numerical studies assume perfectly flat surfaces. The effect of wrinkles and surface defects on the contact angle was also mentioned by Li and Zeng [144], who performed quantum molecular dynamics (QMD) simulations of graphene and hBN monolayers. They also estimated the charges of carbon, boron, and nitrogen atoms in the presence of water using DFT and the Born-Oppenheimer approximation. The effect of temperature and system size on the contact angle of a water droplet on graphite and hBN surfaces was investigated [145], and properties such as the wetting temperature and line tension were calculated but not compared with experimental data. Water-carbon nanotube (CNT) and water-graphene interfaces were studied to investigate the liquid structure near the solid using first principle MD calculations [146]. They reported that different interatomic potentials between the solid and liquid correspond to different liquid behaviors at the interface, demonstrating the necessity of improved fitting procedures for this purpose. Quantum simulations and MD simulations were used to study the wetting properties of a hBN nanolayer by fitting the charges of boron and nitrogen atoms for specific geometries including a rhodium substrate [147]. This showed that the interfacial energy between hBN and water was very close to the surface energy of water. A very recent study presented by Wu et al. [148] proposed to obtain potential parameters by combining diffusion Monte Carlo (DMC), random phase approximation (RPA), and MD methods to simulate the formation of a water droplet over a hBN surface. The nano-droplet contact angle was extrapolated to the macro-scale result by using the modified Young's equation, though the line tension is extremely difficult to measure physically.

The main purpose of this study is to develop a new method to calibrate interatomic potentials at the solid-liquid interface. This involves changing the partial charges of the surface atoms until the simulated surface energy of the interface satisfies Young's equation for the experimental surface energy of the solid and the liquid, and the experimental contact angle. The calibration method is applied to the hBN-water system. hBN is of particular interest due to its advantageous thermal and mechanical properties [92–94]. The effects of different potential parameters and system size on the calculated interfacial potential at the interface, the formation of a nanolayer, and thermal conduction at the interface are investigated.

#### 4.2. Theory and Method

#### 4.2.1. General Approach

The contact angle is one of the major properties of a solid-liquid interface that is measurable from experiment, though the interfacial energy is more readily accessible from simulations. We propose to convert the contact angle to an interfacial energy and to use this to calibrate the interatomic potential. The conversion is accomplished by means of Young's equation:

$$\gamma_s - \gamma_{sl} - \gamma_l \cos(\Theta_C) = 0 \tag{4.1}$$

where  $\Theta_C$  is the contact angle,  $\gamma_l$  is the surface energy of the liquid with vacuum,  $\gamma_s$ is the surface energy of solid with vacuum, and  $\gamma_{sl}$  is the interfacial energy of the solid and liquid. Equation (2.2) is assumed for the interactions between water and hBN atoms. Our intention is to adjust the partial charges of the hBN surface atoms in such a way that  $\gamma_{sl}$  defined by Equation (4.2) and is calculated by Equation (4.3) satisfies Equation (4.1) based on the experimental values of contact angle,  $\gamma_s$ , and  $\gamma_l$ .

Other studies generally attempt to calibrate surface interactions through  $\epsilon_{ij}$ , or simply use the Lorentz-Berthelot rule to specify this parameter. The motivation for changing the partial charge instead of  $\epsilon_{ij}$  is that the partial charge is affected by the presence of other charges in the environment, while the inner shell electron distribution is unlikely to change significantly. Note that the partial charges of nitrogen and boron are assumed to be equal and opposite to maintain charge balance. For a given charge,  $\gamma_{sl}$  is calculated from simulations based on the definition [149]:

$$\gamma = \left(\frac{\partial I}{\partial A}\right)_{S,V,N} \tag{4.2}$$

where I is the internal energy of the system, A is the interfacial surface area, S is the entropy, V is the volume, and N is the number of atoms. This derivative is approximated by the finite difference:

$$\gamma = 0.5 \left( \frac{I_{12l} - I_{8l}}{A_{12l} - A_{8l}} \right)_{S,V,N} \tag{4.3}$$

where the subscripts 12l and 8l correspond to 12-layer and 8-layer models, respectively. The number of layers is selected considering the effect of the number of layers on the thermal properties of hBN [13]. These models are discussed in more detail in the following sections.

#### 4.2.2. Models

Surface energies are calculated by MD simulations using several different models with different dimensions. The 8-layer hBN model is shown in Figure 4.1, and the simulation cell filled with water molecules in the remaining volume is shown in Figure 4.2. The 8-layer and 12-layer models contain same number of borons and nitrogens, and differ in the y-dimension as shown in Figure 4.3. The difference of the internal energies allows  $\gamma_{sl}$  to be calculated by means of Equation (4.3). Since the simulation cells do not involve a droplet, there is no need to use the modified Young's equation. The 8-layer and 12-layer models are used together for the contact angle calibration, and the 8-layer model is also used for the estimation of nanolayer thickness and density analysis in the absence of a thermal load. Temperature, volume and number of atoms were kept constant throughout using the NVT ensemble.

The thermal properties of the interface are calculated using a model with two hBN particles. The two particles have similar structures to the 8-layer particles in the previous models, and each contain 5408 nitrogens and 5408 borons. The particles were located in the intervals 3.7-6 and 11.9-14.2 nm along the z direction in a simulation cell of dimensions  $5.7 \times 6.5 \times 18.3$  nm<sup>3</sup>. The empty simulation volume was filled with 15876 water molecules. This model is used with the Muller-Plathe algorithm for RNEMD.



Figure 4.1: MD models of pure hBN.

## 4.3. Problem Statement

# 4.3.1. Problem Details

The partial charges of boron and nitrogen have been reported to significantly affect the interaction between the two phases in the water-boron nitride nanotube system [150], and the same is expected for the partial charges of the hBN layer at the interface of a hBN particle and a second phase. Furthermore, these are expected to be different from the partial charges of layers in the interior of the particle due to the absence of mitigating partial charges in the external half space. Calibrating the partial charges of the hBN layer at the interface should therefore give a more accurate description of any phenomena there. An experimental contact angle is required to follow the calibration procedure described in Section 4.2, though surface roughness and related defects can change the contact angle as discussed previously [143, 144]. These



Figure 4.2: MD models of one particle hBN.



Figure 4.3: Surface areas of 8-layer and 12-layer models.

studies suggest that roughness increases the hydrophilicity of the surface, and decreases the contact angle. This likely contributes to the difference in experimental [151] and QMD results [144] where the contact angle is reported to be in the interval 33° to 77° and 86°, respectively. The same effect is likely responsible for the variation in other experimental results from 40° to 160° [152–157], where samples with different preparation methods have different surface morphologies. Since the hBN surfaces in our models are atomically flat, we prefer to use experiments with the minimum roughness. The experimental reference value for the contact angle measurement is chosen to be  $67^{\circ}$  from Li *et al.* [154], since they achieved hBN films with very little roughness and a small air-liquid contact friction. The experimental surface energy is taken to be 72 mJ/m<sup>2</sup> from Ref. [151].

Many interface studies assume stationary solid substrates. This is not possible when studying interfacial thermal resistance since kinetic energy must be exchanged between the phases. Allowing motion of substrate atoms introduces a complication as the density calculations to identify the nanolayer must be performed with respect to a moving interface. The position of the surface is calculated as the average z-coordinate of borons and nitrogens in the surface layer.

## 4.3.2. Size Effect

Twelve models with several different dimensions are used to investigate the size effect on our calculations. The x-dimension is roughly 6.1 nm and fixed for all models, the y-dimension is varied to obtain different interface areas, and the initial z-dimension is approximately 11.3 nm for 8-layer models and 17 nm for 12-layer models. The resulting number of atoms and y-dimensions are presented in Table 4.1.

The planar elastic modulus  $c_{11}$  is reported as 750 GPa for hBN, and the resulting strain energy for 1% in plane strain is on the order of 10 mJ/m<sup>2</sup>. Since  $\gamma_{sl}$  is also on the order of 10 mJ/m<sup>2</sup>, the fluctuations in strain energy with NPT boundary conditions can obscure the calculation of the surface energy. We introduce the following procedure to avoid this excessive strain energy difference: The smallest model with 8 layers is created, and the x and y dimensions are recorded after NPT equilibration in all directions. Then the x and y positions of hBN atoms in the larger models are scaled with respect to the dimensions of the smallest model, and the simulation is performed with volume control.

8-layer			12-layer		
$N_{hBN}$	$N_{total}$	$L_y$ (nm)	$\mathbf{N}_{hBN}$	N <sub>total</sub>	$L_y(nm)$
13440	51738	7.59615	13440	51738	5.06468
26880	103482	15.19405	26880	103482	10.12936
40320	155226	22.79107	40320	155226	15.19405
53760	206970	30.38809	53760	206970	20.25873
67200	258714	37.98511	67200	258714	25.32341
80640	315246	45.58214	80640	315246	30.38809

Table 4.1: y-dimension and number of atoms for different models used in the investigation of the size effect.

### 4.3.3. Force Fields

Interactions within the water are described using the flexible TIP3P potential [158]. Interactions within the solid depend on the orientation of the bond. The Tersoff potential with the parameters of Albe *et al.* [109] is used for the covalent bonds between B and N atoms in the plane. The interlayer interactions (z-direction in Figure 4.1) use the LJ 6-12 potential and Coulombic interactions with the parameters from our previous study [13]. Water-hBN interactions include the LJ612 potential and Coulombic interactions, but with three different sets of parameters. The first uses LB mixing to define the LJ 6-12 parameters, using the parameters from our previous work [13]. The second uses the LJ 6-12 parameters and charge values for a water-boron nitride nanotube as given by Hilder *et al.* [150]. The fitting procedure used DFT and considered the interaction between water and B and N in a nanotube geometry. Despite these geometric differences, the parameters of Hilder *et al.* [150] are the best candidates for TIP3P water-hBN interactions in the literature to our knowledge. The third uses the LJ 6-12 parameters of Hilder et al. [150] but adjusts the partial charges of the B and N atoms in the surface layers. For reference, the interfacial Lennard-Jones parameters from the literature are reported in Table 4.2. The regions where each interatomic potential is applied are shown in Figure 4.4.

Table 4.2: Interfacial LJ parameters of 3 different models that are used in this study. LB denotes Lorentz-Berthelot and MC denotes Modified Charges. Parameters of Model 2 and Model 3 are taken from Ref. [150], and those of Model 1 are from

	$\underline{Model 1}$	Model 2	$\underline{Model \ 3}$
	(LB Ref. [13])	(Ref. [150])	(MC Ref. [150])
$\epsilon_{NO}(kcal/mole)$	0.159	0.144	0.144
$\sigma_{NO}(nm)$	0.317	0.303	0.303
$\epsilon_{BO}(kcal/mole)$	-	0.215	0.215
$\sigma_{BO}(nm)$	-	0.310	0.310
q(e)	1.1378	0.975	1.1205

Ref. [13].

Coulombic interactions are calculated using the PPPM solver, the initial velocities of the atoms are uniformly distributed, and the system energy is minimized before equilibration. All simulations are equilibrated with the NVT ensemble as described in Section 4.3.2 for 100 ps, more than enough to observe stabilization of the temperature (300 K), and energy. For surface energy calculations, the potential energy of the system is recorded for 50 ps in the NVT ensemble at 300 K. For simulations with temperature gradients, the system is further equilibrated for a 100 ps in the NVE ensemble while the RNEMD velocity exchange algorithm [76] is applied, and the temperature profile is calculated in the NVE ensemble for further 300 ps. Different procedures are applied after the equilibration stage depending on the properties being investigated. All MD simulations are performed with LAMMPS.



Figure 4.4: Schematic of different potentials used for water, interlayer interactions of hBN, and interface.

### 4.4. Results and Discussions

### 4.4.1. Contact Angle Fitting

The values of  $\gamma_{sl}$  estimated using the Lennard-Jones parameters of Hilder *et al.* [150] as a function of the charge of the surface atoms and system size are shown in Figure 4.5.

There appears to be a noticeable size effect on the calculated  $\gamma_{sl}$  for interface areas smaller than 50 nm<sup>2</sup>, with random fluctuations observed thereafter. The resulting  $\gamma_{sl}$ for each surface charge value is calculated by averaging the  $\gamma_{sl}$  of the largest three models of Figure 4.5, where  $D_A$  is larger than 50 nm<sup>2</sup>. Then the calculated  $\gamma_{sl}$  for different surface charges along with the experimental  $\gamma_{sl}$  are plotted in Figure 4.6.  $\gamma_{sl}$ is observed to depend linearly on the surface charge, and the resulting surface charge is estimated by linear interpolation in Figure 4.6.



