Modeling and simulation of the structural evolution and thermal properties of ultralight aerogel and 2D materials

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2014

Yeo, J. J. (2014). Modeling and simulation of the structural evolution and thermal properties of ultralight aerogel and 2D materials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61804>

<https://doi.org/10.32657/10356/61804>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

School of Mechanical and Aerospace Engineering

**MODELING AND SIMULATION OF THE
STRUCTURAL EVOLUTION AND THERMAL
PROPERTIES OF ULTRALIGHT AEROGEL
AND 2D MATERIALS**

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2014

Abstract

In this thesis, the thermal properties of novel ultralight materials, namely silica aerogels and 2D graphene and silicene, are investigated and established through classical molecular dynamics (MD). In addition, the construct and evolution of the atomic/molecular structures of these ultralight aerogels and 2D materials are explored and realized through various MD simulation schemes.

The aerogel study involves two simulation steps, where the percolated structures of silica aerogel at various densities are first modeled using negative pressure rupturing, while reverse non-equilibrium molecular dynamics (RNEMD) is performed to determine the thermal conductivities of these aerogel samples. Two potential functions were employed in this study, namely the widely used Beest-Kramer-Santen (BKS), and the re-parameterized Tersoff. Results obtained based on the BKS potential followed the power-law variation reminiscent of sintered aerogel characteristics. To achieve a higher accuracy for bulk amorphous silica, the re-parameterized Tersoff potential was found to be superior to the BKS potential, when comparing the vibrational density of states with previous experimental studies. By fitting the results using a power-law variation, the trend of the thermal conductivities successfully mirrored power-law trends of experimental bulk aerogel. Due to finite sizes of pores that can be represented, where increasing simulation length scales leads to an increase in the largest pore size that can be modeled, current quantitative results are consistently higher but within the same order of magnitude as experimental bulk aerogel.

For the analysis of 2D materials, graphene and silicene are considered. There are two major components in this 2D materials simulation study. Firstly, the exfoliation phenomenon of graphite is investigated. This is modeled through MD simulations, where the compression of AB-stacked graphite flakes between hydrogen-terminated silicon substrates leads to the exfoliation of graphene layers. It is shown that this phenomenon occurs through the activation of an inter-layer superlubricity regime, caused by torque-induced spontaneous rotations of the layers due to in-plane shear of graphite during compression. Secondly, the thermal properties of graphene and silicene are established through RNEMD simulations using the adaptive intermolecular reactive empirical bond order (AIREBO) potential. Of special interest in this study is the effects of defects, such as double vacancies and Stone-Thrower-Wales (STW) defects, on the thermal conductivities of graphene nanoribbons when compared with their

pristine structures. It was found that thermal conductivities can fall by more than 80% with just 10% coverage of defect density, and these reductions occur over a wide temperature range of 100K to 600K. Finally, the thermal conductivity of nano- to micron-sized silicene and graphene monolayers are analyzed and compared. Across all length scales, silicene has significantly lower thermal conductivity than graphene, and this was found to be attributed to the lower phonon group velocities of the dominant acoustic modes in silicene.

Acknowledgments

The author would like to express his profound gratitude to his supervisors, Associate Professor Ng Teng Yong and Professor Liu Zishun, for their encouragement, guidance, and support throughout his research. They have brought these and many other interesting research topics to my attention, and patiently guided the author to achieve research excellence. The author is also grateful to his family and close friends, who stood sentry in times of adversity. The author would like to thank Professor Gao Huajian, the Walter H. Annenberg University Professor of Brown University, as well as all members in his research group. The warmth and friendship bestowed during the author's research attachment in Brown University will always be treasured, together with invaluable insights into computational solid mechanics and their applications. The author would also like to thank the staff in HPC@NTU and A*STAR ACRC for providing valuable technical support during the compilation and running of the programs. Many thanks goes out to the staff of Nanyang Technological University as well as the A*STAR Graduate Academy for their kind support throughout my studies. This work is supported by the Agency for Science, Technology and Research (A*STAR), and the Infocomm Development Authority (IDA) of Singapore. Last but not least, I dedicate the finishing of this work to the dear angel who came into my life unexpectedly.

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List of Symbols

A	Cross-sectional area
A_{ij}	Adjustable parameter in interatomic potential functions
B_{ij}	Adjustable parameter in interatomic potential functions
b_{ij}	Bond-order term between atoms i and j
C	Elastic modulus
C_V	Heat capacity at constant volume
C_L	Center of sphere to determine pore sizes
C_v	Velocity autocorrelation function
C_λ	Prefactor in power-law equation for silica aerogel's solid thermal conductivity
C_{ij}	Adjustable parameter in interatomic potential functions
c_i	Adjustable parameter in interatomic potential functions
D	Diameter of sphere to determine pore sizes
D_{ij}	Connectivity switch
d_i	Adjustable parameter in interatomic potential functions
f_i	Vector of forces acting on an atom
f^c	Cutoff function in Tersoff potential
G	Arbitrary system thermodynamic quantity to be determined in statistical mechanics
g	Number of independent momentum degrees of freedom of the system
g_i	Fifth-order spline

H	Hamiltonian function
h_i	Adjustable parameter in interatomic potential functions
i	Atom index
j	Atom index
j^e	Heat flux
K	Kinetic energy function
k	Atom index
k_B	Boltzmann constant
l	Bond length
M	Index for the series of measurements to determine G
m_i	Atomic mass of each atom i
N_m	Number of particles/atoms
N_{swap}	Total number of swaps
n_i	Adjustable parameter in interatomic potential functions
$\mathbf{p}_i$	Vector momenta of each atom i
P	Pressure
P_{ij}	Adjustable parameter in interatomic potential functions
p_i	Scalar momentum of each atom i
$P_{ij}^{\sigma\pi}$	Covalent bond interaction parameter
Q	Fictitious mass of heat bath in Nos é-Hoover thermostat
Q_{ij}	Adjustable parameter in interatomic potential functions
$\mathbf{q}_i$	Generalized vector coordinates of each atom i

q	Atomic charge
$\mathbf{r}_i$	Cartesian vector coordinates of each atom i
$\mathbf{r}_{ij}$	Vector distance between two atoms i and j
R	Adjustable parameter in interatomic potential functions
R_C	Radius of sphere to determine pore sizes
r	Radius of an atom
r_c	Limiting atomic separation cutoff for Lennard-Jones potential
r_{ij}	Scalar distance between two atoms i and j
$\ddot{\mathbf{r}}_i$	Scalar acceleration of atom i
S	Adjustable parameter in interatomic potential functions
S_i	Distance between center of sphere to the i -th atom for determining pore sizes
$S(t)$	Universal switching function
$S'(t)$	Switching function
s	Extended coordinates in Nosé-Hoover thermostat
T	Temperature
t	Time
t_c, t_r, t_b	Scaling functions
U	Potential energy function
U_{ij}^{LJ}	Total Lennard-Jones interaction energy
U_{ij}^{REBO}	Total REBO interaction energy
U_{kijl}^{tors}	Total torsional interaction energy
V^{tors}	Torsional interaction function

V_{ij}^A	Attractive pairwise atomic interaction function
V_{ij}^{LJ}	Lennard-Jones potential
V_{ij}^R	Repulsive pairwise atomic interaction function
v	Velocity of atom
w_{ij}	Interaction weighting factor
α	Cartesian coordinate index
α_{ij}	Adjustable parameter in interatomic potential functions
β	Inverse of the product of the Boltzmann constant, k_B , and temperature, T
β_{ij}	Adjustable parameter in interatomic potential functions
γ_{ij}	Adjustable parameter in interatomic potential functions
δt	Timestep
δt_s	Extended timestep in Nos é-Hoover thermostat
ε_{ij}	Depth of energy well for atomic interactions between atoms i and j
ζ	Exponent in power-law equation for silica aerogel's solid thermal conductivity
$\Theta(t)$	Heaviside step function
θ	Bond angle
λ	Thermal conductivity
λ_s	Solid thermal conductivity of silica aerogel's porous structure
λ_T	Velocity scaling factor
λ_{ijk}	Adjustable parameter in interatomic potential functions
μ	Chemical potential

μ_{ij}	Adjustable parameter in interatomic potential functions
ρ	Density
σ_{ij}	Finite distance over which atomic interactions are zero between atoms i and j
τ_i	Vector of torques acting on an atom
ω	Dihedral angle

Chapter 1

Introduction

Most of the materials presented in this thesis have been published previously in peer-reviewed journals and conferences [1-8]. Driven by the never-ending search for increasingly lighter, stronger, and cheaper engineering materials, numerous classes of ultralight materials have been introduced over the past few decades. One such class of materials is known as aerogels, where the intent is to introduce extreme porosity to dramatically reduce the weight of the material, yet simultaneously attempting to maximize its strength and toughness. Another approach, successfully developed in recent years, is to drastically reduce the thickness of the materials till they are merely a few atoms, or even one atom, in thickness. The thermal and mechanical properties of this novel class of materials have been found to be extremely remarkable. Various materials of this pedigree include those made from carbon (dubbed graphene), and silicon (silicene). In this chapter, an introduction to the background of silica aerogels, graphene, and silicene will be presented, including their synthesis, characterization, and uses.