Figure 4.5: Surface energy results of Equation (4.3) for different interface areas and surface charges.  $D_A$  is the denominator of Equation (4.3) for different sized models.



Figure 4.6: Surface energy results of Equation (4.3) using MD for different surface charges, the surface energy results of Equation (4.1) using experimental data [151], and the linear fit to MD results for interpolation.

The  $\gamma_{sl}$  values found by Equation (4.3) are sensitive to the partial charges, and show a trend similar to that of Vanzo *et al.* [138] for the graphene-water system. Moreover, a preliminary calculation considering the interaction with three water molecules above a hBN surface suggest that the derivative of Coulombic energy per unit area with respect to surface charge is on the order of  $10^2 \text{ J/m}^2$ e, similar to the slope in Figure 4.6. The resulting surface charge is found to be 1.1205 *e* using linear interpolation.

#### 4.4.2. Nanolayering Near the Surface

The number density of water molecules in the vicinity of the hBN surface is measured to identify the effect of the surface charges on nanolayering. The bins are slabs of depth ranging from 0.01 to 0.1 nm perpendicular to the surface, and are defined relative to the average position of atoms in the surface layer of the hBN particle. The number density of water molecules in a slab is estimated by averaging the number of oxygen atoms per volume every 10 fs for 300 ps after equilibration. The results are averaged over the two surfaces of the hBN particle, normalized with respect to the bulk number density of water. The effect of interface area on the nanolayer density calculations is considered first, and presented in Figure 4.7 for different interface areas with Model 3. Changing the interfacial area has no visible effect on the nanolayer density profile. Therefore, the smallest model with a 45 nm<sup>2</sup> surface area is used in the rest of the chapter.

Figure 4.8 shows the nanolayer density profile as a function of distance from the surface. The density peak around 0.31 nm from the surface is an indication of nanolayering, in agreement with previous radial distribution calculations for solid-liquid problems [159]. Our analysis obeys the simulation symmetry though, whereas a radial distribution function would not. There is no significant change in the position or height of the nanolayer peak between Model 2 and Model 3; however, there is a substantial difference between those two cases and and Model 1 where LB mixing is used for the LJ 6-12 parameters. Models 2 and 3 lead to a 45% density increase with respect to Model 1 at the peak density position. We conclude that the LJ parameters have a significant effect on the density of the nanolayer, whereas no significant surface charge



Figure 4.7: Density profile of nanolayer for 8-layer one particle models with different interface area using Model 3.  $N^*$  is the number density of water molecules normalized with respect to bulk water and r is the distance from the surface.



Figure 4.8: Density profile of nanolayer for 8-layer one particle model.  $N^*$  is the number density of water molecules normalized with respect to bulk water and r is the distance from the surface. Parameters of the models are taken from Table 4.2.

effect is observed between Models 2 and 3.

## 4.4.3. Interfacial Thermal Resistivity

Interfacial thermal resistance has been studied extensively in the literature, and most studies calculate the Kapitza length using an interaction potential with LJ 6-12 parameters given by the Lorentz-Berthelot rule. Figures 4.5 and 4.6 suggest that these models could give unreasonably weak interactions and underestimate the thermal conductivity enhancement of the nanolayer. This motivated our study of the thermal characteristics of the water-hBN interface using RNEMD with the Muller-Plathe algorithm for the two particle model.



Figure 4.9: Density profile of nanolayer for 8-layer model at different surface temperatures according to Model 1 of Table 4.2.  $N^*$  is the number density of water molecules normalized with respect to bulk water and r is the distance from the surface.

The number density profiles of water molecules near the surface are shown in Figures 4.9, 4.10 and 4.11 for the three different solid-liquid interactions (given in Table 4.2). The temperature gradient induced by velocity swapping in the RNEMD algorithm raises the temperature of one side of the surface to 326 K and lowers the other to 300 K.



Figure 4.10: Density profile of nanolayer for 8-layer model at different surface temperatures according to Model 2 of Table 4.2.  $N^*$  is the number density of water molecules normalized with respect to bulk water and r is the distance from the surface.



Figure 4.11: Density profile of nanolayer for 8-layer model at different surface temperatures according to Model 3 of Table 4.2. N\* is the number density of water molecules normalized with respect to bulk water and r is the distance from the surface.

Figures 4.9, 4.10 and 4.11 show that the nanolayer is denser with increasing temperature. The distance from the surface that the water reaches the bulk density is consistently around 0.3 nm. This distance is used as the starting point to create bins that are slabs of depth (0.1 nm) perpendicular to the surface to measure the temperature profile. The size effect on the temperature profile is quantified first, as it was done for the density calculations. The temperature profiles for different interfacial areas using Model 3 were estimated by averaging the temperature of each bin over samples taken every 10 fs for total 300 ps, and are presented in Figures 4.12, 4.13 and 4.14.

Figure 4.12 shows that a linear temperature profile is achieved with the Muller-Plathe algorithm; this exchanges the velocities of pairs of particles in specified cold and hot regions (20, 40 and 60 oxygen atoms for 45 nm<sup>2</sup>, 90 nm<sup>2</sup> and 135 nm<sup>2</sup> interface areas, respectively), and does not control the temperature directly. For this reason the maximum temperature and the temperature gradient in the liquid are not the same in all cases. The most significant feature of Figures 4.12, 4.13 and 4.14 is the temperature jump at the interfaces indicating the existence of an interfacial thermal resistance that depends on the choice of potential. The thermal resistivity and thermal conductivity are calculated as

$$R = \frac{\Delta T}{q''} \tag{4.4}$$

$$k = \frac{q''}{\delta T / \delta z} \tag{4.5}$$

where R is the thermal resistivity,  $\Delta T$  is the temperature difference between the surface and the liquid slab 0.27 nm from the surface, k is the thermal conductivity, q'' is the heat flux rate obtained with the Muller-Plathe algorithm, and  $\delta T/\delta z$  is the temperature difference divided by distance  $\delta z$ . The interfacial thermal resistivity (ITR) and interfacial thermal conductivity (ITC) are estimated using the temperature difference at the interface (between points 2-3 for the cold surface and points 4-5 for the hot surface in Figure 4.12), and the overall thermal conductivity (OTC) of the system is estimated using the maximum and the minimum temperature values of the system (between points 1 and 6 in Figure 4.12). The interfacial thermal resistivity and thermal conductivity are reported in Figures 4.13) and 4.14).



Figure 4.12: Temperature profile using the two particle 8-layer model with different interface areas using Model 3. T is the temperature and z is the z-coordinate of the simulation box.



Figure 4.13: Thermal resistivity of the interface as functions of interfacial area using the two particle 8-layer model with Model 3.

The surface area is found to have no significant effect of the thermal resistivity and thermal conductivity at the interface. Therefore, the thermal properties for



Figure 4.14: Thermal conductivity of the interface as functions of interfacial area using the two particle 8-layer model with Model 3.

different surface charges are measured using the  $45 \text{ nm}^2$  interfacial area. The temperature profiles for different interface potentials are presented in Figure 4.15, and the corresponding interfacial properties are reported in Table 4.3.



Figure 4.15: Temperature profile using the two particle 8-layer model. T is the temperature and z is the z-coordinate of the simulation box. Parameters of the models are taken according to Table 4.2.

Table 4.3 indicates that the surface charge modification of this chapter lowers the interfacial thermal resistivity and raises the thermal conductivity of both the interface and overall. Surface charge modifications are found to enhance the overall thermal conductivity, suggesting that a poor choice of potential could be the cause of the underestimation of the heat transfer enhancement in NEMD studies of nanofluids. Specifically, Model 3 leads to an approximately 21.4% reduction in ITR, 28.1% enhancement in ITC, and 11.8% increase in OTC with respect to Model 1.

Table 4.3: MD estimates of interfacial thermal properties for three different potentials presented in Table 4.2.

	Surface at 300 K		Surface at 326 K			
	Model 1	Model 2	Model 3	Model 1	Model 2	Model 3
$ITR(\mu \text{ K/mW})$	1.045	1.028	0.887	0.918	0.884	0.664
ITC(W/m.K)	0.301	0.306	0.355	0.343	0.356	0.474
	Model 1		Model 2		Model 3	
OTC(W/m.K)	1.193		1.	18	1.3	334

## 4.5. Conclusions

Water-hBN surface interactions and more specifically nanolayering and interfacial thermal resistivity are studied using molecular dynamics simulations. Most studies in the literature use the Lorentz-Berthelot rule to define the Lennard-Jones parameters in the interphase interactions, though there is little formal justification for doing so. To our knowledge, there is no other extensive study in the literature where the effect of the solid-liquid interactions on both the density and thermal properties of the interface are considered.

A new calibration procedure for interfacial interactions is introduced to find the partial charge of atoms in the solid surface. Specifically, the partial charges of the surface atoms are adjusted until the surface energies are consistent with the experimental surface energy of water, experimental contact angle of water on a hBN surface, and Young's equation. A potential with Lennard-Jones 6-12 parameters given by the Lorentz-Berthelot rule is used as a reference for the other sets of potentials considered in this study.

The formation of a water nanolayer in the vicinity of the hBN surface was quantified by applying a dynamical analysis where the bins used to calculate the number density of water molecules were defined relative to the position of the hBN surface. The effect of the choice of interfacial interactions on the nanolayer (the lower interfacial thermal resistivity with the proposed surface charge optimization) was investigated.

The RNEMD method with the Muller-Plathe algorithm was applied to investigate the thermal resistivity and thermal conductivity of the water-hBN interface using Fourier's law. We found that tuning the surface charge to reproduce the experimental interfacial energy reduced the thermal boundary resistivity at the interface, and that this is a possible explanation for the underestimation of the thermal conductivity of nanofluids in NEMD studies.

Considering these results and the fact that wetting properties of a solid surface strongly depends on the Lennard-Jones parameters and surface charges, we suggest that interface interactions should be directly calibrated for the materials being investigated, rather than relying on standard parameter mixing procedures.

# 5. THERMAL CHARACTERIZATION ASSESSMENT OF RIGID AND FLEXIBLE WATER MODELS IN A NANOGAP USING MOLECULAR DYNAMICS

### 5.1. Introduction

Water plays a key role in biological, chemical, and a variety of engineering systems. The estimation of water properties in the past generally relied on empirical correlations and equations of state [160], whereas the molecular dynamics (MD) approach has recently become more common with the increase in computational capabilities [161]. Gulliot [60] counted 46 water models in the literature, and this number continues to increase with recently developed models such as the Four-Site Transferrable Intermoleculer Potential (TIP4P) and Five-Site Transferrable Intermoleculer Potential (TIP5P). These models are usually classified as rigid, flexible, or polarizable [162].

Mao and Zhang [52] state that one of the major challenges with water models is to reproduce experimental data including the melting and boiling points, specific heat, viscosity, and thermal conductivity. Thermal conductivity is one of the properties most infrequently considered, and requires the use of specific techniques such as Equilibrium Molecular Dynamics (EMD) or Non-equilibrium Molecular Dynamics (NEMD). EMD relies on the Green Kubo formalism and the calculation of the autocorrelation function. The significant computational time involved means that estimates of water thermal conductivity using the EMD technique are limited in the literature. Bresme *et al.* [163] estimated the thermal conductivity of supercooled TIP4P/2005 water model [164] using EMD and found higher results than the experiments. Rosenbaum *et al.* [165] presented EMD results of the thermal conductivity for SPC/E [48], TIP4P-Ew [166] and TIP4P-FQ [167] potentials and achieved 10-20% relative errors with respect to the experiments. English and Tse [51] also used EMD technique with TIP5P potential of Mahoney and Jorgensen, [168] and reported good agreement with experiments for the thermal conductivity predictions. Sirk *et al.* [50] reported both NEMD and EMD thermal conductivity results that agreed with experiments and suggested further investigation of the thermal behavior of water-solid interfaces. They studied several different water models, reported that the bond and angle stretching in water molecules do not significantly contribute to the heat transport, and did not find any significant difference in thermal conductivity for the rigid TIP3P, TIP4P and SPC/E models. Kumar and Stanley [53] found very high thermal conductivity results using NEMD and rigid TIP5P potential of Mahoney and Jorgensen [168], but Mao and Zhang [52] reported good agreement with experiments for the TIP5P potential re-parametrized by Rick [62].