1.1. Silica Aerogel

The exceedingly porous material dubbed silica aerogel was initially synthesized in the early 1930s by S. S. Kistler [9, 10], when he attempted to remove liquid from a wet gel through supercritical drying. Supercritical drying is a method of removing liquid from a gel, by allowing the liquid-gas phase boundary to become indistinguishable due to high temperatures and pressures. Simply drying the gels by evaporating the liquid in air would result in high surface tensions, generated due to the formation of liquid-vapor interfaces. This caused the collapse and shrinkage of the gel to form xerogels [11], with porosities that

reached only about 50%. Formation of the nanostructures comprising the solid network of aerogels requires a multistep process, involving polymerization, gelation, hydrolysis, and condensation. Polymerization involves the crosslinking of linear oligomers of particulate colloidal silica. The gelation stage is where the liquid gel undergoes a sol-gel transition continuously. These two processes are driven by hydrolysis and condensation of the water or alcohol. The first precursor used to create the silica gels was sodium metasilicate Na_2SiO_3 [9]. Nowadays, alkoxides of $\text{Si}(\text{OR})_4$ are frequently used. R and OR denotes alkyl and alkoxide groups respectively. Newer and faster methods of producing silica aerogels include hydrolyzing tetramethoxysilane (TMOS), where a methyl group CH_3 comprises the R group. This is dissolved in methanol, following the reaction,

Another possible precursor is tetraethoxysilane (TEOS), where the R group is ethyl. Polycondensation results in the silica molecules forming a coherent network within the alcohol and can be dried supercritically.

A wide list of precursors (and mixtures of these precursors) derived from alkoxide are in use today, such as 3-(2-aminoethylamino) propyltrimethoxysilane (EDAS), polyethoxysilane (PEDS), and perfluoroalkylsilane (PFAS) [10]. The reason for such a varied range of precursors is that some precursors can enhance certain desired chemical properties of the resulting gel. The nature of the solvent, nature and concentration of the catalyst, the molar ratio of precursors to water, and the concentration of precursors are all important parameters that can alter the nanostructures and properties of the resulting

aerogel. Some of the properties that can possibly be varied include the pore size distribution and density [10].

Furthermore, aerogels can potentially be based on many other materials, resulting in aerogels that are not silica-based and having widely-varying properties. This allows for the tailoring of the properties to suit the specific application desired, especially useful since silica aerogels have rather poor mechanical properties. These gels can also be made opaque, and electrically and thermally conductive, amongst many other possibilities. Some examples of other precursors that are not based on silica include carbon, sodium silicate, zirconium dioxide, and many other organic and inorganic materials. A comprehensive compendium of aerogels outside of silica aerogels are detailed in the Aerogel Handbook [10].

The mechanical properties of pure silica aerogels tend to be very poor, and they are largely dependent on the density and connectivity of the silica network. Elastic compression of silica aerogels can be easily achieved, reaching approximately 50% contraction as compared to its length [10]. Strengthening of silica aerogels can be attained through processes like hybridization, doping, and aging. Despite these drawbacks, silica aerogels have numerous desirable properties. These include being non-toxic to the environment, extremely low thermal conductivities, and being translucent [12]. Due to these properties, silica aerogels are highly suitable for applications in dielectrics for integrated circuits (ICs), passive solar energy collection devices, and thermal and acoustic insulation in buildings and appliances [13]. Plastics produced from chlorofluorocarbons, used in thermal insulation of refrigerators, can also be substituted by aerogels. The most well-known application was in Cherenkov radiators as Cherenkov counters [14]. Their extremely low

density for a solid is another crucial characteristic. Silica aerogel's density can go as low as 0.003g/cm^3 . This value is only three times higher than that of air which is approximately 0.0012g/cm^3 . Thus, drastic weight savings can be obtained if silica aerogels can be modified for usage in various monolithic structures. Other applications of silica aerogels include the sorption, entrapment, storage, and release of a huge range of nanoparticles and molecules. These functions are possible due the extremely high porosity of the aerogel [10].

Large-scale commercial production of modern porous aerogel is encouraging greater proliferation of the usage of silica aerogels as thermal insulators [15-17]. These aerogels generally take the form of granular beads due to the greater flexibility in terms of tailoring the optical and thermal properties for the required application when used as fillers [18]. Some examples include thermal insulation of windows [19, 20], passive solar windows [21], as well as cryogenic thermal insulation systems on space launch vehicles [22, 23]. It was also theoretically found that a window using aerogel as insulation could possibly reduce its thermal conductance by more than half using just 5mm thick aerogel [19]. This was a reduction that was significantly more than those of double-glass windows. Another study also stated that using silica aerogels enabled the two recent Mars Rovers, Spirit and Opportunity, to be kept at relative steady temperatures, despite the fact that there were more than $100\text{ }^{\circ}\text{C}$ variations in temperatures on the surface of Mars [22].

Figure 1.1. The extremely low thermal conductivity of silica aerogel is demonstrated through the lighting of a burner underneath the translucent blue aerogel, and the flower shows no signs of excessive heat. Image courtesy of www.aerogel.org

Experimental characterizations of the thermal transport mechanisms in aerogels have been performed in previous studies through various methods [24-27]. The total thermal conductivity of monolithic silica aerogels can be broken down into separate components of gaseous, solid, and radiative thermal conductivity. There is negligible coupling between the different modes of heat transfer, and gases do not convect heat within the pores [24]. Experimental studies showed that the high amount of pores effectively restricted the movement of local excitations within the skeletal aerogel backbone. This led to significant reductions in the solid thermal conductivity of silica aerogels in comparison with non-porous monolithic forms of amorphous silica.

Furthermore, a power-law variation of the solid thermal conductivity with density was found, such that

$$\lambda_s = C_\lambda \rho^\zeta \quad (1.1)$$

where the factor C_λ changes according to the connectivity of the particles within the aerogel, and for silica aerogels with densities, ρ , between 0.3 to 1g/cm³, ζ was approximately 1.6 [28].

Numerical characterizations of the mechanical properties of silica aerogel have also been attempted in many previous studies; various methods were used, and they mainly focused on accurate reproductions of the porous and fractal nature of silica aerogels [29-35]. Fractal geometry is frequently used to describe the architecture of silica aerogels, where fractality refers to self-similar patterns that appear geometrically similar when viewed up close or from afar. The degree of fractality of a structure is typically described by the fractal dimension. The fractal dimension of silica aerogels can be determined experimentally through methods such as small-angle neutron scattering (SANS) spectroscopy, adsorption of molecules of different cross-sectional areas, or small or ultra-small-angle x-ray scattering (SAXS/USAXS).

In terms of molecular dynamics (MD) simulation of silica aerogels, Kieffer and Angell [29] used an interaction potential of the Born-Mayer form to gradually expand a well-thermalized sample of amorphous silica. This expansion caused the Si-O bonds to rupture under negative pressures and, upon relaxation, form fractal structures. This method was dubbed negative pressure rupturing by Kieffer and Angell [29]. The fractal dimension was

determined to be somewhat similar to experimental porous silica. In a similar vein, Nakano *et al.* [30] also gradually expanded an amorphous silica sample to the required density and studied the structural correlations of such porous samples, using an interaction potential that consists of two- and three-body terms, known as the Vashishta potential [36]. The internal surface area, pore surface-to-volume ratio, pore-size distribution, fractal dimension, correlation length, and mean-particle size were determined as a function of the density. Murillo *et al.* [35] developed an expanding, heating, and quenching method to characterize the mechanical properties of silica aerogels. They found that their method was able to achieve a good fit for the elastic moduli as compared with experimental results, but not the strength. Other methods are also available to model silica aerogels [31-34] but these are generally more complex or requires greater computational power. For example, in a later work, Kieffer *et al.* [33] used a reactive force field in MD with charge transfer to model sol-gel synthesizing in an aqueous environment.

However, these methods have not been utilized to characterize the thermal properties of silica aerogel. In contrast, all these studies largely concentrated on characterizing the geometrical, mechanical, and chemical properties of silica aerogel as mentioned above. It is still not known whether these methods of producing the aerogel porous skeleton can also reproduce the thermal features of bulk aerogel, especially their extremely low thermal conductivities. This is an interesting issue that requires further investigation. Further discussion of the simulation of silica aerogels using MD will be presented in Section 2.3.

1.2. Graphene

There is a remarkable increase in interest in the very unique properties of many novel two-dimensional materials synthesized or theorized of late. These materials typically consist of a single atomic plane, and the properties can be further functionalized or tailored, through atomic doping or defects. One such material is a carbon monolayer, known as graphene. The successful synthesis of graphene [37] has led to the advent of many new possible technological developments [38], largely due to its exceptional electronic and thermal properties [39-42]. Graphene is a two-dimensional, single layer of carbon atoms arranged in a honeycomb lattice structure with sp^2 bonds. It is the constitutive component in most carbon-based materials, including graphite and carbon nanotubes (CNTs). Early attempts to isolate graphene layers were through chemical intercalation and exfoliation of bulk graphite. However, this resulted in a sludge largely made up of scrolled and restacked graphene sheets. This form of graphene attracted limited attention due to their uncontrollable nature. Some attempts have also been made to grow graphene in the same way as CNTs, but this resulted in highly layered graphene with the number of layers in the region of hundreds [38].

Recent advances in the production of graphene resulted in multiple possible methods of preparing graphene in numerous varieties, allowing graphene of different quality, shapes, sizes, and quantity to be produced. If the focus is only placed on the methods which are scalable, the main methods are chemical vapor deposition (CVD), exfoliation of graphite (or other layered materials to produce other monolayers) in solvents, and graphene growth on various substrates (typically silicon carbide) [43]. Polycrystalline graphene can be deposited as large and uniform films on copper substrates through CVD, and transferred to another substrate desired [44]. This method proves to be very promising for many

applications, even though many defects are present. Future research in this area is focused on the deposition of graphene on arbitrary surfaces, as well as minimizing the defects while maximizing the area covered. The method of exfoliating graphite using solvents involves exposing graphite to solvents that favorably maximizes the total area of graphite due to surface tension. This is treated with sonication and centrifugation to yield large amounts of monolayered graphene flakes [45]. Another similar alternative is to oxidize graphite pellets, exfoliate through sonication in a solution, centrifugated, deposited on a substrate, and reduced back to graphene. Creating graphitic layers through sublimation of silicon atoms in silicon carbide wafers is another possible route. Such a method has been found to be capable of controllably creating high quality graphene [46], albeit at high cost, and high temperatures are needed.

In our study of the mechanical properties of graphene, we have also uncovered for the first time another possible method of exfoliating graphene by activating a phenomenon known as superlubricity [47-49] between graphite layers. This phenomenon causes a systematic drop in the friction between two crystalline surfaces, due to incommensurate contact. Some conditions required to activate superlubricity includes crystallinity, atomic flatness and hardness, and passivation of the underlying substrate activating the superlubricity in graphite. Plastic deformations or disorder of the surfaces in contact could result in the inability to activate superlubricity [50, 51]. Passivation of the substrate surface prevents the formation of covalent bonds and keeps the surface chemically stable at ambient conditions to be appropriate for activating superlubricity [52]. An example of this is hydrogen-terminated (H-terminated) silicon substrates which we will be using in our MD studies. Superlubricity can be observed to occur through forced rotation of the layers in lamellar materials with respect to each other, such as molybdenum disulphide [53] and the afore-

mentioned graphite at micrometer scales [54, 55]. Sliding of graphite flakes on crystalline substrates has also been observed to give rise to spontaneous rotations in the layers due to superlubricity [56].

There are also several methods of characterizing exfoliated graphene, in order to determine properties such as its thickness and crystallinity. One of the first methods used that is still widely used today is atomic force microscopy (AFM). This is mainly used to estimate the number of graphene layers [57]. Another technique is through X-ray diffraction (XRD). Employing copper K-alpha radiation with a wavelength 0.154nm, graphite induces an acute (002) Bragg reflection where 2θ is approximately 26° . As the number of layers decrease, this peak broadens gradually, and this broadening can be used together with the Scherrer formula to estimate the number of graphene layers [58]. A relatively more accessible and low-cost method of approximating graphene's average thickness is through the Brunauer, Emmett, and Teller (BET) surface area. The specific surface area of single-layer graphene is known to be $2,630\text{m}^2/\text{g}$. As layer thickness increases, this value will decrease [58]. Another very useful and commonly used technique is Raman spectroscopy, as the differences in the Raman spectra across different graphene layers are very significant. The intensity of the G Raman band of monolayered graphene will be half that of the 2D band, while the 2D band is weaker than the G band in double-layered graphene, with an additional shift to a higher wavenumber and possessing a different shape. Lastly, transmission electron microscopy (TEM) can directly observe suspended graphene's atomic structure.

Graphene holds much promise in nanoelectronics applications, as it is a semiconductor with zero bandgap with significantly higher electron mobility compared to silicon, hence

graphene is a very promising next-generation semiconductor material [38, 41]. Additionally, as graphene also possesses excellent thermal conductivity properties, many potential engineering applications are expected for graphene in the realm of thermal management [59]. Thermal dissipation has been one particularly important area that received much attention in experimental, as well as theoretical, research efforts [42, 60-67]. The mechanical properties of single-layered graphene were directly measured using nanoindentation [68]. This was performed using AFM to indent suspended graphene monolayers, and the stress-strain curve was derived. The stress-strain curve of graphene was eventually non-linear as strain increased, and fractured when strain exceeded 20%. Young's modulus was found to be approximately 1,000 GPa. Density functional theory (DFT) analysis of the stress-strain curve of single-layered graphene found good agreement with experimental results [69]. It was determined that at high strains, crystallographic direction significantly affect the deformation behavior of graphene. The strength was found to be approximately 107 to 121 GPa, in good agreement with experimental values.

Recently, several experimental measurements using Raman spectroscopy have found very high thermal conductivities of pristine graphene ranging from 2,500 to 5,300 W/(m K) [42, 60, 64]. However, theoretical analyses of pristine graphene using MD suggests that due to edge effects, graphene possesses significant anisotropic thermal conduction [62, 63, 65, 67]. Moreover, the synthesis, processing, and integration of graphene and CNTs could result in various defects, which could significantly affect the properties of graphene. These include defects such as point vacancies, impurities, and dislocations [70], among others. These defects could also be intentionally manufactured or applied, for the purpose of adjusting the properties of graphene to suit the requirements of the application, in the same spirit as methods that are currently applied in the nanodesign of nanomaterials [71-74]. Such defects

are known to have profound influences on chemical and physical properties. For instance, increasing defect concentration could significantly decrease the electronic conductivity in CNTs, as well as lowering reaction barriers [75, 76].

In an earlier work [63], the effects of vacancies and edge roughness on the thermal conductivity of graphene nanoribbons (GNRs) have been studied through MD. GNRs are thin graphene strips with finite widths and edges, as opposed to infinitely wide monolayers of graphene. It was found that an increasing number of vacancies led to a significant decrease of almost 50% in the thermal conductivity of GNRs at room temperature. Also, another MD study found that random hydrogenation of pristine graphene led to drastic decreases in its thermal conductivity, up to a certain amount of hydrogen coverage [77]. Another class of topological defects that has significant effects on the properties of graphene is the Stone-Thrower-Wales (STW) defect [78, 79]. STW defects are the result of a 90 degree rotation of two carbon atoms relative to the midpoint of their pairwise bond. With the recent advancements in high-resolution transmission electron microscopy, more STW defects can be observed and characterized in graphene [80]. STW defects are known to have an impact on various properties of graphene. Experimentally, it was found that STW defects could quench the spin-polarized gap state caused by adsorption of hydrogen atoms on graphene sheets, and also change the local density of states [81, 82]. Moreover, it has been theoretically and experimentally shown that STW defects can be created through methods such as ion irradiation, electron irradiation and scanning tunneling microscopy [72, 83, 84]. However, it is not eminently clear whether STW defects significantly affect the thermal conductivity of GNRs, due to a lack of both experimental and theoretical evidence.

1.3. Silicene

Along with the significant attention to graphene, significant interest has also been generated in new single-layered materials synthesized from silicon (dubbed silicene), boron nitride, and molybdenum disulphide. While silicon and carbon possess electronic configurations that are very much alike, honeycomb structures are not spontaneous and energetically favorable in silicon due to the fact that sp^3 hybridization in silicon is more stable than sp^2 [85], in contrast with carbon, where the reverse is true. Owing to the prevalence and maturity of silicon and its corresponding production technology in electronics, it seems to be a logical extension to synthesize graphene-like structures from silicon [86-89], in order to take advantage of existing technology to create new products.

The first likely synthesis of a silicene-like material is reported by Nakano *et al.* [90], where CaSi_2 is chemically exfoliated to produce Mg-doped, oxygen-bonded silicon sheets. Currently, the focus of efforts in this area of research has so far been on the epitaxial growth of single- and multi-layered silicon [86, 87, 91-93], typically on silver substrates with different surface orientations such as on Ag(111), Ag(110), and Ag(100) surfaces. These researches have revealed that silicene possessed structures that are very similar to the honeycombs of graphene. Latest research also indicates the ability to create multi-layered silicene [91].

Theoretical studies of the mechanical and thermal properties are relatively scarce compared to the somewhat more extensive literature on their electronic properties [93, 94]. At the point of writing this thesis, there is yet to be any experimental characterizations of the mechanical and thermal properties of silicene to the best of the author's knowledge. Jing *et al.* [95] employed *ab initio* calculations and MD simulations to jointly determine and

corroborate the mechanical properties of silicene nanoribbons. For the MD simulations, results from different potentials were compared, such as the environment-dependent interatomic potential (EDIP) [96], the Stillinger–Weber (SW) [97], the Erhart-Albe [98], and the modified embedded-atom (MEAM) [99] potentials. It was found that silicene's Young's modulus as predicted by EDIP is of a closer match to *ab initio* calculations than the other potentials used. *Ab initio* calculations determined Young's moduli of 148.5GPa and 140.7GPa for zigzag and armchair silicene respectively. Uniaxial tensile test on bulk silicene also found lower values of critical strain and stress in the armchair direction than in the zigzag direction. Size effects were also found, where increases in the size of the nanoribbons led to increases in the Young's modulus. In another approach, Roman and Cranford [100] used MD simulations and the reactive force-field (ReaxFF) [101] and determined that the in-plane stiffness of silicene is approximately one-fifth that of graphene's stiffness, and its strength approximately 15% of graphene's. They found that the likely reason, as determined by the ReaxFF, is that silicon's single bond is half as stiff and strong as that of carbon's. The ultimate strain was also found to be approximately 18%, and the effective bending stiffness was quantified to be 38.63eV per unit width.

Mechanical or chemical means of exfoliation of creating free-standing silicene should not be too far off in the scientific horizon, as knowledge and expertise in this area become more enhanced. For now, silicene's properties are poorly understood due to its novelty; hence, theoretical characterization of silicene is being delved into first, such as through tight binding and density functional theory to analyze silicene's geometric and electronic structures, and the adsorption and hydrogenation of silicene. In this study, the thermal properties of silicene will be determined using MD and compared with that of graphene.

1.4. Research Objectives

The objectives of this thesis are as follows. Firstly, a new exfoliation phenomenon which produces single-layered graphene is presented. We found that compression of AB-stacked graphite flakes between hydrogen-terminated silicon substrates leads to the exfoliation of graphene layers. We will show that this phenomenon occurs through the activation of an inter-layer superlubricity regime, caused by torque-induced spontaneous rotations of the layers due to in-plane shear of graphite during compression. Several parameters will be varied to more precisely determine the conditions allowing such exfoliations to occur.