NEMD, proposed by Muller–Plathe [76], effectively reproduces the experimental procedure by imposing a heat flux on the system and is often more computationally efficient than EMD; however, the size effect and thermal gradient dependence should be carefully considered when extrapolating to bulk properties [78]. NEMD was initially developed for simple monoatomic substances, and afterwards extended to polyatomic substances [169] and rigid molecules [170]. Bedrov and Smith [170] applied NEMD to rigid water molecules such as those in the TIP5P model, but this required that a classical MD solver be modified to include an implementation of the rigorous algorithm they describe. More generally, the calculation of the temperature of rigid molecules by means of the equipartition theorem requires careful consideration of the number of degrees of freedom within the domain [169, 171]. A simple and rigorous approach to calculate the temperature of rigid molecules that can intersect the domain boundary in NEMD studies would be valuable.

This chapter proposes a new method to calculate the temperature and thermal conductivity in MD simulations, and compares the performance of the proposed method for the rigid TIP5P and flexible TIP3P water models with that of Mao and Zhang [52]. The proposed method is found to give more reasonable temperature profiles than that of Mao and Zhang [52] when molecules are rigid and the atomic density is non-uniform due to the presence of solid-liquid interfaces. Solid blocks are introduced to apply Muller–Plathe algorithm [76] without the need to implement the algorithm of Bedrov and Smith [170]. Temperature profiles using NEMD and the thermal conductivity predictions of both NEMD and EMD are presented to compare with experimental data.

#### 5.2. Methodology

## 5.2.1. Non-equilibrium Molecular Dynamics

Two copper blocks are separated by regions filled with water molecules in a simulation box with periodic boundary conditions in all directions, as shown in Figure 5.1. The simulation box has initial dimensions of 3.2x3.2x6.9 nm<sup>3</sup> and contains 2592 copper atoms and 1448 water molecules. We applied the velocity swapping of the Muller–Plathe algorithm [76] to the monoatomic copper atoms to generate a thermal gradient and estimate the thermal conductivity of the intervening water regions. This obviated the need to swap the momentum and angular momentum of rigid molecules, and considerably simplified the procedure.

A TIP5P model with the parameters of Rick [62], or a TIP3P model with the parameters of Jorgensen *et al.* [65], was used for the water molecules, and a Lennard-Jones pair potential was used for the copper atoms [12]. The water-Cu interactions followed the LB rule. The net z-momentum of each copper block was set to zero every 10 fs to avoid translation through the simulation cell. The system was equilibrated in the NPT ensemble for 100 ps at 300 K and 1 atm with a timestep of 1 fs, after which the NVE ensemble was used for a 1 ns production run. As described above, the velocities of atoms in the copper blocks were swapped rather than applying the velocity swapping algorithm of Bedrov and Smith [170] directly to the rigid TIP5P molecules. The velocities of three copper atoms were swapped every 200 fs, and LAMMPS [79] was used for MD calculations.

The system was divided into 20 bins along the z-direction (perpendicular to the water-copper interface) and the temperature in each bin was calculated by two different approaches. The first defined an atomic temperature for each atom as proposed by Mao



Figure 5.1: MD model of TIP5P-Cu system, containing two Cu blocks with periodic boundary conditions.

and Zhang [52]:

$$T_i = \frac{2KE_i}{k_B M_i^I} \tag{5.1}$$

where  $KE_i$  is the kinetic energy of the atom,  $k_B$  is Boltzmann's constant and  $M_i^I$  is the number of degrees of freedom (DOF) for that atom. The DOF is calculated as:

$$M_i^I = 3 - \frac{C_i}{2}$$
(5.2)

where  $C_i$  is the number of distance constraints that involve atom *i*, and angle constraints are viewed as distance constraints on non-adjacent atoms. Note that  $C_i$  is not always an integer, e.g., there is no way to equitably distribute five angle constraints on four hydrogens in rigid methane without allowing fractional constraints. Once the atomic temperatures are calculated using Equation 5.1, they are averaged over the atoms in a bin to find the temperature of that bin. This is denoted as Method 1 in this study.

We propose a new method to calculate the temperature of a domain containing rigid molecules, and denote this as Method 2. The temperature is defined by means of the equipartition theorem:

$$T = \frac{2\sum_{i} KE_{i}}{k_{B}\sum_{i} M_{i}^{II}}$$
(5.3)

where the sums are performed over all atoms in the domain. The number of degrees of freedom  $M_i^{II}$  of atom *i* is given by:

$$M_i^{II} = 3(m_i + I_i) \tag{5.4}$$

where  $m_i$  and  $I_i$  are the fractional contribution of atom *i* to the mass and to the moment of inertia of the rigid molecule. An atom without constraints is considered to be a rigid molecule of one atom and has no moment of inertia. This is believed to more equitably distribute the degrees of freedom of the rigid molecule among the constituent atoms, and is particularly important when a rigid molecule is only partly contained in the domain. The resulting DOF for atoms in the TIP5P model are summarized in Table 5.1.

Table 5.1: DOF for the atoms in the TIP5P model as calculated by two different methods.  $M_O$  is for oxygen,  $M_H$  is for hydrogen, and  $M_L$  is for the ghost atoms of the

TIP5P model.					
	$M_O$	$M_H$	$M_L$		
Method 1	1	1.25	1.25		
Method 2	2.782	1.609	0		

Temperatures of the bins were calculated using Eqns. (5.1) or (5.3) and time averaged over 1000 data points taken for each of 10 equal intervals during the 1 ns production run. Theil-Sen regression [172] was used for the temperature gradient calculation to minimize the effect of outliers. The mean and standard deviation of the temperature gradient were calculated using bootstraping with 10000 resampled temperature data [173]. Once the temperature gradient was estimated for a given heat flux, the thermal conductivity was calculated by Fourier's law [76] (Equation (3.15)) for both water regions as seen in Figures 5.2, 5.3 and Figures 5.4 and 5.5, and they were averaged for the overall result. The temperature gradient was estimated by ignoring the outlier points for Method 1 with TIP5P as seen by the regression lines in Figure 5.2.

## 5.2.2. Equilibrium Molecular Dynamics

The EMD technique was performed using cubic simulation boxes with 1331 water molecules. The edge length of the simulation box converged to 3.38 nm for TIP3P and 3.42 nm for TIP5P after a 100 ps NPT equilibration at 300 K and 1 atm, giving respective densities of 1.03 kg/m<sup>3</sup> and 0.99 kg/m<sup>3</sup>. For the GK calculations, Equation (2.7) is used. McGaughey and Kaviany [174] reported that the correlation is short-lived for low thermal conductivity materials, and different sampling times ranging between 2-50 ps are used in the literature [50, 51, 163]. The timestep chosen was 1 fs [163] and the HCAF converged over a 20 ps sampling time. The micro-canonical ensemble (NVE) was used during the production run, and the thermal conductivity was calculated by averaging over the x, y and z directions (water is isotropic). Further details of the GK calculations can be found elsewhere [12].

#### 5.3. Results and Discussion

The temperature profile of the water region as calculated by the two methods discussed above is presented in Figures 5.2 and 5.3 for the TIP5P and TIP3P water models. The variation in the number of atoms per bin as shown in Figures 5.4 and 5.5 is mainly a result of the formation of a nanolayer near the surface. Vertical bars indicate the average boundaries of the copper regions, and the difference in the z-dimensions and the bin positions of the TIP3P and TIP5P models are due to the different surface interactions. The energy parameter of the LJ potential between oxygen and copper differs by 30% for the TIP3P and TIP5P models, and this affects the nanolayer density [131].

Method 1 strongly depends on the number of atoms in the bin for the rigid water model. More specifically, if an inhomogeneity causes the proportion of atomic species in a bin to differ significantly from that of the rigid water molecule, and the degrees of the rigid molecule are not equitably distributed among the atomic species, then the calculation of degrees of freedom in the bin will be inaccurate. With this in mind, we observe the relative excess of oxygens in the bins adjacent to the copper blocks in Figure 5.4. There are also some copper atoms observed outside of the vertical bars due to the random drift of the copper blocks along the z-dimension during the simulation. This does not affect our thermal transport predictions though, since the bulk water regions are used for the Fourier law calculations. By comparison, Method 2 gives a linear temperature profile within the bulk of the water, with temperature jumps that result from the thermal resistance of the nanolayers, and no apparent systematic error from the density variations.

The same variation in the temperature for Method 1 is not observed for the flexible TIP3P molecules in Figure 5.3, and the two method leads to very similar temperature profiles. While the average ratio of the atomic kinetic energy and degrees of freedom in Method 1 is in general not equivalent to the ratio of the average atomic kinetic energy and average degrees of freedom in Method 2, the two methods are equivalent for flexible molecules where every atom has the same number of DOF. Nevertheless, Method 2 (proposed here) adheres more closely to classical statistical mechanics and gives more physically reasonable results for rigid molecules than Method 1, and therefore should be preferred in general.

For the EMD calculations, the normalized HCAF along the x-direction for the last 20 ps interval is plotted for the flexible TIP3P and rigid TIP5P models in Figures 5.6 and 5.7. The substantial difference in the rate of decay of the fluctuations of the TIP3P and TIP5P models is attributed to the bond stretching in the TIP3P model, in agreement with the findings of Sirk *et al.* [50]. The resulting thermal conductivities are presented in Figure 5.8. The thermal conductivity converges after approximately 500 ps, and the average thermal conductivity is calculated for the 600 ps to 1000 ps interval.



Figure 5.2: Temperature calculation by Method 1 and Method 2 for TIP5P water model. Vertical lines denote the average boundaries of the copper regions.



Figure 5.3: Temperature calculation by Method 1 and Method 2 for TIP3P water model. Vertical lines denote the average boundaries of the copper regions.


Figure 5.4: Number density calculation for TIP5P. Vertical lines denote the average boundaries of the copper regions.



Figure 5.5: Number density calculation for TIP3P. Vertical lines denote the average boundaries of the copper regions.



Figure 5.6: Normalized HCAF in the x-direction for rigid TIP5P model.



Figure 5.7: Normalized HCAF in the x-direction for rigid TIP3P model.



Figure 5.8: Thermal conductivity results of TIP3P and TIP5P models using EMD.

Table 5.2: Thermal conductivity results of TIP5P and TIP3P water models using different methods, the experimental value is 0.63 W/mK [175].All entries are reported

in units of W/mK.				
	Method	TIP3P	TIP5P	
This work	EMD	$0.983\pm0.038$	$0.65\pm0.032$	
Ref. [51]	EMD	-	$0.67\pm0.031$	
Method 1	NEMD	$0.882\pm0.09$	$0.382\pm0.016$	
Method 2	NEMD	$0.843\pm0.08$	$0.79\pm0.063$	
Ref. [53]	NEMD	-	$1.5\pm0.07$	

The results in Table 5.2 indicate that the TIP3P model has a higher thermal conductivity than the TIP5P model. This is in agreement with the results of Mao and Zhang [52], and Sirk *et al.* [50] even reported that flexible models generally have higher thermal conductivity than rigid models. The atomic temperature calculation (Method 1) gives a substantially lower thermal conductivity than experiments for the rigid TIP5P model, but is in agreement with EMD for the TIP3P model. This is consistent with the atomic temperature calculation incorrectly assigning atomic degrees of freedom in rigid molecules and consequently overestimating the thermal gradient in our TIP5P simulations. Method 2 gives much more consistent thermal conductivity results, slightly below those of EMD for the TIP3P model and slightly above those of EMD for the TIP5P model. While this suggests that Method 2 in preferable to Method 1 for rigid molecules, we observe that the NEMD results generally do not fall within the confidence intervals of the EMD results (and vice versa). This is quite possibly follows from additional sources of systematic error in NEMD that can be difficult to control, but our results show significant amount of improvement when compared to the results of Kumar and Stanley [53]. Specifically, the EMD result for TIP5P is in agreement with the findings of English and Tse [51] has a relative error of 3%, whereas the NEMD result using the temperature calculation in Equation 5.3 has a 25% relative error with respect to experiment.