Secondly, an appropriate model will be formulated, enabling rapid and reasonable reproduction of the geometrical, mechanical, and thermal properties, of bulk experimental porous silica aerogel across a wide range of different densities. As mentioned in Section 1.1, the major deficiency in current models is that all of them have yet to be employed in characterizing silica aerogel's thermal properties. Further investigations are necessary to determine whether current models require tweaking to ensure full representation of all characteristics of silica aerogel, or whether an entirely new model is needed. More advanced methods of simulating silica aerogel are computationally intensive and require more simulation time as well, thus this research will attempt to balance the proposed models' accuracy with efficiency too. Moreover, these models could possibly be extended to model other forms of aerogels, such as carbon aerogels, which have not been characterized numerically.

This thesis will describe the MD procedures that allows for such a balance between accurately characterizing the geometrical and thermal properties of silica aerogels, and the computational efficiency. By using existing MD aerogel models and interatomic interaction

potentials, it will be shown that different models and potentials give drastically differing thermal conductivities. Two models will be explored, namely the method of negative pressure rupturing first introduced by Kieffer and Angell [29], as well as the heating, expanding, and quenching, scheme first proposed by Murillo *et al.* [35]. These are modeled using the BKS and re-parameterized Tersoff potential respectively. The most accurate model is established in terms of the thermal conductivity, and the reasons for the better accuracy are discussed, together with an analysis of the shortcomings and the possible improvements that can be made to this model.

Thirdly, there exists a distinct gap of knowledge with regard to the influence of STW defects on the thermal properties of GNRs, as mentioned in Section 1.2. MD simulations will be used to investigate the changes in the thermal conductivity of graphene of differing chiralities, and containing different number densities and arrangements of STW defects. Comparisons will also be made between the different impact of STW defects and double vacancies. Furthermore, larger scale comparisons will be made between nano- to micron-sized graphene and silicene monolayers. Currently, there is a dearth of information with regard to the thermal properties of silicene, as it is a novel single-layered material that has yet to be synthesized as a free-standing sheet.

To achieve consistency, and meaningful comparisons, with previous reported results, the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential will be employed to determine and compare between pristine and defective graphene. The known shortcoming of the AIREBO potential is that it cannot accurately depict the vibrational modes in graphene, leading to underestimation of the thermal conductivity of pristine graphene [102]. This problem is further compounded by the fact that the lengths of the

GNRs modeled in our studies are far lower than the phonon mean free path of graphene, leading to greater underestimation of the thermal conductivity of the GNRs. This phenomenon has also been extensively observed in other reported computational studies as well [61, 63, 65, 102]. In order to make meaningful comparisons for large nano- to micron-sized monolayers without consideration of the edge effects, an optimized Tersoff potential for graphene will be used [103], leading to more realistic depiction of the phonon density of states and phonon dispersion in graphene. These results will be compared with those obtained from silicene, and the disparity will be discussed in detail.

1.5. Organization of Thesis

The organization of this thesis is as follows. The following chapter, Chapter 2, will be a literature review of the methods used for all MD simulations in this thesis. In Chapter 3, the procedures of all the present simulations will be laid out. Simulations of the new exfoliation mechanism of graphite will also be presented and discussed in this chapter. Chapter 4 will describe and discuss in detail the results obtained in determining accurate models to depict the solid thermal conductivity of silica aerogels. Chapter 5 will lay out the results obtain from the study of defects and their effects on the thermal conductivity of graphene, as well as making comparisons with silicene. Finally, Chapter 6 will summarize the present research efforts, and an overview of the future work to be done will also be presented.

1.6. Publications Arising from this Thesis

The following is a list of publications that arose from the research results presented herein, arranged in reverse chronological order.

Peer-reviewed Journal Papers

J.J. Yeo, T.Y. Ng, Z.S. Liu. Molecular dynamics analysis of the thermal conductivity of graphene and silicene monolayers of different lengths. *Journal of Computational and Theoretical Nanoscience*, (2013) (Accepted)

J. Lei, Z. Liu, **J. Yeo**, T.Y. Ng, Determination of the Young's modulus of silica aerogels - an analytical-numerical approach, *Soft Matter*, 9 (2013) 11367-11373.

T.Y. Ng, **J. Yeo**, Z. Liu, Molecular dynamics simulation of the thermal conductivity of shorts strips of graphene and silicene: a comparative study, *International Journal of Mechanics and Materials in Design*, (2013) 1-10.

J. Yeo, Z. Liu, T. Ng, Enhanced thermal characterization of silica aerogels through molecular dynamics simulation, *Modelling and Simulation in Materials Science and Engineering*, 21 (2013) 075004.

J.J. Yeo, Z.S. Liu, T.Y. Ng, Comparing the effects of dispersed Stone–Thrower–Wales defects and double vacancies on the thermal conductivity of graphene nanoribbons, *Nanotechnology*, 23 (2012) 385702.

T.Y. Ng, **J.J. Yeo**, Z.S. Liu, A molecular dynamics study of the thermal conductivity of graphene nanoribbons containing dispersed Stone–Thrower–Wales defects, *Carbon*, 50 (2012) 4887-4893.

T.Y. Ng, **J.J. Yeo**, Z.S. Liu, A molecular dynamics study of the thermal conductivity of nanoporous silica aerogel, obtained through negative pressure rupturing, *Journal of Non-Crystalline Solids*, 358 (2012) 1350-1355.

Conference Presentations

J.J. Yeo, S. Shakouri, T.Y. Ng, Z.S. Liu, H.K. Taylor, Exfoliation of graphene through activation of superlubricity. Oral Presentation delivered at 5th Asia Pacific Congress On Computational Mechanics & 4th International Symposium On Computational Mechanics (APCOM & ISCM), Singapore, December, 2013.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Molecular dynamics modelling of silica aerogel. Oral Presentation delivered at International Graduate Summer School in Aeronautics and Astronautics, Beijing, China, July, 2013.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Comparing thermal conductivities of graphene and silicene through molecular dynamics. Oral Presentation delivered at 7th International Conference on Materials for Advanced Technologies (ICMAT), Singapore, June, 2013.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Comparisons of the effects of different classes of defects on the thermal conductivity of graphene - A molecular dynamics study. Oral Presentation delivered at 4th International Conference on Computational Methods (ICCM), Gold Coast, Australia, November, 2012.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Geometrical and thermal characterization of silica aerogel using classical molecular dynamics. Oral Presentation delivered at European Congress on Computational Methods in Applied Sciences and Engineering (ECCOMAS), Vienna, Austria, September, 2012.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Thermal conductivity of defective graphene nanoribbons – A molecular dynamics study. Oral Presentation delivered at International Congress on Theoretical and Applied Mechanics (ICTAM), Beijing, China, August, 2012.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Numerical characterization of silica aerogel using Molecular Dynamics and the re-parameterized Tersoff potential. Poster Presentation delivered at 5th MRS-S Conference on Advanced Materials, Singapore, March, 2012.

J.J. Yeo, T.Y. Ng, Z.S. Liu, Investigating nanoporous silica aerogel obtained through negative pressure rupturing - A molecular dynamics study. Oral Presentation delivered at Tenth Young Researchers' Conference, Belgrade, Serbia, December, 2011.

Chapter 2

Molecular Dynamics – Theory and Formulation

In this chapter, a literature review of MD simulations will be given. The potentials used in MD simulations pertaining to the materials of silica, silica aerogels, carbon, graphene, and silicene, will be introduced. Methods of simulating these materials and determining their thermal conductivities will also be covered.

2.1. Molecular Dynamics (MD) Simulation

Rapid advances in the synthesis and high-resolution microscopy of nanostructures are causing a paradigm shift in the methods with which scientists look at, and experiment with, materials. The incredible miniscule level with which one can now view, manipulate, create, and probe atoms and molecules is unprecedented, allowing researchers to study the very fundamentals of materials. The advent of large-scale sophisticated computational techniques and resources further contributes to these remarkable advances, where such techniques and resources are now widely available as compared to mere decades ago where highly parallel multi-million atomic simulations were inconceivable.

The past decade has seen the rapid emergence of the field of materials modeling, where theory, simulation, and experiments are integrated in a huge melting pot. This field of research is highly notable for its unique capabilities of analyzing and predicting broad ranges of material structures and phenomena. Increasingly, computational modeling is approaching parity, in terms of prestige and importance, with the traditional methods of theoretical and experimental research. Previous intractable problems in describing the properties of matter fundamentally are now resolvable through simulations and their

analysis. These benefits are strengthened by the fact that materials modeling requires substantial knowledge from all branches of knowledge in science and engineering, creating a multi-disciplinary, fertile breeding-ground for cross-interactions within the scientific community [104].

Figure 2.1. Different methods of computational modelling over a wide range of time- and length-scales.

Typically, more than one order of time- or length-scales is necessary to fully describe many physical phenomena. For instance, non-equilibrium processes to determine properties such as shear viscosity and thermal conductivity are usually the province of MD simulations, while processes such as electronic structures and transport in solid-state physics are typically dealt with through *ab initio* methods such as density functional theory (DFT).

Traditionally, four somewhat discrete and distinct levels of length- and time-scales are identifiable in materials modeling, illustrated in Figure 2.1.

On the smallest scale of less than a few angstroms, the main issues dealt with are electronics properties determined through *ab initio* methods of quantum mechanics and the Schrödinger equation. As a consequence of the intensive computational power required to solve such problems, the applications of these methods are severely limited to very small simulation systems of about a few hundred atoms and processes in the order of femtoseconds. However, due to the rigorous nature of these methods, they are very well suited to develop and validate descriptions of systems that more approximate. The next level of atomistic simulations can span length-scales ranging from a few angstroms to a few microns, as well as time-scales ranging from picoseconds to nanoseconds. The more well-developed of these techniques are Monte Carlo (MC) and MD. These methods ignore electron contributions, and hence are of reduced reliability when compared to *ab initio* methods. However, MD is of particular importance to our study as it can efficiently model atomic heat transport phenomena on the nanoscale, and yet naturally incorporate anharmonic vibrations and interactions as a result of the treatment of atoms with empirical interatomic potentials.