A frequent source of systematic error is the so-called size effect [176], which is evaluated here by increasing the simulation length along the z-direction (Figure 5.1). We ran simulations with z-dimensions of 3, 5, 7, 9 and 11 nm, and observed an insignificant size effect on our thermal conductivity predictions. A second source of error could be the presence of unreasonably high thermal gradients. The thermal gradients for the TIP3P and TIP5P models are presented in Table 5.3 along with the reported values of Sirk et al [50]. and Mao and Zhang [52]. While thermal gradients of these magnitudes are indeed unphysical, the ones in our simulations are less so than for other established results in the literature.

(K/Å).				
	TIP3P	TIP5P		
This work	1.39	1.68		
Ref. [50]	1.77	-		
Ref. [52]	2.51	3.34		

Table 5.3: Average thermal gradient results of TIP5P and TIP3P water models

### 5.4. Conclusion

The temperature calculation for rigid and flexible water models in non-equilibrium molecular dynamics simulations with a nanogap between solid walls is considered. A new method is proposed and compared with that of Mao and Zhang [52]. Both methods give similar temperature results for flexible TIP3P molecules, but only the proposed method gives a reasonable temperature profile and thermal conductivity for rigid TIP5P water model between solid walls. This is achieved by distributing the degrees of freedom of a rigid molecule among its atoms according to our formulation in Equation 5.4. The thermal conductivity calculations using equilibrium molecular dynamics and non-equilibrium molecular dynamics for TIP3P and TIP5P models are compared with experiments, and the proposed technique is found to give more accurate thermal conductivity results among the non-equilibrium molecular dynamics predictions.

# 6. ORTHOTROPY AND AGGLOMERATION ANALYSIS OF HEXAGONAL BORON NITRIDE NANOPARTICLES

### 6.1. Orthotropic Nanoparticles

## 6.1.1. Introduction

Most MD studies of nanofluids in the literature consider nanoparticle with isotropic heat transfer properties. However, a nanofluid with orthotropic nanoparticles could be engineered to improve the thermal performance by adjusting the nanoparticle morphology. This chapter specifically considers the effect of changing hBN nanoparticle morphology on the thermal properties of a water-hBN nanofluid.

## 6.1.2. Method

<u>6.1.2.1. Simulation Details.</u> The simulation cell has dimensions of  $9.93 \times 9.93 \times 4.66$  nm<sup>3</sup>, and contains 14400 water molecules with 724 B atoms, and 724 N atoms. Two identical nanoparticles (one of them is shown in Figure 6.1) in the simulation, positioned symmetrically with respect to the middle plane in the *x*-direction. The particles have 4 layers, and all atoms along the edges have at least 2 covalent bonds to prevent spurious interlayer bonding. The potential function for the interlayer hBN interactions is that of Chapter 3, and the water model and water-hBN interactions are those of Chapter 4. All simulations use a 100 ps NPT equilibration, a 100 ps NVE equilibration with the Muller-Plathe algorithm, and a 500 ps production run to measure the thermal properties by RNEMD. The system is divided into 20 bins along the *x*-direction, and the velocities of 10 oxygen atoms are exchanged between the hot and cold bins every 20 fs.



Figure 6.1: Hexagonal Boron Nitride nanoparticle specifically designed for RNEMD studies. The atoms that are used for orientation calculations are indicated with red circles. Water molecules are not shown.

<u>6.1.2.2.</u> Orthotropy Analysis. Let **P** be a moving frame attached to the top surface of the suspended nanoparticle, and **Q** be the global fixed frame of the simulation box as seen in Figure 6.2 ( $\vec{p_3}$  is perpendicular to the top layer). The relative orientation of these frames enables us to calculate the rotation of the nanoparticle with respect to its initial orientation.



Figure 6.2: The moving frame,  $\mathbf{P}$  attached to the nanoparticle in the nanofluid. Water molecules are not shown.

Let the components of **P** be written as  $\vec{p_1} = a_1\hat{i} + b_1\hat{j} + c_1\hat{k}$ ,  $\vec{p_2} = a_2\hat{i} + b_2\hat{j} + c_2\hat{k}$ and  $\vec{p_3} = a_3\hat{i} + b_3\hat{j} + c_3\hat{k}$  where  $\vec{p_i}$  is a normalized vector. Let **Q** consist of unit normal vectors along x, y and z directions. Then the rotation matrix that transforms a column of the **P**-coordinates of a vector into a column of the **Q**-coordinates of the same vector is:

$$\mathbf{R} = \begin{bmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{bmatrix}$$
(6.1)

The elements of  $\mathbf{R}$  are found from the coordinates of atoms in the top layer. An arbitrary vector on the top layer of hBN along *x*-direction is denoted as  $\vec{p_1}$ . The cross product of  $\vec{p_1}$  and any non-parallel vector in the same hBN layer  $\vec{p_2}$  gives  $\vec{p_3}$ , and then  $\vec{p_3} = \vec{p_2} \times \vec{p_1}$ . This gives the frame  $\mathbf{P}$  which follows the position of the flat surface of the hBN nanoparticle during the simulation, and the corresponding transformation matrix,  $\mathbf{R}$ .

Once the transformation matrix is found, the following system of equations is considered:

$$\mathbf{K}' = \mathbf{R}\mathbf{K}\mathbf{R}^T \tag{6.2}$$

where  $\mathbf{K}'$  is the TC matrix in the  $\mathbf{R}$  frame as measured by RNEMD, and  $\mathbf{K}$  is the TC matrix in the  $\mathbf{P}$  frame following the nanoparticle orientation.

The thermal conductivity and the components of  $\mathbf{R}$  are calculated every 200 fs by averaging 10 data points with 20 fs intervals. Theil-Sen regression is used to calculate the thermal gradient, and Fourier's law is used for the thermal conductivity with the same RNEMD procedure as in the previous chapters. 500 ps production run with Muller-Plathe algorithm leads to 2500 set of values for  $\mathbf{R}$  and  $\mathbf{K}'$  in one direction. All three Cartesian directions are considered which physically correspond to three different configurations. First is the initial configuration where *c*-axis of the hBN nanoparticle coincides with the direction of heat flux as shown in Figure 6.3 and denoted with  $k_{zz}$ . The other two cases correspond to initial configuration where layers coincide with the direction of heat flux as shown in Figure 6.4 and denoted with  $k_{xx}$  or  $k_{yy}$ .

### 6.1.3. Results and Discussion

The results of xx, yy and zz components of **K** are found to be  $k_{xx} = 1.09$ ,  $k_{yy} = 1.06$  and  $k_{zz} = 1.03$  W/mK, with the standard deviations on the order of  $10^{-2}$ . This implies that the orientation of the nanoparticle does not have any significant effect on the heat transfer. Considering the physical mechanisms involved, Brownian



Figure 6.3: A schematic of the  $k_{zz}$  component of **K**.



Figure 6.4: A schematic of the  $k_{xx}$  or  $(k_{yy})$  component of **K**.

motion is believed to be a minor contribution to the heat transfer enhancement of the nanofluids as discussed in the current literature and Section 2.3.5 for Cu nanoparticles, however, the effect orthotropy on the enhanced heat transfer by Brownian motion is unknown.

The nanolayering in a solid-liquid system is studied in Chapter 4, where the properties of the interface are found to affect the heat transport in a water-hBN nanofluid by up to 12%. Those results fo not consider the nanolayering effect at the edges of the hBN nanoparticle though. It is expected that B and N atoms with two covalent bonds at the edge of a layer (such as the circled ones in Figure 6.1) will bond with  $H^ OH^+$ ions in the water, and introduce different edge-water interactions; this is not within the scope of this dissertation. However, the aspect ratio of the hBN aggregates may change the heat transport significantly. hBN nanoaprticles with large planar surfaces and a small number of layers would presumably increase any orthotropic effects of the material on the thermal transport.

A preliminary analysis is done for a nanoparticle with aspect ratio of approximately 10, following the calculation procedure of Section 6.1.2.2, and thermal conductivities are found as  $k_{xx} = 1.05$ ,  $k_{yy} = 1.08$  and  $k_{zz} = 0.89$  W/mK. This shows that the aspect ratio of the hBN nanoparticle may change the directional thermal transport in a nanofluid system. The hBN nanoparticles with larger planar surfaces and low number of layers would have higher orthotropic effect on the thermal transport of nanofluids when compared to case of nanoparticles with similar planar and z-dimensions.

### 6.2. Agglomeration and Aspect Ratio

Nanoparticle agglomeration may be the most significant mechanism of Keblinski's mechanisms [3], given recent studies of nanolayering and the Brownian motion effect as discussed in Section 2.1. Heat transfer should be enhanced with particle agglomerates where energy can be transported along a higher conductive medium than the fluid; however, agglomeration is also an important source of shear viscosity increase. Agglomeration can contribute to precipitation in nanofluids as well, since large particles are more likely to settle out. This leads to stabilization problems that will discussed briefly in later sections.

It is known that different surfactants can be used to decrease the attractive forces between nanoparticles and overcome stabilization problems [10]. However, controlling agglomeration using surfactants is difficult to achieve in practice. Therefore, a detailed analysis of the phenomena by means of simulations would be valuable.

MD simulations nanofluids with multiple nanoparticles are theoretically possible, but the the collective behavior of a large number of particles with diameters of a few nanometers could require microsecond simulation times. A preliminary study using the orthotropic properties of hBN nanoparticles is performed here.

## 6.2.1. Method

6.2.1.1. Experimental Images. hBN nanoparticles have two characteristic dimensions. This can be observed from SEM images, and the hBN aggregates without any liquid (dry nanoparticles) are shown in Figure 6.5. We assume that the aggregates in the image can be treated effectively as single large nanoparticles. Hexagonal BN aggregates with different in-plane and out-of-plane dimensions are shown in Figure 6.5 with red circles, and the aspect ratio (AR) is defined as the ratio of the twese two dimensions (in-plane divided out-of-plane). Aggregation on longer length scales is shown in Figure 6.6.

hBN nanoparticles can also be observed in SEM images of hBN-water nanofluids as in Figure 6.7, but the resolution is not sufficient to measure the aspect ratio. Only the planar dimensions can be observed for most of the particles, except perhaps for the one with the red circle.

Since it is not possible to simulate nanofluids with nanoparticle dimensions of a few hundred nanometers, this section makes only preliminary calculations into the effect of AR on the thermal transport. Eleven different nanoparticles are identified



Figure 6.5: SEM image of dry hBN nanoparticles. Red circles demonstrate aggregates with different sizes, which have similar structure to the single particles used in simulations.



Figure 6.6: SEM image of dry hBN nanoparticles.



Figure 6.7: SEM image of hBN-water nanofluid with 0.5% volume fraction.

from the SEM images of dry hBN, and their ARs are calculated and presented in Figure 6.8. The AR of most of the particles is about 5, though much more data would be necessary for statistically accurate results.

<u>6.2.1.2. Simulation Details.</u> Molecular dynamics simulations are used to investigate the effect of AR on the thermal conductivity of the nanofluid. Four different models (2, 4, 6 and 8 layers) are created with nanoparticles having different ARs but similar volumes and correspondingly similar volume fractions as in Figure 6.9. There are approximately 735 BN pairs and 14600 water molecules in each of the models with dimensions of  $9.93 \times 9.93 \times 4.66$  nm<sup>3</sup>. The same simulation parameters as Section 6.1.2.1 are used for theb potential functions, equilibration, production runs and Muller-Plathe algorithm. The pure water thermal conductivity is also calculated in order to find the relative enhancement as in Section 2.3.4.



Figure 6.8: Measured aspect ratios of 11 nanoparticles using SEM images of dry hBN.



Figure 6.9: Nanoparticles with different aspect ratios and equal volumes. Water molecules are excluded from the figure.

# 6.2.2. Results and Discussion

Thermal conductivity enhancement results from 4 different nanofluid simulations with different AR hBN nanoparticles are shown in Figure 6.10. While there is no consistent nanofluid TC results between ARs of 0.5 and 3, the AR of 10 (a 2 layer nanoparticle) has higher TC than the others. This should be expected since high thermal conductivity plane of the nanoparticle is much larger than the low conductivity direction. Interpolating the data in Figure 6.10 would give a thermal enhancement of around 3% for an AR of 5, much less than the 10% observed in experiments [10]. The underestimation is attributed to the following effects:

- The results of Figure 6.8 are biased to small particles that are easier to detect and measure. The average AR could change significantly when a larger number of particles is considered. If the nanoparticles used in experiments have a larger average AR, then the results in Figure 6.10 may agree better with experiment.
- The measured thermal conductivity of TIP3P water having the same dimensions as the nanofluid models is around 1 W/mK. This agrees with the RNEMD results of Mao and Zhang [52], but is much higher than the experimental value, and could lead to lower enhancement ratios.



Figure 6.10: Thermal conductivity enhancement of different AR models with respect to the base fluid.

Suggestions relating to the concerns above will be discussed in Chapter 7.2 as future work. We continue to believe that the thermal effect of hBN aggregation could be investigated using image processing of electron microscopy images (preferably high resolution TEM or HRTEM ones) and MD simulations.

# 7. CONCLUSION AND RECOMMENDATION OF FUTURE WORK

### 7.1. Conclusion

Molecular Dynamics simulations are used in this dissertation and stand between the electronic structure methods and mesoscale approaches. This is believed to be a feasible alternative among different simulation techniques to study the nanofluids, since the atomic interactions are particularly considered. Water based nanofluids with hexagonal boron nitride nanoparticles are studied in general believing that the properties of hexagonal boron nitride may result in enhanced performance of nanofluids. High thermal conductivity, chemical stability, low shear forces between the layers, and the recent developments in the synthesis procedures can be thought as some of these advantageous features.

Different potential derivations, surface charge optimizations and thermal transport calculations have been developed and used in this dissertation as mentioned above. Several results are reported as an output of these techniques and these results may be valuable for further simulations of hexagonal boron nitride or water-hexagonal boron nitride systems. In addition to these contributions, the developed methodologies also contribute to the literature as they can be used for solution of different problems. For example, a new potential can be calibrated between graphite layers by following the method of Chapter 3, surface charges can be optimized for any ceramic-polar liquid interface with the help of Chapter 4, and the temperature calculation technique proposed in Chapter 5 can be useful for non-equilibrium thermodynamics model of any liquid system. The studies conducted in this dissertation can be summarized with the following steps:

• Water models have been studied using different potential functions for benchmark and understanding the method. Their transport properties have been estimated for validation using MD simulations.

- Cu nanoparticles have been introduced in the water as a benchmark case for nanofluid models. Thermal conductivity enhancement, shear viscosity increase of water-Cu nanofluids and Brownian motion effect have been studied by using equilibrium MD.
- A new interlayer potential for hBN has been developed, mechanical and thermal properties have been estimated and validated. This potential has been aimed to be used in further two-phase models with hBN.
- A new approach to describe solid-liquid interactions have been developed using hBN-water interface, and the effect of interface interactions on the interfacial thermal transport has been studied.
- The thermal properties of rigid and flexible water models have been studied in a nanogap geometry and a new formulation has been derived to estimate temperature profile in Non-Equilibrium Molecular Dynamics (NEMD) simulations.
- The effect of orthotropic properties of hBN nanoparticles on the thermal properties of water-hBN nanofluid has been studied, and the agglomeration has been briefly interpreted based on microscopic images and preliminary simulation results.
- Recommendations for future studies considering the findings of this dissertation have been discussed to lead to new questions, perspectives, novel approaches and to beyond the state of the art.

Simpler water-Cu system is studied as a benchmark in the first chapter of this dissertation, water models are tested and thermal conductivity and shear viscosity results are calculated by providing a statistical assessment of Green-Kubo method. Thermal conductivity enhancement and shear viscosity increase of nanofluids with respect to basefluid are predicted. Brownian motion and its effect on the thermal properties are also quantified by tracking the movement of Cu nanoparticle and the associated kinetic energy. The thermal enhancement beyond the Maxwell limit and experiments, and the shear viscosity increase in agreement with the theoretical relations have been observed. Insignificant effect of Brownian motion of the nanoparticle on the

thermal enhancement has also been found.

Water-hexagonal boron nitride nanofluid is studied in the next chapter where no thermal enhancement is found in the preliminary simulations. The performance of potentials for hexagonal boron nitride and hexagonal boron nitride-water interface are studied to clarify the weakness of the preliminary models, and it is observed that there are questionable foundations of the potential functions available in the literature for the desired purposes. Hexagonal boron nitride is a material that has been recently attracting attention with complex atomic structure and there exist no accurate and computationally cheap potential in the literature that represents the interlayer dynamics of multilayered hexagonal boron nitride. Since potential parameters have significant effect on molecular dynamics results, a new potential function in the form of classical Lennard-Jones 6-12 and Coulomb potentials is derived for the interlayer interactions of hexagonal boron nitride layers using the recent experimental data and quantum simulation results. It has been shown that the derived potential leads to better molecular dynamics predictions of c-axis properties hexagonal boron nitride than the older potentials in the literature with respect to the experiments. This enables us to define accurate interactions for the suspended hexagonal boron nitride nanoparticles in the nanofluid system.

Additionally, it has been observed that hexagonal boron nitride-water interactions are not well defined in the literature, and most of the molecular dynamics studies use Lorentz-Berthelot rule without any justification. As a result, water-hexagonal boron nitride interactions are also tuned by changing the partial charges of surface layers of hexagonal boron nitride, instead of fitting weak Van der Waals interactions. It is assumed that the effect of polar molecules on the partial charges of solid surface atoms are more significant than the associated change in the Van der Waals forces at the interface. It has been shown that the interfacial thermal resistance and the overall thermal conductivity of the solid-liquid system changes significantly with the proposed potential, and Lorentz-Berthelot rule is found as a possible source of the artificially high interfacial thermal resistance in the non-equilibrium molecular dynamics simulations nanofluids.

Water is one of the most common substances that is studied in atomic scale approaches and there is a large literature for the modelling techniques, molecular interactions and resulting properties. However, the thermal transport using molecular dynamics has not been fully understood yet, and there is just a few studies reporting thermal conductivity and shear viscosity of water and water-based nanofluids resulting to close agreement with the experiments. Green-Kubo results of water are extensively studied in the previous chapter, but it is aimed to use non-equilibrium molecular dynamics techniques for further simulations of water-hexagonal boron nitride due to the limitations in computational power. Therefore, water properties are estimated using non-equilibrium molecular dynamics simulations considering a reference study, where excellent agreement with the experiments are reported with TIP5P water model. However, it has been found that the accuracy of the proposed technique significantly changes in NEMD models, when there are interfaces and resulting non-uniform density profile of water in the vicinity of the surfaces. A new temperature calculation method is proposed for the NEMD and the robustness of the formulations is shown by comparing its performance for flexible, rigid water models, and non-uniform density profiles.

In the last part of the dissertation, the effect of the orthotropy of hexagonal boron nitride nanoparticles on the thermal transport of nanofluids is studied. A new mathematical approach considering the orientation of suspended nanoparticle is developed and molecular dynamics results of thermal conductivity is used. It has been shown that there is no orthotropy effect of the particle for the thermal conductivity of nanofluid, but this observation is valid for particles having aspect ratio in the order of 1, which corresponds to similar dimensions of planar and z-direction (c-axis) of hexagonal boron nitride nanoparticle. However, it is believed that orthotropy might have more significant effect for the nanoparticles with high planar surface area. It is observed from microscopy images of the water-hexagonal boron nitride nanofluids that the aggregated nanoparticles have similar geometric properties with the single particles in the simulations. Therefore, aspect ratio is studied using reverse non-equilibrium molecular dynamics to investigate the effect of particle shape and agglomeration. It has been found that the effect of agglomeration can be further investigated by determining the particle sizes from experimental images and comparing the simulations results with experimental measurements.

The potential functions and their performance are mainly studied in this dissertation except the first water-copper simulations. This is believed to be a very fundamental issue for molecular mechanics, and it has been observed that there are numerous molecular dynamics simulation studies using the potentials in the literature rather than developing or testing them considering the aim of the simulations. This should be done very carefully since the potential functions are derived using some targeted properties of the material, but this does not guarantee the accuracy of their performance when they are used to predict properties that are different than the targeted ones of the derivation. It can be observed in the literature that this is not considered much for most of the molecular dynamics simulations, and this unfortunately reduces the reliability of the results in general. In this dissertation, it is aimed to develop the mathematical form of the interactions considering the physics of the problem, instead of forcing insufficient potential parameters to get results from molecular dynamics simulations. This is believed to be the ideal perspective of the researchers to have a cumulative valuable scientific knowledge in the computational materials science community.

In summary, it is aimed to investigate several nanoscale physical mechanisms associated with nanofluids and solid nanomaterials, solid-liquid interfaces, liquid models. This dissertation provides different potential functions for a nanofluid system and methodologies for potential derivation or molecular dynamics calculations. The three major heat transfer enhancement mechanisms of nanofluids that are Brownian motion, nanolayering and agglomeration are discussed and quantified, different water models are considered and several equilibrium or non-equilibrium molecular dynamics simulations are studied. The extension of these studies are discussed as future work considering different ways that this research can be leaded to.

# 7.2. Recommendation of Future Work

This dissertation has aimed to investigate the transport properties of water-hBN nanofluids. This is important for several reasons including that there is an increasing research focus on nanofluids with low-dimensional nanomaterials such as graphene or graphite [177] and hexagonal boron nitride [178] in the current literature. These materials have orthotropic or anisotropic behavior where thermal transport is very effective in one direction when compared to other. Several mathematical models have been developed to simulate this phenomena, and water models, interlayer interactions of hBN layers and water-hBN interactions have also been studied. It is believed that these potentials will constitute a robust basis for the future studies of nanofluids with low-dimensional nanoparticles. The future challenges and developments of the proposed models will be discussed in this section, from the point of the author of this dissertation.

## 7.2.1. Edge Phenomena of Suspended hBN Nanoparticles

The interactions between water and hBN nanoparticle should be examined in two different directions (Surface and Edge) as shown in Figure 7.1 considering the orthotropic structure of hBN as discussed extensively in Section 6.1. The physical mechanisms should ideally be treated differently for these two sides of the particle, and the surface interactions are studied in Chapter 4 with a detailed analysis of surface charges and Lorentz-Berthelot rule.

The study of the edges are suggested as a future work in this dissertation. There are two covalently bonded B and N atoms at the edges without any edge treatment in the simulations, and physically it is expected to have some type of bonding between the ions in the water and the B or N atoms at the edge. Since graphene has a very similar chemical structure with hBN, water-graphene studies also deliver insight for the edge bonding where OH ions are usually bonded with C atoms, leading to hydroxyl groups at the edges for both simulations [179, 180] and experiments [181]. Also the recent experiments of Lee *et al.* [178] provide the chemical structure of the edge of



Figure 7.1: MD simulation snapshot with two hBN nanoparticles, showing the two different interface phenomena.

hBN nanosheets in an ethylene-glycol (EG) nanofluid.

It is necessary to define interactions at the edges with a careful selection of potentials to investigate any physical effect accurately. Cha *et al.* [180] use COMPASS (Condensed-Phase Optimised Molecular Potentials for Atomistic Simulation Studies) force field [182] to define interactions between edge C atoms and OH group. This potential function uses LJ 6-9 form instead of LJ 6-12, and might be a good starting point for the edge decoration of hBN. There are also quantum simulation approaches for H decoration of hBN nanosheets in the literature [183,184], where useful information can be found. Edge decoration of hBN might have some effect for the nanofluid properties, and the procedure developed can also be utilised for different functional groups on the nanoparticle. Cha *et al.* [180] investigated the effect of different functional groups that are attached to the graphene nanoparticles in EG and proposed a new approach to functional groups considering the stability of the nanofluid. In addition to the control of the aggregation of the particles, functional groups may also be useful to reduce the interfacial thermal resistance at the nanoparticle-basefluid interface as suggested by Keblinski *et al.* [185]. Therefore, simulations of edge decoration and other functional groups may be valuable for clarifying the stability problem of the nanofluids and for the enhanced heat transport at the solid-liquid interfaces; however, improved potential functions might be necessary to obtain accurate models.