Moving on from the atomistic scale, we gradually approach simulations with length-scales of more than a few microns, involving simulation process such as coarse-grained MD and finite element methods (FEM). Typically, the information needed to carry out these simulations can be obtained from calculations of the previous atomistic or *ab initio* methods, providing inputs such as the stiffness matrix or other physical parameters specific to the material at hand. The same can be said for continuum methods of simulation,

including computational fluid dynamics (CFD) and continuum elasticity (CE). These methods also tend to be the most critical when it comes to the design and implementation of materials, as properties in much larger scales are typically governed by the microstructures determined at this level.

Classical MD simulation is an extremely powerful and useful technique to solve classical many-body problems in the context of atomistic studies of matter. Classical N -body problems generally lack an analytical solution; the best alternative available in such events is numerical studies. MD attempts to reproduce the behaviors of atomistic systems using model systems, reducing the need to deduce these systems experimentally. Rapidly increasing computational power enables the employment of MD in problems of swiftly escalating complexity while still providing meaningful solutions. Many branches of science, including physics, chemistry, and biochemistry, apply MD as an indispensable tool [105-108].

MD is underpinned theoretically by Newton's laws of motions, and also embodies many important analytical mechanics results derived by Euler, Hamilton, and Lagrange. In its simplest form involving structureless particles, MD becomes merely an exemplification of Newton's second law. In one of the earliest MD studies [109, 110], Alder and Wainwright simulated a system of hard spheres, experiencing perfectly elastic collisions as these spheres moved at constant velocity.

Increasing complexity of problems require the use of Euler equations, Hamilton's quaternions, and Lagrange's method of geometric constraints. By averaging out the motion of the electrons, the Hamiltonian of a system of atoms can be expressed as a function of

their nuclear variables through the Born-Oppenheimer approximation. Assuming a classical description of a system is adequate, the Hamiltonian H of a system of N_m number of particles can be expressed as a sum of its potential U , and kinetic K energy functions. K and U in turn are functions of the set of coordinates $\mathbf{q}_i$ and momenta $\mathbf{p}_i$ of each atom i , such that

$$\mathbf{q} = (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{N_m}) \quad (2.1)$$

$$\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_{N_m}) \quad (2.2)$$

$$H(\mathbf{q}, \mathbf{p}) = K(\mathbf{p}) + U(\mathbf{q}) \quad (2.3)$$

Variables in bold indicates vectors. Typically, the set of Cartesian coordinates $\mathbf{r}_i$ of each atom in the system makes up the generalized coordinates $\mathbf{q}$. This would be different in the case of rigid molecules, where $\mathbf{q}$ is the Cartesian coordinates of the corresponding center of mass of each molecule, coupled with variables specifying molecular orientation. In either event, the corresponding set of conjugate momenta is represented by $\mathbf{p}$. This set of positions and momenta can be said to be the coordinates of a multidimensional space, known as phase space. Consequently, the kinetic energy K is of the form

$$K = \sum_{i=1}^{N_m} \sum_{\alpha} \frac{p_{i\alpha}^2}{2m_i} \quad (2.4)$$

where m_i is the atomic mass, and K is summed over the x-, y-, and z-components, represented by the index α , of the momenta of each atom i . Furthermore, as will be discussed in Section 2.2, most of the information of interest, due to intermolecular interactions, is contained within the potential energy function U . From the Hamiltonian H ,

the Hamiltonian, Lagrangian, or Newtonian form of equation of motion governing the mechanical properties and time evolution of the system can be derived, with the added assumption that U is fairly well-behaved [111]. By calculating the torques, τ_i , and forces, f_i , acting on the atoms from U , the solution of the equation of motion can be obtained. The equilibrium distribution of the atomic position and momenta are also determined by the Hamiltonian. What all these imply is that the basic inputs for a MD simulation is the potential energy function U , which is usually broken up into terms accounting for pair, triplet, or larger groups, of interactions.

MD is also steeped in statistical mechanics, dealing with ensemble averages. Usually, a small set of parameters, such as the pressure P , the temperature T , and the number of atoms N_m , can sufficiently define the thermodynamic state of a one-component macroscopic system. By understanding the fundamental equations of thermodynamics as well as the equations of state, thermodynamic properties like the heat capacity, C_V , and the chemical potential, μ , can be derived. For example, in the canonical ensemble, where temperature T and number of particles N_m of the system is fixed, the average of a certain quantity, G , at equilibrium can be found in terms of integrals containing the potential energy, $U(\mathbf{r}_1, \dots, \mathbf{r}_{N_m})$,

$$\langle G \rangle = \frac{\int G(\mathbf{r}_1, \dots, \mathbf{r}_{N_m}) e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_{N_m})} d\mathbf{r}_1 \dots d\mathbf{r}_{N_m}}{\int e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_{N_m})} d\mathbf{r}_1 \dots d\mathbf{r}_{N_m}} \quad (2.5)$$

where $\beta = 1/k_B T$, and k_B is the Boltzmann constant. A series of measurements is taken over an ensemble of independent systems to find this average [106]. Subsequently, measurements taken over the evolution of a single system in equilibrium is related to the

ensemble average via the ergodic hypothesis. This hypothesis states that the same result should be produced by both kinds of measurement assuming the typical behavior is captured through samplings that are sufficiently thorough.

The averages produced by MD over a series of M measurements are of the form,

$$\langle G \rangle = \frac{1}{M} \sum_{i=1}^M G_i(r_1, \dots, r_{N_m}) \quad (2.6)$$

There are four commonly used ensembles in MD, listed in Table 2.1, such that the thermodynamic variables listed are fixed or specified.

Table 2.1. List of commonly used ensembles in MD simulations.

Ensemble	Constant Variables
Canonical	NVT
Microcanonical	NVE
Grand canonical	μVT
Isothermal-isobaric	NPT

The term “canonical” implies that this ensemble is the simplest or most standard ensemble, pertaining to statistical mechanics. Therefore, the canonical ensemble is central to a lot of MD simulations, and the other ensembles are special cases or extensions of this particular assembly of systems. MD performed with constant NVT implies that the system is closed, such that the number of atoms and the volume of the simulation box are held constant

throughout the simulation. The temperature of the entire system is also held constant typically through the coupling of the system to a heat bath. Thermostats that can perform such a function in MD are described in Section 2.3.

A special subset of the canonical ensemble is termed the microcanonical ensemble or NVE ensemble. By completely isolating the systems under study, every member of this statistical ensemble possesses constant total energy, volume, and number of particles. Due to the conservation of energy, a microcanonical ensemble will not change over time despite the fact that every system within this ensemble is in motion. However, perfectly conserved energy will not be observed in MD simulations due to computational truncation and rounding-off.

The canonical ensemble can be extended into the final two ensembles: the grand canonical and the isothermal-isobaric ensembles. Due to the coupling and exchanging of both energy and particles with a reservoir while maintaining the same volume, the grand canonical ensemble can be described as an open system. Every possible state within this ensemble can possess diverse values of total energy and number of particles. On the other hand, the isothermal-isobaric ensemble extends the canonical ensemble by allowing for volume changes, thus allowing for all possible states of the system to reside in a particular pressure. A simple practical approach is the implementation of a piston which regulates pressure by altering the volume of the system.

2.2. Interatomic Potentials in MD Simulations

The most fundamental interactions assumed by MD occur between a pair of atoms, providing two main features of interatomic forces; the repulsion at close range and the attraction over a range of distances. These characteristics are exhibited through the use of a suitable potential function. For the simplest case of a system consisting of N_m -atoms, the potential energy is a function with terms that rely on the coordinates of individual atoms, pairs, triplets, and so forth, such that

$$U = \sum_i U_1(\mathbf{r}_i) + \sum_i \sum_{j>i} U_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (2.7)$$

where the pairs, triplets, etc., terms are summed over distinct pairs, triplets, etc., respectively. $U_1(\mathbf{r}_i)$ corresponds to the effects exerted by an external force field on the system, such as container walls. $U_2(\mathbf{r}_i, \mathbf{r}_j)$ is the pair potential of the system, which solely depends on $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, the magnitude of the pair separation.

Based on the interactions possible within the system, further terms can comprise of processes such as varying bond angles, bond stretching, and rotations about single bonds [112]. When these bonds and angles deviate from their equilibrium or reference value, energy penalties can be introduced. An important feature of representing the potential energies in this specific manner is that it allows for easier understanding of the effects on performance due to variations in the parameters, as well as aiding the process of parameterization.

An example of such a functional form exemplifying the above can be given by

$$\begin{aligned}
 U(\mathbf{r}_1, \dots, \mathbf{r}_{N_m}) = & \sum_{bonds} \frac{k_l}{2} (l_i - l_{i,0})^2 + \sum_{angles} \frac{k_\theta}{2} (\theta_i - \theta_{i,0})^2 + \sum_{torsions} \frac{V_n}{2} (1 + \cos(n\omega - \gamma)) \\
 & + \sum_{i=1}^{N_m} \sum_{j=i+1}^{N_m} \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)
 \end{aligned} \tag{2.8}$$

where l is the bond length; θ the bond angle; ω the dihedral angle; and q the atomic charge, which accounts for the Coulombic interactions. The subscript 0 denotes the reference or equilibrium values.

The forces corresponding to a potential is written as,

$$f = -\nabla U(r) \tag{2.9}$$

and the equations of motions are determined from Newton's second law,

$$m\ddot{\mathbf{r}}_i = \mathbf{f}_i = \sum_{j=1(j \neq i)}^{N_m} \mathbf{f}_{ij} \tag{2.10}$$

where m is the atomic mass of the atom under consideration. Some commonly used interatomic potentials will be discussed in the subsequent subsections, and the interatomic potentials used in our simulations are also explained in greater detail.