### 7.2.2. Nanofluid Property Optimization

Thermal conductivity and shear viscosity are estimated for a water-Cu nanofluid system in Chapter 2; however, it is found that this procedure is not straightforward to apply for water-hBN problem due to the insufficient potentials available. We therefore focussed on the interlayer interactions of hBN and water-hBN interface which were the major issues to be improved in the first place. It is now believed that much better approximation of water-hBN interactions can be achieved by using the results of Chapters 3 and 4 when compared to the previous literature, and the future investigation of TC and SV may be studied based on this dissertation. As an example, Franca *et al.* [186] recently improved the solid liquid interactions in a suspension of ionic liquid and carbon nanomaterials (similarly in Chapter 4) and made conclusions about chemical structure of the interface, nanolayering, nanoparticle orientation, thermal conductivity and Kapitza length using MD technique. Similar approaches by using the outcomes of this dissertation can be designed for water-hBN nanofluid to investigate several physical aspects.

Water models have also not been fully clarified in terms of MD predictions, and it is believed that Chapter 5 may also serve as a benchmark for any water based nanofluids study. Numerical characterization studies should include careful validations with respect to the experiments and have great importance for designing nanofluids. It is strongly suggested that once the chemical structures at the edges are achieved, TC and SV of water-hBN nanofluids should be investigated by using different methods (NEMD or EMD) and the results should be interpreted with Prasher *et al.*'s [30] formulation to justify the feasibility. Considering the experimental data of high TC enhancement and limited SV increase of water-graphene and water-hBN nanofluids [10, 177, 178], it is believed that efficient nanofluids may be achieved with these materials, and physical mechanisms can be investigated and manipulated for design and optimization of different parameters such as stability, particle size and shape, volume fraction, edge and surface treatments.

### 7.2.3. Agglomeration and Stability of Nanofluids

Percolation is believed to be one of the most significant effects for the thermal transport in the nanofluids and there is still much to do for clarifying the phenomena. Novel nanofluids with percolating structures are designed to achieve stable suspensions with maximum thermal enhancement and minimum viscosity increase may be a very important step for the commercial nanofluids in the future.

The analogy between the aspect ratio of hBN and the aggregates, and a new method to discover the effect of agglomeration on the thermal properties of the nanofluids have been mentioned in Section 6.2. That is believed to be a promising approach constructing a bridge between simulations and experiments and has also potential to investigate the aggregation effect on shear viscosity increase in nanofluids. Therefore, extending this approach for different nanoparticle designs in terms of different parameters such the aspect ratio and volume fraction is suggested for the future work. As an example, dispersed hBN flakes can also be studied (being similar with the work of Cha *et al.* [180] with graphene layers) and the results can be compared with the case of MLhBN nanoparticles.

Aggregated nanoparticles might also have effect on the discussion of Section 6.1 where the orientation of the orthotropic structure of hBN nanoparticles may influence the thermal conductivity of the nanofluid. It should be considered that the nanoparticles with high AR values might lead to different results than the Section 6.1, where nanoparticles with ARs in the order of 1 have been studied. If the enhanced heat transfer is achieved with the specific configuration of hBN nanoparticles with large planar surfaces (high AR value), then controlling their orientation may have significant importance for increasing the thermal efficiency of the system. Aligning 2D materials in a specified direction is usually achieved by mechanical stress, electric or magnetic field as discussed by Lin *et al.* [187] who also controlled the alignment of graphene flakes with micro-magnets in a water suspension. Hong *et al.* [188] and Philip *et al.* [189] used this idea in nanofluids by controlling the orientation of aggregated Fe<sub>2</sub>O<sub>3</sub> nanoparticles with magnetic field and reported significant amount of thermal enhancement up to 300%. Magnetic field concept for nanofluids has been extensively reviewed by M'hamed *et al.* [190] and their study showed that most of the studies are limited with metallic nanoparticles, and suffered from stability problems and high costs. Magnetic control of suspended nanoparticles may be a promising approach for the nanofluids with low-dimensional nanoparticles to achieve stable nanofluids with improved thermal enhancement.

The recent literature suggests that there is a significant dependence between the shape of the aggregates and the stability. Neogy *et al.* [191] have studied the thermal enhancement using Au nanoparticles. They used one-step method to produce the nanofluids with aggregated particles having network structure as shown in Figure 7.2. This configuration has different chains consisting of spherical nanoparticles and it has been shown that 35% enhancement is achieved with this structure when compared to dispersed nanoparticles case. It has also been reported that network like structure of Au particles are stable in the nanofluid (without any sedimentation) and did not lead to any further increase in shear viscosity. This is a similar phenomena with the nanofluids with 2D nanomaterials where surface area to the volume ratio is very high, showing how nanofluid properties substantially change with the shape of the aggregates. Therefore, this effect should be further investigated for the stabilization problems, and it is believed that the aspect ratio of hBN nanoparticles may be a reference parameter for the suggested purpose.

Another important effect for the aggregates and resulting stabilization would be the type of basefluid. In most of the experimental studies where the nanofluids are reported as being stable, EG is preferred instead of water [178, 191, 192]. This selection is easier to obtain stable nanofluids since cohesion has significant effect on the agglomeration, and the aggregation behavior of the particles in water should also be investigated considering the discussion of Section 7.2.1.



Figure 7.2: Network structure of Au nanoparticle aggregates in EG suspension, synthesized by Neogy *et al.* [191].

Long term stability of nanofluids are required for the operational conditions of all heat transfer fluids and it has been experimentally studied by various researchers [32]. Current techniques mainly use surfactants to decrease the attraction forces between particles [10], and it has also been reported that synthesis method has also significant effect on the dispersion of the suspended particles. However, there is no standard surfactant or synthesis method for the nanofluids and this creates some discrepancies among the experimental results. Ghadimi *et al.* [32] reviewed more than 25 experimental studies of nanofluids and showed that only a few of them have been reported as stable. Sedimentation is even not mentioned in half of those studies, but it is important since more stable nanofluids does not necessarily have enhanced thermal characteristics.

Simulations are an alternative and feasible approach to problems where experimental procedures are limited or not consisted with each other, as in the case of stabilization problems of nanofluids. There are just a few stability analysis of nanofluids using MD simulations to our knowledge, such as the study of Dang *et al.* [193] for CNT nanoparticles with different basefluids that are water, hexane and methanol, and also the study of Jahangiri and Yenigun [194] for CNT-polymer solutions. These specifically focus on the physical mechanism of repulsion forces between suspended nanoparticles and effect of functional groups (as surfactants) on the sedimentation. Similar approach would also be valuable for water-hBN nanofluids using the results of this dissertation and would enable us to understand the design parameters of hBN nanoparticles to get stable nanofluids, such as the particle size, aspect ratio and volume fraction. The study of Farzaneh et al. [195] is also a good benchmark for our future suggestions since his MD simulations investigate temperature and particle size effect on the stabilization, which is also crucial for the operation conditions of nanofluids. The stability has been studied examining the interparticle forces using MD in their study, and this method can be easily applied to the proposed models in Chapter 6. It is believed that water-hBN nanofluids with a realistic edge decoration as suggested in Section 7.2.1 may also enhance the accuracy of simulations, which might aim to investigate stability. This phenomena is believed to be linked with agglomeration of the particles as sedimentation is expected for larger aggregates. Therefore, aggregation effect on the stability of water-hBN nanofluids may be studied as a future work, as an example starting point. The time dependent z-position (direction of gravity) of the center-of-mass of hBN nanoparticles having different aspect ratios can be compared between different simulations. However, the required simulation time for this analysis is unknown at the moment.

# 7.2.4. Water-hBN Nanofluid Flow

There is a growing number of nanofluid simulation results in recent years where nanoparticles are introduced in a basefluid and different mechanisms are investigated. There are still open questions regarding to this problem. However, our knowledge of the nanofluids has been increasing, and the extension of this problem to the flow systems is important as a next step. There are numerous macro-scale studies (such as CFD) of these kind of problems, but the resulting designs have not been used in any application different than a research project yet. The nano-scale analysis approaches as conducted and suggested in this dissertation aims to guide future macro-scale designs and experiments, and there is also potential to find some new results for the nanofluids with flow conditions defined. Molecular Dynamics simulations for nanoscale liquid flows have been studied previously for nanochannels and nanofluidics applications [68], and MD results have also been used in CFD calculations [196]. However, nanofluid flow using MD has limited number of results in the literature, and these studies are restricted to nanochannels due to the computational expense. Poiseuille and Couette flows of Ar-Cu nanofluid system confined in a nanochannel have been studied by different groups and some mechanisms have been investigated such as enhanced nano-convection effect around the nanoparticle in a shear flow [197, 198], viscous drag due to the flow, effect of wall-nanofluid interactions [44], or aggregation structure of nanoparticles in a pressure-driven flow [199]. However, a novel and a more practical system such as water-hBN suspension flow has not been investigated. For example, the orientation of hBN particles with different aspect ratios in a pressure-driven internal flow would be valuable for thermal enhancement predictions of flowing water-hBN nanofluid, and also new insight can be gained for the agglomeration in flow. In addition the thermal conductivity and shear viscosity results, study of Ge et al. [200] can be extended to predict convective heat transfer properties as well. However, the results would be valid for a nanofluidics system, and may require large number of atoms and simulation times, i.e. Ge et al. [200] used more than 100000 argon atoms and 9.5 ns simulation time.

## 7.2.5. Mesoscale Approaches for Nanofluids

Molecular Dynamics is one of the most widely used simulation tool in computational materials science, but the required computational power is still a major problem and limits the capability of the method. Therefore, nanofluid simulations having the exact size of the nanoparticles that are used in the experiments are rare among the MD studies. This makes size and time scales crucial as discussed throughout this dissertation. Alternative approach to overcome these problems is to use an upper-scale method, where larger particles that are comprised of collection of atoms instead of individual atoms are considered to solve the equation of Newton's second law. The mathematical procedure of such a method is very similar to MD, but forces (such as contact, body, drag, Brownian, hydrodynamic, etc.) are directly defined into the system instead of using potential functions. This approach is called Discrete Element Method (DEM) that is first developed to study rock mechanics [201], and has been used to model flow of colloidal systems with many particles [202]. In addition to the various flow problems that DEM can be applied, there are a few DEM simulations of nanofluids in the literature. Macpherson *et al.* [203] studied particle aggregation in ethylammonium nitrate liquid and investigated effect of Brownian forces on the kinetics of self-assembly of a nanoparticle suspension.

A similar approach to DEM is called Dissipative Particle Dynamics (DPD) and it is more commonly used for liquid models in the literature. Dissipative Particle Dynamics method has been first introduced by Hoogerbrugge and Koelman [204] and has capability of modelling hydrodynamics and colloidal behavior of the system. Therefore, it has been usually used for modelling complex fluids. However, defining the force field is a fundamental drawback since there is no standard procedure developed [205]. The most commonly used force model for liquids was derived by Groot and Warren [206], where repulsion, dissipative and random forces are defined for a water droplet containing three water molecules. This motivated the development of DPD models of nanofluids since the modelling granular particles will require much less computational time than modelling each atom, and nanoparticle sizes, which are comparable with the ones in experiments, can be simulated with this approach. There are a few DPD models of nanofluids in the literature such as Min et al. [207] who studied the interaction between graphene nanosheets and surfactant in aqueous phase and suggested their method for surface functionalization and agglomeration analysis. Yamada etal. [208] predicted the thermal conductivity of water based  $Al_2O_3$  and CuO nanofluids using DPD method and their results are partially in agreement with the experiments. They attributed the differences to nanoparticle shape, agglomeration and pH value that are different between DPD simulations and experiments. In the current literature, there haven't been following studies for those references yet, but DEM/DPD simulations of hBN-water nanofluid system with or without surfactant and functionalized groups would shed light on the aggregation and stability mechanisms. However, this necessitates the careful definition of the resulting forces, and it is believed that

the particle interactions can be described accurately using different MD methodologies proposed in this dissertation, such as the nanoparticle-nanoparticle, nanoparticle-liquid or nanoparticle-surfactant interactions can be used for defining forces. However, it is suggested to obtain an accurate basefluid model first, since it has a significant effect in nanofluid simulations.