2.2.1. Lennard-Jones Potential

One of the most well-known pair potential functions is the '12-6' Lennard-Jones (LJ) potential [106, 113], expressed as:

$$U(r_{ij}) = \begin{cases} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & \text{for } r_{ij} < r_c \\ 0 & \text{for } r_{ij} \geq r_c \end{cases} \quad (2.11)$$

where the parameter ε_{ij} is the depth of the potential well which dictates the strength of interatomic interactions, σ_{ij} the finite distance over which the interactions are zero, and r_c a limiting separation cutoff as the interatomic separation gets progressively larger. The LJ potential assumes each atomic pair interacts independently; the other atoms in their neighborhood do not exert any effect on their forces. The r_{ij}^{-12} term accounts for the interatomic repulsion at short ranges, attributable to the overlap of electron orbitals. On the other hand, the r_{ij}^{-6} term describes the long-range attractive force, i.e. the van der Waals (vdW or dispersion) force [114].

This potential simply models the interactions of smooth, soft, and colliding particles, held together by the walls of a container. The LJ potential can only represent limited types of systems as it is very simplistic. On its own, it can only accurately model low density gases, such as argon [115, 116]. However, it has garnered wide usage through coupling with other potentials, in order to add dispersive interactions to some potentials to model a much broader range of systems [117-120], together with the Lorentz-Berthelot mixing rules [105] to approximate interactions between dissimilar atoms.

This mixing rule is defined as

$$\sigma_{ij} = \sigma_{ji} = \frac{\sigma_i + \sigma_j}{2} \quad (2.12)$$

$$\varepsilon_{ij} = \varepsilon_{ji} = \sqrt{\varepsilon_i \varepsilon_j} \quad (2.13)$$

Increasing complexity in the systems that researchers wished to analyze led to further developments of such pair potentials, culminating in potentials such as the Morse potential and the Buckingham potential [105, 112, 114], as well as further extensions resulting in the potentials discussed next.

2.2.2. van Beest, Kramer, and van Santen (BKS) Potential

In this thesis, one of the primary interaction potential used to model silica is introduced by van Beest, Kramer, and van Santen (BKS) [121, 122], as implemented on the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [123]. LAMMPS is distributed as an open-source classical molecular dynamics code, with many interatomic interaction potentials for a wide variety of materials, such as solid-state elements, soft biological matter, and coarse-grained or mesoscopic systems. It is also a highly parallel particle simulator at the atomic, meso, or continuum scale, using message-passing techniques and spatial-decomposition of the simulation domain.

The interaction terms for two atoms i and j in the BKS potential are

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (2.14)$$

where r_{ij} is the separation between atoms i and j ; q_i and q_j their atomic charges; and A_{ij} , B_{ij} , and C_{ij} the different constants for different pairs of atoms i and j . The first term in Equation 2.14 is the long-range Coulombic interaction; the second and third terms are the short-range attraction and repulsion of atoms respectively. There are three different pairs of atoms of Si-Si, Si-O, and O-O, since silica consists of only silicon and oxygen atoms.

These constants defined by van Beest *et al.* [121] are $A_{SiSi} = 0.0\text{eV}$, $A_{SiO} = 18,003.7572\text{eV}$, $A_{OO} = 1,388.7730\text{eV}$, $B_{SiSi} = 0.0\text{\AA}^{-1}$, $B_{SiO} = 4.87318\text{\AA}^{-1}$, $B_{OO} = 2.760\text{\AA}^{-1}$, $C_{SiSi} = 0.0\text{eV} \cdot \text{\AA}^6$, $C_{SiO} = 133.5381\text{eV} \cdot \text{\AA}^6$, $C_{OO} = 175.0\text{eV} \cdot \text{\AA}^6$, $q_{Si} = 2.4\text{e}$, and $q_O = -1.2\text{e}$. These parameters were derived via fitting to *ab initio* calculations [121]. A short-range interaction cut-off was set at $8\text{\AA}$, and long-range Coulombic interactions beyond this cut-off were calculated in reciprocal space via LAMMPS' particle-particle particle-mesh solver.

The BKS potential was able to more accurately predict the properties of various silica polymorphs [121, 122], as compared to other pair potentials such as the Tsuneyuki, Tsukada, Aoki, and Matsui (TTAM) potential [124]. Parameters of this potential were fitted to both experimental macroscopic data as well as microscopic *ab initio* studies, including data for α -quartz. This leads to accurate depiction of the geometrical and mechanical properties of various silica polymorphs, such as the unit-cell dimensions and elastic moduli

respectively. Table 2.2 shows the comparisons between the calculated elastic moduli and data from experiments.

Table 2.2. Comparison of elastic moduli between experimental data [125] and results from BKS potential [121], where the ratio shows that the results were largely similar.

Elastic Modulus	Experiment, GPa	BKS potential, GPa	Ratio between experiment and BKS potential
C_{11}	8.68	9.05	1.04
C_{33}	10.58	10.70	1.01
C_{44}	5.82	5.02	0.86
C_{66}	3.99	4.12	1.03
C_{12}	0.70	0.81	1.16
C_{13}	1.91	1.52	0.80
C_{14}	-1.80	-1.76	0.98

Moreover, the BKS potential was found to be easily extendable to model aluminophosphates and zeolites [122]. The BKS potential had been widely used to model amorphous silica [126-132], including silica nanowires and nanoparticles [131], and nanoporous silica thin films [132]. These studies have shown that the BKS potential can predict, with reasonable accuracy, various properties of bulk silica, such as its structure [129] and thermal conductivity [128]. For instance, Jund and Jullien [128] found reasonable

reproductions of the thermal conductivity in amorphous silica in comparison with experimental data. The BKS potential approximates the order of magnitude of the thermal conductivity pretty well within the temperature range of 20-400K, achieving quantitative agreement, and reproducing the conductivity plateau at 10K after finite-size corrections. Coquil *et al.* [132] found qualitative agreement with experimental results for the thermal conductivity at room temperature of amorphous silica possessing monodispersed spherical pores, establishing that the thermal conductivity for such nanofilms was dependent only on porosity.

Also, the BKS potential is a two-body potential, which is computationally advantageous. Comparatively, alternative potentials such as the re-parameterized Tersoff potential [133], Vashishta potential [36], and ReaxFF force fields [134] are more complex and time-consuming in their implementation, leading to far greater computational times. This is due to the fact that these potentials are two- and three-body bond-order potentials allowing for variable bonding states and, in the case of ReaxFF, even allows for variable electrostatic reactions.

Before creating the aerogel structure, it was necessary to produce a sample of amorphous silica, where the system was heated to its liquid state and subsequently quenched to an amorphous solid state. The quenching process can cause atoms to approach each other too closely at very high temperatures, leading to uncontrollable dynamics. The BKS potential alone cannot effectively handle the strong repulsive forces in such scenarios [130, 131, 135]. A modification of the BKS potential was necessary to maintain cohesion in such situations.

Basically, a '24-6' LJ potential was added to the BKS potential to obtain [135]

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{c_{ij}}{r_{ij}^6} + 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{24} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.15)$$

The parameters ε_{ij} and σ_{ij} are $\varepsilon_{SiSi} = 13.20\text{eV}$, $\varepsilon_{SiO} = 1.12 \times 10^{-2}\text{eV}$ and $\varepsilon_{OO} = 4.78 \times 10^{-4}\text{eV}$; $\sigma_{SiSi} = 0.40\text{\AA}$, $\sigma_{SiO} = 1.35\text{\AA}$ and $\sigma_{OO} = 2.20\text{\AA}$ [130]. The '24-6' LJ term essentially gives the BKS potential a steep repulsive capability as interatomic distances becomes very small to prevent atoms from approaching too closely to each other at extremely high temperatures. The addition of the '24-6' LJ term did not require any adjustments of the constants in the BKS terms [131, 132, 135].

2.2.3. AIREBO Potential

The AIREBO potential [117] is a classical potential that is able to model changes in covalent bonding empirically, even though such changes are inherently quantum mechanical. It allows for formation and dissociation of bonds during the MD run. Terms accounting for many-body interactions help to account for the local coordination environment of each atom, thus augmenting the conventional pairwise interactions. The AIREBO potential is an improvement over a previously derived potential, known as the second-generation REBO potential [136]. The REBO potential was first developed for modeling the chemical vapor deposition of diamond, and subsequently it has been extended to simulations of many varied properties of hydrocarbons and solid carbons [117]. However, due to the lack of nonbonded and dispersion terms in the REBO potential, it limits the systems that can be simulated. This is particularly significant when modeling thin layers of graphene, graphite, and some fullerenes. Also, the REBO potential lacks a torsional

potential to model the torsional limits about a single bond. This prohibits its modeling of large hydrocarbon systems, and limits its accuracy. The AIREBO potential attempts to address all these deficiencies.

From the original REBO potential, the pairwise covalent interactions, based on the form of the Tersoff potential [137], are given as

$$U_{ij}^{REBO} = V_{ij}^R(r_{ij}) + b_{ij}V_{ij}^A(r_{ij}) \quad (2.13)$$

where V_{ij}^R and V_{ij}^A are the repulsive and attractive pairwise interaction terms respectively.

The b_{ij} bond-order term accounts for the various strength of the covalent bond which allows, for example, heavier weighting towards triply coordinated sp^2 carbon atoms than quadruply coordinated sp^3 carbon atoms. It approximates the chemical concept of a bond order, adapting the strength of a bond as the local environment changes, such that for stronger bonds, b_{ij} gets larger.

The repulsive term is given as

$$V_{ij}^R(r_{ij}) = w_{ij}(r_{ij}) \left[1 + \frac{Q_{ij}}{r_{ij}} \right] A_{ij} e^{-\alpha_{ij}r_{ij}} \quad (2.14)$$

where the values pair parameters Q_{ij} , A_{ij} , and α_{ij} , and other potential parameters are listed in Table 2.3.