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## APPENDIX A: APPENDIX

#### A.1. Ewald Summation for Long Range Coulombic Interactions

The Coulombic interaction between two atoms (atom A and atom B) is defined using Coulomb's law;

$$E_C = \frac{K_C q_A q_B}{r_{AB}} \tag{A.1}$$

where  $K_C$  is Coulomb constant, q is the partial charge and r is the distance between two atoms. However, summing these interactions for all the atoms in a lattice leads to a conditionally-convergent series that is incompatible with the use of a cutoff distance. One widely used alternative is the Ewald summation which was introduced in 1921 to sum the long range interactions between particles and their periodic images [209]. The derivation starts with the definition of an error function:

$$\frac{1}{|t|} = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-t^2 \rho^2) d\rho$$
 (A.2)

where  $\rho$  is a dummy variable. For the calculation of the electrostatic interaction of atoms in hBN, let the vertical translation vector be  $\vec{z}$ , the horizontal translation vector be  $\vec{l}$ , and the vector for the horizontal shift of subsequent layers be  $\vec{u}$ . Then the total Coulombic energy between atoms can be written as a summation over Equation (A.1) using Equation (A.2), up to a multiplicative constant:

$$\sum_{\vec{l}} \left| \frac{1}{\vec{l} + \vec{u} + \vec{z}} \right| = \frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-\vec{z}^2 \rho^2) \sum_{\vec{l}} \exp[-(\vec{l} + \vec{u})^2 \rho^2] d\rho \tag{A.3}$$

Applying a Fourier transformation and inverse Fourier transformation in sequence leads to the following expression:

$$\begin{split} \sum_{\vec{l}} \left| \frac{1}{\vec{l} + \vec{u} + \vec{z}} \right| &= \frac{2}{\sqrt{\pi}} \int_0^\infty \left[ \frac{1}{2\pi} \int_{-\infty}^\infty \exp(-izk) \int_{-\infty}^\infty \exp(-izk) \exp(-z^2 \rho^2) dz dk \right] \\ &\sum_{\vec{l}} \exp[-(\vec{l} + \vec{u})^2 \rho^2] d\rho \end{split}$$
(A.4)

denoting z as a scalar quantity in the right hand side since it is the displacement only along the vertical direction. Using the following definition from the Fourier transform tables:

$$\int_{-\infty}^{\infty} exp(-izk) \exp(-z^2 \rho^2) dz = \frac{\sqrt{\pi}}{\rho} \exp\left(\frac{-k^2}{4\rho^2}\right)$$
(A.5)

Equation (A.4) can be written as:

$$\sum_{\vec{l}} \left| \frac{1}{\vec{l} + \vec{u} + \vec{z}} \right| = \frac{1}{\pi} \int_0^\infty \int_{-\infty}^\infty \frac{1}{\rho} \exp(-izk) \exp\left(-\frac{k^2}{4\rho^2}\right) \sum_{\vec{l}} \exp[-(\vec{l} + \vec{u})^2 \rho^2] dk d\rho$$
(A.6)

where another Fourier and inverse Fourier transformation can be applied to the summation term at the end of the equation (A.6):

$$\sum_{\vec{l}} \exp[-(\vec{l}+\vec{u})^2 \rho^2] = \sum_{\vec{g}} \exp(-i\vec{g}\cdot\vec{u}) \frac{1}{A} \iint_A \sum_{\vec{l}} \exp[-(\vec{l}+\vec{u})^2 \rho^2] \exp(-i\vec{g}\cdot\vec{u}) d\vec{u}$$
(A.7)

where A is the unit cell and  $\vec{g}$  is the reciprocal lattice vector. Fixed lattice sites are assumed for hBN atoms as they are vibrating around their positions in the crystal structure with a change of variable  $\vec{j} = \vec{l} + \vec{u}$ , and considering that  $\vec{j}$  has non-zero components in the planar directions, Equation (A.7) can be written as:

$$\sum_{\vec{l}} exp[-(\vec{l}+\vec{u})^2 \rho^2] = \sum_{\vec{g}} \exp(-i\vec{g}\cdot\vec{u}) \frac{1}{A} \int_{-\infty}^{\infty} \exp(-j_1^2 \rho^2) \exp(-ij_1 g_1) dj_1$$

$$\int_{-\infty}^{\infty} \exp(-j_2^2 \rho^2) \exp(-ij_2 g_2) dj_2$$
(A.8)

The integral in this equation can also be replaced using the definition in Equation (A.5):

$$\sum_{\vec{l}} \exp[-(\vec{l}+\vec{u})^2 \rho^2] = \sum_{\vec{g}} \exp(-i\vec{g}\cdot\vec{u}) \frac{1}{A} \frac{\pi}{\rho^2} \exp\left(-\frac{g_1^2 + g_2^2}{4\rho^2}\right)$$
(A.9)

When Equation (A.9) is inserted in Equation (A.6), the following expression is obtained:

$$\sum_{\vec{l}} \left| \frac{1}{\vec{l} + \vec{u} + \vec{z}} \right| = \frac{1}{A} \sum_{\vec{g}} \exp(-i\vec{g}.\vec{u}) \int_{-\infty}^{\infty} \exp(-iz.k) \int_{0}^{\infty} \frac{1}{\rho^{3}} \exp\left(-\frac{(k^{2} + g_{1}^{2} + g_{2}^{2})}{4\rho^{2}}\right) dkd\rho$$
(A.10)

Now with the change of variable  $r = 1/\rho^2$ , the integral with respect to  $\rho$  in the right of the equation above is straightforward:

$$\int_0^\infty \frac{1}{\rho^3} \exp\left(-\frac{(k^2 + g_1^2 + g_2^2)}{4\rho^2}\right) d\rho = \frac{2}{k^2 + g_1^2 + g_2^2} \tag{A.11}$$

Equation (A.11) is put into Equation (A.10). Rearranging the terms and using the Fourier transform tables again gives:

$$\sum_{\vec{l}} \left| \frac{1}{\vec{l} + \vec{u} + \vec{z}} \right| = \frac{2\pi}{A} \sum_{\vec{g}} \exp(-i\vec{g}.\vec{u}) \frac{1}{|\vec{g}|} \exp(-|\vec{g}||\vec{z}|)$$
(A.12)

Using Euler's relations and the orthogonality of vectors  $\vec{g}$  and  $\vec{u}$ , the final expression for the Ewald summation is derived:

$$\sum_{\vec{l}} \left| \frac{1}{\vec{l} + \vec{u} + \vec{z}} \right| = \frac{2\pi}{A} \sum_{\vec{g}} \cos(\vec{g}.\vec{u}) \exp(-|\vec{z}||\vec{g}|) \frac{1}{|\vec{g}|}$$
(A.13)

### A.2. LAMMPS Script Examples

A.2.1. Thermal Conductivity and Shear Viscosity Calculation of Water-Cu nanocolloid system using Green-Kubo formalism

```
units real
atom_style full
log vf105_cu2_tip3p.lammps
variable Na equal 6.02214179
variable Pequal 1
variable T equal 300
variable V equal vol
variable dt equal 1.0
variable p equal 10000 # correlation length
variable s equal 2
                         # sample interval
variable
         d equal $p*$s # dump interval
# convert from LAMMPS real units to SI
variable
         kB equal 1.3806504e-23
                                 # [J/K] Boltzmann
variable atm2Pa equal 101325.0
variable A2m equal 1.0e-10
variable fs2s equal 1.0e-15
variable
         kCal2J equal 4186.0/6.02214e23
variable
           convert_v equal ${atm2Pa}*${atm2Pa}*${fs2s}*${A2m}*
     ${A2m}*${A2m}
variable
           convert_k equal ${kCal2J}*${kCal2J}/${fs2s}/${A2m}
              3
dimension
boundary
              ррр
              hybrid lj/cut/coul/long 10 coul/long 10 lj/cut 6.3
pair_style
bond_style
             harmonic
angle_style
             harmonic
read_data
             vf105_187_d20.data
lattice
           fcc 3.63
```

Figure A.1: LAMMPS script for the transport properties of a water-Cu nanocolloid

system

```
NANOP sphere 41.85 41.85 41.85 8.5
region
    side in units box
create_atoms
                3 region NANOP
dihedral_style none
improper_style none
kspace_style pppm 0.00001
group tip3p type 1 2
group oxygen type 1
group hydrogen type 2
group copper type 3
pair_coeff 1 1 lj/cut/coul/long 0.102 3.188
pair_coeff 2 2 coul/long
pair_coeff 1 2 coul/long
pair_coeff 3 3 1j/cut 9.4469 2.5129
pair_coeff 1 3 lj/cut/coul/long 0.9816 2.85
pair_coeff 2 3 coul/long
bond_coeff 1 450 0.9572
angle_coeff 1 55 104.52
neighbor
              1 bin
neigh_modify every 1 delay 0 check yes
velocity
               all create 300 432567 dist gaussian
fix 1 all box/relax iso 1.0
minimize 1.0e-4 1.0e-6 1000 1000
unfix 1
fix
           NPT all npt temp $T $T 100.0 iso $P $P 1000.0
timestep
               ${dt}
write_restart water_3p.restart
dump
         positions all atom 1000 cu2_tip3p_vf105.lammpstrj
thermo
             1000
thermo_style custom step temp 1x 1y 1z pxx pyy pzz press
      etotal density
```

```
50000
run
### GREEN-KUBO
reset_timestep 0
unfix
            NPT
fix
          NVE all nve
             myKE all ke/atom
compute
             myPE all pe/atom
compute
             myStress all stress/atom NULL virial
compute
compute
             flux all heat/flux myKE myPE myStress
             JJ all ave/correlate $s $p $d c_flux[1] c_flux[2]
fix
        c_flux[3] type auto file J0Jt_vf105_cu2_tip3p.dat
        ave running
variable
             scale equal ${convert_k}/${kB}/$T/$T/$V*$s*${dt}
             k11 equal trap(f_JJ[3])*${scale}
variable
variable
             k22 equal trap(f_JJ[4])*${scale}
variable
             k33 equal trap(f_JJ[5])*${scale}
variable
             k equal (v_k11+v_k22+v_k33)/3.0
variable
             pxy equal pxy
variable
             pxz equal pxz
variable
             pyz equal pyz
fix
             SS all ave/correlate $s $p $d v_pxy v_pxz v_pyz
        type auto file SOSt_vf105_cu2_tip3p.dat ave running
variable
             scale equal ${convert_v}/(${kB}*$T)*$V*$s*${dt}
variable
             v11 equal trap(f_SS[3])*${scale}
variable
             v22 equal trap(f_SS[4])*${scale}
             v33 equal trap(f_SS[5])*${scale}
variable
             20000
thermo
thermo_style custom step temp pxy pxz pyz v_k11 v_k22 v_k33
        v_k v_v11 v_v22 v_v33
             1000000
run
```

#### A.2.2. Calculation of elastic constants of multi-layer hBN

```
units real
atom_style
            full
#Define temperature
variable T equal 300
dimension
               З
boundary
               ррр
log
       green05tension.lammps
pair_style
               hybrid lj/cut/coul/long 8 tersoff
kspace_style ewald 0.0001
#Read data file of hBN with 12 layers
read_data
               12layers.data
lattice fcc 1
#Tersoff potential of Albe
pair_coeff * * tersoff slotmant.tersoff B N B N
#Akiner et al. interlayer parameters
               0.1 bin
neighbor
neigh_modify delay 10 every 2 check yes
               all create T 123456789 dist gaussian
velocity
timestep
               1
variable dens equal 1.66*mass(all)/vol
dump positions all atom 1000 akiner_et_al.lammpstrj
fix 1 all box/relax aniso 0.0
minimize 1.0e-4 1.0e-6 100 1000
unfix 1
fix
          NPT all npt temp 300.0 300.0 100.0 x 0.0
0.0 1000.0 y 0.0 0.0 1000.0 z 0.0 0.0 1000.0
yz 0.0 0.0 1000.0 xz 0.0 0.0 1000.0 xy 0.0
0.0 1000.0 nreset 1000
thermo
             100
```

```
thermo_style custom step temp etotal press pxx
pyy pzz pxy pyz pxz v_dens
run
                 20000
write_restart hbn.restart
# Apply strain
unfix NPT
reset_timestep 0
# Initial length
variable
            lz0 equal lz
fix
                NVT all nvt temp T T 1000 drag 0.4
               100
thermo
thermo_style
              custom step temp etotal press pxx pyy pzz
   pxy pyz pxz lz
run
               100000
unfix NVT
reset_timestep 0
#Compression
              all z delta -0.1 0.1 remap units box
change_box
fix
               NVT all nvt temp T T 1000 drag 0.4
# Relax atoms positions
           1.0e-4 1.0e-6 100 1000
minimize
               100
thermo
thermo_style custom step temp etotal press pxx pyy
   pzz pxy pyz pxz
               100000
run
```