The bonds are weighted by the factor

$$w_{ij}(r_{ij}) = S'(t_c(r_{ij})) \quad (2.15)$$

When the pairwise distance exceeds the specified bonding distance, the REBO interactions are switched off, and the switching function is of the form

$$S'(t) = \Theta(-t) + \Theta(t)\Theta(1-t)\left(\frac{1}{2}\right)[1 + \cos(\pi t)] \quad (2.16)$$

and a scaling function is applied for the switching region for each type of bond

$$t_c(r_{ij}) = \frac{r_{ij} - r_{ij}^{min}}{r_{ij}^{max} - r_{ij}^{min}} \quad (2.17)$$

Next, a triple exponential describes the attractive pair interactions in Equation 2.13,

$$V_{ij}^A = -w_{ij}(r_{ij}) \sum_{n=1}^3 B_{ij}^{(n)} e^{-\beta_{ij}^{(n)} r_{ij}} \quad (2.18)$$

For long-ranged interactions, this function is smoothly switched off using the bond weight.

The bond-order term in Equation 2.13 is given by

$$b_{ij} = \frac{1}{2} (p_{ij}^{\sigma\pi} + p_{ji}^{\sigma\pi}) + \pi_{ij}^{rc} + \pi_{ij}^{dh} \quad (2.19)$$

The terms in b_{ij} are dependent on the bonding environment, thus providing many-body contributions.

The terms detailing the covalent bond interactions are the main contributors to the bond-order, such that

$$p_{ij}^{\sigma\pi} = \left[1 + \sum_{k \neq i, j} w_{ik}(r_{ik}) g_i(\cos \theta_{ijk}) e^{\lambda_{ijk}} + P_{ij} \right]^{\frac{1}{2}} \quad (2.20)$$

where the $\mathbf{r}_{ji}$ and $\mathbf{r}_{ki}$ vectors determines the bond angle θ_{jik} . A penalty is imposed on bonds that approaches each other too closely, through the fifth-order spline, g_i . The rest of the terms are small correction factors. Going back to Equation 2.19, other than covalent interactions, the remaining terms account for the radical and conjugation effects, and penalties imposed for rotations around multiple bonds.

To include a mechanism for intermolecular interactions, as compared to the intra-molecular interactions of REBO, a '12-6' LJ potential, as described in Section 2.2.1, was implemented. This was further augmented using a distance-dependent switch to determine whether and at what distance the LJ interactions are turned off. This adaptive decision is based on the pairwise separation distance, the strength of existing bonding interactions between them, and the network of bonds connecting them. Generally, if the two atoms are deemed unlikely to form a chemical bond, LJ repulsion at short distances will be imposed.

Mathematically, this is represented by

$$U_{ij}^{LJ} = S\left(t_r\left(r_{ij}\right)\right)S\left(t_b\left(b_{ij}^*\right)\right)D_{ij}V_{ij}^{LJ}\left(r_{ij}\right)+\left[1-S\left(t_r\left(r_{ij}\right)\right)\right]D_{ij}V_{ij}^{LJ}\left(r_{ij}\right) \quad (2.21)$$

where $V_{ij}^{LJ}\left(r_{ij}\right)$ is the LJ potential given by Equation 2.8. This is coupled to multiple switching functions.

$S(t)$ is a universal switching function, such that

$$S(t) = \Theta(-t) + \Theta(t)\Theta(1-t)\left[1-t^2(3-2t)\right] \quad (2.22)$$

where $\Theta(t)$ is the Heaviside step function, and $t_r(r_{ij})$ is a scaling function used to rescale the domain of $S(t)$. It is given by

$$t_r\left(r_{ij}\right) = \frac{r_{ij} - r_{ij}^{LJ \min}}{r_{ij}^{LJ \max} - r_{ij}^{LJ \min}} \quad (2.23)$$

The switching region $\left[r_{ij}^{LJ \min}, r_{ij}^{LJ \max}\right]$ is constrained such that $r_{ij}^{LJ \min} = \sigma_{ij}$, and

$r_{ij}^{LJ \max} = 2^{\frac{1}{6}}\sigma_{ij}$. These constraints help to prevent artificial reaction barriers due to LJ repulsions at short distances when LJ interactions are switched off, as well as maintaining the same LJ potential well minimum from the unswitched interaction. It also guarantees the second derivative of the potential is continuous at $r_{ij}^{LJ \min}$.

The scaling function $t_b(b_{ij})$ is given by

$$t_b(b_{ij}) = \frac{b - b_{ij}^{LJ \min}}{b_{ij}^{LJ \max} - b_{ij}^{LJ \min}} \quad (2.24)$$

When covalent bonding is likely to occur, the repulsive LJ interactions will not be present as $t_b > 1$. Conversely, when covalent bonding is unlikely, LJ interactions will be included, varying according to the value of b_{ij} . The bond-order b_{ij}^* term in Equation 2.21 is evaluated as

$$b_{ij}^* = b_{ij} \big|_{r_{ij}=r_{ij}^{min}} \quad (2.25)$$

The connectivity switch is represented by the parameter D_{ij} in Equation 2.21, and are manipulated through bond weights, such that

$$D_{ij} = 1 - \max \left\{ w_{ij}(r_{ij}), w_{ik}(r_{ik}) w_{kj}(r_{kj}), \quad \forall k \right. \\ \left. w_{ik}(r_{ik}) w_{kl}(r_{kl}) w_{lj}(r_{lj}), \quad \forall k, l \right\} \quad (2.26)$$

The bond torsional potential is given by

$$V^{tors}(\omega_{kijl}) = \varepsilon_{kijl} \left[\frac{256}{405} \cos^{10} \left(\frac{\omega_{kijl}}{2} \right) - \frac{1}{10} \right] \quad (2.27)$$

This potential is implemented in AIREBO with bond weights at different dihedral angles,

$$U_{kijl}^{tors} = \frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i, j} \sum_{l \neq i, j, k} w_{ij}(r_{ij}) w_{jk}(r_{jk}) w_{kl}(r_{kl}) \times V^{tors}(\omega_{kijl}) \quad (2.28)$$

Finally, the total system energy as determined by the AIREBO potential will be a summation,

$$U = \frac{1}{2} \sum_i \sum_{j \neq i} \left[U_{ij}^{REBO} + U_{ij}^{LJ} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} U_{kijl}^{tors} \right] \quad (2.29)$$

All parameters have been empirically fitted and are given in the study by Stuart *et al.* [117].

The parameters for carbon-carbon interactions are detailed in Table 2.3.

Researchers have found many varied uses of the AIREBO potential in carbon-related MD simulations [138-141]. For example, it has been used to study the effects of low-energy ion irradiation of both individual CNTs and CNT bundles [138]. 10nm long single-walled nanotubes (SWNTs) suspended at their ends were irradiated with Ar ions with energies between 50 to 3,000eV. This caused a proliferation of defects in the SWNTs, such as single vacancies, defects related to vacancies, carbon adatoms which are doubly-coordinated, STW defects, and amorphous regions. In another study [139], Ag(111) was bombarded by clusters of C₆₀ ions at 15keV, in order to determine the sputtering yield. This study showed that craters approximately 10nm in diameter can develop on the Ag surface due to the bombardment, similar to Au surfaces being bombarded by Au₃. In comparison with

bombardments with 15keV Ga atoms, C₆₀ bombardments led to 35 times increase in the yield of Ag₃ ions, and approximately 16 times increase in the yield of Ag atoms.

Table 2.3. Parameters for the AIREBO potential [117] used in LAMMPS.

Parameters	Values
Q_{ij} (Å)	0.313460296
α_{ij} (Å ⁻¹)	4.746539061
A_{ij} (eV)	10953.54416
$B_{ij}^{(1)}$ (eV)	12388.79198
$B_{ij}^{(2)}$ (eV)	17.56740647
$B_{ij}^{(3)}$ (eV)	30.71493208
$\beta_{ij}^{(1)}$ (Å ⁻¹)	4.720452313
$\beta_{ij}^{(2)}$ (Å ⁻¹)	1.43321325
$\beta_{ij}^{(3)}$ (Å ⁻¹)	1.382691251
r_{ij}^{min} (Å)	1.7
r_{ij}^{max} (Å)	2.0

$\rho_{ij} \text{ (\AA)}$	0.0
$r_{ij}^{LJ \text{ min}} \text{ (\AA)}$	3.4
$r_{ij}^{LJ \text{ max}} \text{ (\AA)}$	3.816370964
$b_{ij}^{LJ \text{ min}}$	0.77
$b_{ij}^{LJ \text{ max}}$	0.81
$\varepsilon_{ij} \text{ (eV)}$	0.002843732
$\sigma_{ij} \text{ (\AA)}$	3.4
$\varepsilon_{kijl} \text{ (eV)}$	0.307885109

The AIREBO potential was also frequently used to characterize various properties in graphene, including its thermal characteristics [102, 142-152]. Zhao *et al.* [142] found that the MD prediction of fracture strength, Young's modulus, and fracture strain of bulk graphene agreed reasonably with experimental results. It was also determined that size and chirality played an important role in the mechanical properties of graphene, such that graphene with armchair chirality undergoing uniaxial tension possesses much lower fracture strain and strength in comparison with the zigzag chirality. Moreover, the stiffness increased as the length of the nanoribbon increased. Shen *et al.* [146] simulated single-layered graphene sheets of different aspect ratios, subjecting them to uniform pressure in the transverse direction, uniaxial tensile tests, and shear loading. The temperature was varied from 300 to 700K. They determined that the mechanical properties are temperature-

dependent, size-dependent, as well as being anisotropic. The shear modulus showed weak dependence on changes in temperature, while the Young's modulus increased as temperature decreased.