#### A.2.3. Temperature profile calculation for water-hBN interface

```
units real
atom_style
           full
variable
           dt equal 1
log akiner_temperature_q11378rev_LB.lammps
dimension
               3
boundary
               ррр
pair_style
               hybrid coul/long 9 lj/cut/coul/long 9 tersoff
bond_style
               harmonic
angle_style
               harmonic
read_data
               water_hbn_2particle_8layers_60x75x182_q11378.data
dihedral_style none
improper_style none
kspace_style pppm 0.00001
group water type 1 2
group oxygen type 1
group hbn type 3 4 5 6
group 11 molecule 19150
group 12 molecule 19151
group 13 molecule 19152
group 14 molecule 19153
group 15 molecule 19154
group 16 molecule 19155
group 17 molecule 19156
group 18 molecule 19157
lattice fcc 1
####BORON-NITRIDE
pair_coeff * * tersoff slotmant.tersoff NULL NULL B N B N
#B−B
pair_coeff 3 5 coul/long
#N−N
```

Figure A.3: LAMMPS script for the thermal behavior of water-hBN interface

```
pair_coeff 4 6 lj/cut/coul/long 0.2496 3.1461
#B−N
pair_coeff 4 5 lj/cut/coul/long 0.007 3.75
pair_coeff 3 6 lj/cut/coul/long 0.007 3.75
#WATER
pair_coeff 1 1 lj/cut/coul/long 0.102 3.188
pair_coeff 2 2 coul/long
pair_coeff 1 2 coul/long
####CROSS-RELATIONS
###WITH OXYGEN
#lorentz-berthelot
pair_coeff 1 4 lj/cut/coul/long 0.15956 3.16705
pair_coeff 1 3 coul/long
#lorentz-berthelot
pair_coeff 1 6 lj/cut/coul/long 0.15956 3.16705
pair_coeff 1 5 coul/long
###WITH HYDROGENS
#BN has only Colombic interactions with hydrogen of water
pair_coeff 2 3 coul/long
pair_coeff 2 4 coul/long
pair_coeff 2 5 coul/long
pair_coeff 2 6 coul/long
bond_coeff 1 450 0.9572
angle_coeff 1 55 104.52
neighbor
                0.1 bin
neigh_modify
                delay 0 every 1 check yes
velocity
                all create $T 432567 dist uniform
            NPT all npt temp 300.0 300.0 100.0 x 0.0 0.0
fix
1000.0 y 0.0 0.0 1000.0 z 0.0 0.0 1000.0
couple none nreset 1000
minimize 1.0e-4 1.0e-6 200 1000
```

```
timestep
               ${dt}
dump positions all atom 10000 akiner_temperature_size2dump.lammpstrj
write_restart water_hbn_nanolayer_akiner.restart
               10000
thermo
thermo_style custom step temp pxx pyy pzz lx ly lz
               100000
run
reset_timestep 0
unfix NPT
fix NVE all nve
#### RNEMD ####
## Equilibrate the system for imposed heat flux
fix heat_swap_eq oxygen thermal/conductivity
200 z 20 swap 20
compute surf1_com l1 com
compute surf2_com 18 com
               10000
thermo
thermo_style custom step temp etotal press c_surf1_com[3]
c_surf2_com[3]
               100000
run
unfix heat_swap_eq
#T calculation using kinetic theory
fix heat_swap oxygen thermal/conductivity
200 z 20 swap 20
## FIRST SURFACE
variable zhigh_s1_1 equal c_surf1_com[3]-2.7
variable zlow_s1_1 equal c_surf1_com[3]-3.7
variable zhigh_s1_2 equal c_surf1_com[3]-3.7
variable zlow_s1_2 equal c_surf1_com[3]-4.7
variable zhigh_s1_3 equal c_surf1_com[3]-4.7
variable zlow_s1_3 equal c_surf1_com[3]-5.7
variable zhigh_s1_4 equal c_surf1_com[3]-5.7
```

```
variable zlow_s1_4 equal c_surf1_com[3]-6.7
variable zhigh_s1_5 equal c_surf1_com[3]-6.7
variable zlow_s1_5 equal c_surf1_com[3]-7.7
variable zhigh_s1_6 equal c_surf1_com[3]-7.7
variable zlow_s1_6 equal c_surf1_com[3]-8.7
region nanolayer_r1_1 block INF INF INF INF
${zlow_s1_1} ${zhigh_s1_1}
region nanolayer_r1_2 block INF INF INF INF
${zlow_s1_2} ${zhigh_s1_2}
region nanolayer_r1_3 block INF INF INF INF
${zlow_s1_3} ${zhigh_s1_3}
region nanolayer_r1_4 block INF INF INF INF
${zlow_s1_4} ${zhigh_s1_4}
region nanolayer_r1_5 block INF INF INF INF
${zlow_s1_5} ${zhigh_s1_5}
region nanolayer_r1_6 block INF INF INF INF
${zlow_s1_6} ${zhigh_s1_6}
compute nanolayer_n1_1 water temp/region
nanolayer_r1_1
compute nanolayer_n1_2 water temp/region
nanolayer_r1_2
compute nanolayer_n1_3 water temp/region
nanolayer_r1_3
compute nanolayer_n1_4 water temp/region
nanolayer_r1_4
compute nanolayer_n1_5 water temp/region
nanolayer_r1_5
compute nanolayer_n1_6 water temp/region
nanolayer_r1_6
#SECOND SURFACE
variable zhigh_s2_1 equal c_surf2_com[3]+2.7
```

```
variable zlow_s2_1 equal c_surf2_com[3]+3.7
variable zhigh_s2_2 equal c_surf2_com[3]+3.7
variable zlow_s2_2 equal c_surf2_com[3]+4.7
variable zhigh_s2_3 equal c_surf2_com[3]+4.7
variable zlow_s2_3 equal c_surf2_com[3]+5.7
variable zhigh_s2_4 equal c_surf2_com[3]+5.7
variable zlow_s2_4 equal c_surf2_com[3]+6.7
variable zhigh_s2_5 equal c_surf2_com[3]+6.7
variable zlow_s2_5 equal c_surf2_com[3]+7.7
variable zhigh_s2_6 equal c_surf2_com[3]+7.7
variable zlow_s2_6 equal c_surf2_com[3]+8.7
region nanolayer_r2_1 block INF INF INF INF
${zhigh_s2_1} ${zlow_s2_1}
region nanolayer_r2_2 block INF INF INF INF
${zhigh_s2_2} ${zlow_s2_2}
region nanolayer_r2_3 block INF INF INF INF
${zhigh_s2_3} ${zlow_s2_3}
region nanolayer_r2_4 block INF INF INF INF
${zhigh_s2_4} ${zlow_s2_4}
region nanolayer_r2_5 block INF INF INF INF
${zhigh_s2_5} ${zlow_s2_5}
region nanolayer_r2_6 block INF INF INF INF
${zhigh_s2_6} ${zlow_s2_6}
compute nanolayer_n2_1 water temp/region
nanolayer_r2_1
compute nanolayer_n2_2 water temp/region
nanolayer_r2_2
compute nanolayer_n2_3 water temp/region
nanolayer_r2_3
compute nanolayer_n2_4 water temp/region
nanolayer_r2_4
```

```
compute nanolayer_n2_5 water temp/region
nanolayer_r2_5
compute nanolayer_n2_6 water temp/region
nanolayer_r2_6
compute Tsurf1 11 temp
compute Tsurf2 18 temp
compute T12 12 temp
compute T13 13 temp
compute T14 14 temp
compute T15 15 temp
compute T16 16 temp
compute T17 17 temp
fix swap_heat all ave/time 100000 1 100000
f_heat_swap file heat_q11378LB.out mode scalar
thermo
                10
thermo_style custom step temp etotal press c_nanolayer_n1_6
c_nanolayer_n1_5 c_nanolayer_n1_4 c_nanolayer_n1_3
c_nanolayer_n1_2 c_nanolayer_n1_1 c_Tsurf1 c_T12
c_T13 c_T14 c_T15 c_T16 c_T17 c_Tsurf2
c_nanolayer_n2_1 c_nanolayer_n2_2 c_nanolayer_n2_3
c_nanolayer_n2_4 c_nanolayer_n2_5 c_nanolayer_n2_6
c_surf1_com[3] c_surf2_com[3]
               300000
run
```

# A.2.4. Muller-Plathe algorithm and temperature calculation for a TIP5P water and Cu system

```
units real
atom_style full
variable
               dt equal 1
log
          tip5p_copper_block68x68x194.lammps
variable
               Na equal 6.02214179
dimension
               3
boundary
                ррр
                hybrid lj/cut/coul/long 9 coul/long 9 lj/cut 9
pair_style
bond_style
                none
angle_style
                none
read_data
                tip5p_copper_block68x68x194.data
                nanoparticle1r sphere 14.2570 14.2998 24.8650 5
region
  side in units box
            nanoparticle2r sphere 14.0070 14.0498 76.9715 5
region
  side in units box
         nanoparticlesr union 2 nanoparticle1r nanoparticle2r
region
create_atoms
              4 region nanoparticlesr
       nanoparticles region nanoparticlesr
group
#Visualization of the nanoparticles and surrounding water
region visualr block INF INF 0 15 INF INF units box
group visual region visualr
dihedral_style none
improper_style none
kspace_style pppm 0.00001
group tip5p type 1 2 3
group copper type 4
group oxygen type 1
group hydrogen type 2
group lone type 3
```

Figure A.4: LAMMPS script for the thermal behavior of TIP5P water in a nanogap
```
##WATER
#TIP5P
pair_coeff 1 1 lj/cut/coul/long 0.178 3.097
pair_coeff 1 2 coul/long
pair_coeff 1 3 coul/long
pair_coeff 1 4 lj/cut 1.2967 2.8049
pair_coeff 2 2 coul/long
pair_coeff 2 3 coul/long
pair_coeff 2 4 none
pair_coeff 3 3 coul/long
pair_coeff 3 4 none
pair_coeff 4 4 lj/cut 9.4469 2.5129
               1 bin
neighbor
neigh_modify
               delay 0 every 1 check yes exclude molecule tip5p
velocity
               all create 300 432567 mom yes rot yes dist uniform
run O
velocity all scale 300
fix RIGID tip5p rigid/npt/small molecule temp 300.0 300.0
100.0 x 1.0 1.0 1000.0 y 1.0 1.0 1000.0 z 1.0 1.0
1000.0 couple none
            NPT copper npt temp 300.0 300.0 100.0 x 1.0 1.0
fix
1000.0 y 1.0 1.0 1000.0 z 1.0 1.0 1000.0 couple none
dump positions visual atom 100 tip5p_copper_np.lammpstrj
timestep
               ${dt}
write_restart water_tip5p.restart
fix
      mom_copper copper momentum 10 linear 0 0 1
                1
thermo
thermo_style custom step temp 1x 1y 1z pxx pyy pzz press etotal
                1000000
run
reset_timestep 0
unfix RIGID
```

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Figure A.4 (Cont.)

```
unfix NPT
fix RIGID tip5p rigid/nve/small molecule
fix NVE copper nve
fix heat_swap_eq copper thermal/conductivity
200 z 20 swap 3
               10000
thermo
thermo_style custom step temp etotal press f_heat_swap_eq
               1000000
run
unfix heat_swap_eq
reset_timestep 0
compute ke all ke/atom
variable zmin equal zlo
variable dz equal (zhi-zlo)/20
compute cc1 all chunk/atom bin/1d z ${zmin} ${dz} units box
fix KE all ave/chunk 10000 10 100000 cc1 c_ke temp
norm all file ke.profile
compute nO oxygen property/chunk cc1 count coord1
compute nH hydrogen property/chunk cc1 count coord1
compute nL lone property/chunk cc1 count coord1
fix N all ave/time 10000 10 100000 c_nO[*] c_nH[*] c_nL[*]
file atoms.out mode vector
fix heat_swap copper thermal/conductivity 200 z 20 swap 3
                100000
thermo
thermo_style custom step temp etotal press f_heat_swap
               1000000
run
```

Figure A.4 (Cont.)