In terms of the characterization of the thermal properties of graphene, Pei *et al.* [150] performed NEMD on hydrogenated graphene and determined the variation in the thermal conductivity as hydrogen coverage increased. When the graphene was randomly hydrogenated, increasing coverage till approximately 30% led to rapid decreases in the thermal conductivity, beyond which there was little change. When the hydrogenation is patterned such that the hydrogen stripes and the heat flux were parallel, increasing coverage led to gradual decreases in the thermal conductivity, even up till 100% coverage. When these stripes and the heat flux were perpendicular, thermal conductivity deteriorated by 60% even with merely 5% coverage.

Furthermore, Pei *et al.* [151] found drastic decreases in the thermal conductivity of graphene doped with carbon isotope, due to interfacial thermal resistance existing between the isotopes and graphene. Thermal rectification was also found to arise in this interface. The thermal rectification and afore-mentioned interfacial thermal resistance can also be increased by applying tensile strain to graphene. Luo and Lloyd [152] determined the interfacial thermal conductance in graphene and polymer interfaces using NEMD. At the graphene-polymer interfaces, thermal transport is significantly affected by graphene's long wavelength phonons. Interfacial thermal transport can be improved through strong coupling between the polymer and graphene spectra, due to the presence of low frequency out-of-plane modes between 2 to 16THz. Strong interfacial interaction strength also led to increases in the thermal conductance.

2.2.4. Tersoff Potential

Introduced by Tersoff in 1988 [153], the Tersoff potential was initially formulated to address the strong interest in the development of interatomic potentials which are simple, and yet allows the energetics and structural properties of complex systems such as semiconductors to be determined directly. As mentioned in Section 2.2, models of simpler systems such as gases can be adequately described using more basic pair potentials like the LJ, Morse, and Buckingham potentials. These pair approaches are limited in their ability to model far more interesting, but structurally and chemically complex, materials such as polymers, ceramics, and semiconductors. This problem is further compounded when the element has multiple possible polymorphs, like the case of silicon and carbon.

In order to address these issues, Tersoff employed the idea that the strength of each bond (i.e. the bond order, which was introduced in Section 2.2.3) is dependent on the conditions within the local environment. For instance, atoms with fewer neighboring atoms form stronger bonds than atoms with many neighbors. Such dependence adequately stabilizes structures in covalent materials, due to low neighbor counts (atomic coordination). Explicit involvement of this dependence does not significantly increase the computational expense of these potentials, yet helping to solve various problematic issues with regards to descriptions of covalent systems.

The mathematical form of the potential is as follows:

$$U = \sum_i U_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (2.30)$$

$$V_{ij} = f^c(r_{ij}) [V^R(r_{ij}) + b_{ij} V^A(r_{ij})] \quad (2.31)$$

A repulsive pair potential is represented by the function V^R in Equation 2.31, while V^A is the attractive portion, related to atomic bonding. A function to smoothly limit the potential to short interaction ranges is given by f^c ; this helps to significantly reduce computational expense for many applications of this potential. In the same manner as the AIREBO potential in Section 2.2.3, the bond order is introduced through the function b_{ij} , which decreases monotonically depending on the coordination of atoms i and j . The bond order is also similarly limited to short range interactions within the first neighbor shell. V^R and V^A are taken to be exponential functions in a manner similar to the Morse potential. This gives several desirable bonding features, beyond our scope of discussion [154, 155].

$$V^R(r_{ij}) = A_{ij} \exp(-\gamma_{ij} r_{ij}) \quad (2.32)$$

$$V^A(r_{ij}) = B_{ij} \exp(-\mu_{ij} r_{ij}) \quad (2.33)$$

$$A_{ij} = (A_i + A_j)^{\frac{1}{2}}, B_{ij} = (B_i + B_j)^{\frac{1}{2}} \quad (2.34)$$

$$\gamma_{ij} = \frac{\gamma_i + \gamma_j}{2}, \mu_{ij} = \frac{\mu_i + \mu_j}{2} \quad (2.35)$$

The cutoff function is given as

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos\left(\pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), & R_{ij} < r_{ij} < S_{ij} \\ 0, & r_{ij} > S_{ij} \end{cases} \quad (2.36)$$

$$R_{ij} = (R_i R_j)^{\frac{1}{2}}, S_{ij} = (S_i S_j)^{\frac{1}{2}} \quad (2.37)$$

The cutoff function and its derivative are continuous for all r_{ij} , with the function taking values between 0 and 1 to only include first-neighbor interactions using the limits R_{ij} and S_{ij} . The bond order term is

$$b_{ij} = \chi_{ij} \left(1 + \beta_i^{n_i} \zeta_{ij}^{n_i}\right)^{-\frac{1}{2n_i}} \quad (2.38)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_c(r_{ik}) \omega_{ik} g(\theta_{ijk}) \quad (2.39)$$

$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos \theta_{ijk})^2} \quad (2.40)$$

where, similar to Section 2.2.3, θ_{ijk} denotes the bond angle between the bonds of atoms i and j , and i and k . Strengthening or weakening of the heteropolar bonds is dictated by the parameter χ_{ij} in Equation 2.35. The remaining terms in the Tersoff potential such as A , B , and n are parameters that can be fitted to experimental or *ab initio* data to parameterize the Tersoff potential to obtain structures and energies similar to the system under investigation.

The parameters derived by Munetoh *et al.* and implemented in LAMMPS are listed in Table 2.4.

Table 2.4. Parameters for Si-Si, Si-O, and O-O interactions used in the re-parameterized Tersoff potential [133], employed in LAMMPS.

Parameter	Silicon	Oxygen
A (eV)	1.8308×10^3	1.88255×10^3
B (eV)	4.7118×10^2	2.18787×10^2
γ ($\text{\AA}^{-1}$)	2.4799	4.17108
μ ($\text{\AA}^{-1}$)	1.7322	2.35692
β	1.1000×10^{-6}	1.1632×10^{-7}
n	7.8734×10^{-1}	1.04968
c	1.0039×10^5	6.46921×10^4
d	1.6217×10^1	4.11127
h	-5.9825×10^{-1}	-8.45922×10^{-1}
R ($\text{\AA}$)	2.5	1.7
S ($\text{\AA}$)	2.8	2.0
$\chi_{\text{Si-O}} = 1.17945$		

Many different parameterizations of the Tersoff potential exist, enabling the modelling of various covalent structures using MD simulations. Tersoff parameterized it for silicon initially [137, 153]. Subsequently, he expanded the parameters to include interactions between silicon and carbon, as well as silicon and germanium [156, 157]. This allows for the modelling of pure silicon, pure carbon, pure germanium, binary silicon carbide, and binary silicon-germanium. It was also parameterized for pure gallium, pure nitrogen, and binary gallium nitride by Nord *et al.* [158]. Further parameterizations include those for boron carbide, boron nitride, and nitrogen-carbon interactions [159]. Of greater interest to us is the re-parameterization by Munetoh *et al.* [133] to model silica interactions. The re-parameterized Tersoff potential has been frequently used in thermal MD studies recently [160-162] due to its unique capability of reproducing the vibrational density of states (vDOS) of bulk amorphous silica, with good agreement with experimental data [163]. This will be demonstrated and compared with the BKS potential in Chapter 4.

Ong and Pop [160] used NEMD and the re-parameterized Tersoff potential to probe the coupling of thermal energy between amorphous silica and CNTs. They found proportionate scaling of the phonon thermal boundary conductance per unit of CNT length with the strength of vdW interactions. It was also proportionate to the diameter of the CNT, and possessed a power-law relation with temperature, where the temperature investigated ranged from 200 to 600K. For a single CNT, the thermal relaxation time was also found to be independent of its diameter. These results were found to be comparable to experimental data. Chen *et al.* [162] investigated the Kapitza resistance (i.e. the interfacial thermal resistance) of a heterojunction. This junction was created using crystalline silicon and amorphous silica. They showed that the Kapitza resistance was highly dependent on the strength of the coupling of the interfaces. At the limit of weak interfacial coupling, the

length of the junction and the interfacial structure was the strongest influence on the Kapitza resistance. On the other hand, at the limit of strong interfacial coupling, the value was approximately constant, showing insensitivity to the same factors of length and structure.

The Tersoff potential was also employed in our analysis and comparisons of very large graphene and silicene monolayers that approaches 1000nm in length. The Tersoff potential had been optimized from the original parameters [153] for this purpose for graphene [103], leading to drastically enhanced conformity with structural data. The authors showed that it also gives much better fits to data from graphite's in-plane phonon dispersion, providing acoustic phonon velocities agrees very well with experimental data. Their simulation data using this optimized Tersoff potential also led to significantly better comparisons of the lattice thermal conductivity in single-walled CNTs with experimental results. The parameters for this potential are listed in Table 2.5.

Table 2.5. Parameters for C-C interactions used in the optimized Tersoff potential [103], employed in LAMMPS.

Parameter	Values
A (eV)	1.3936×10^3
B (eV)	4.3000×10^2
γ ($\text{\AA}^{-1}$)	3.4879
μ ($\text{\AA}^{-1}$)	2.2119
β	1.5700×10^{-7}
n	7.2751×10^{-1}
c	3.8000×10^4
d	4.3484
h	-0.93
R ($\text{\AA}$)	1.95
S ($\text{\AA}$)	0.15

2.3. Thermostats

In order to generate the equilibrium ensembles that pertain to a particular system temperature, such as in the NVE or NVT ensembles as discussed in Section 2.1, computational thermostats are required. The most frequently used, also the thermostat that is employed in all our studies, is the Nosé-Hoover thermostat [164]. Other popular and more basic thermostats include the method of velocity rescaling and the Berendsen [165] thermostat. The kinetic energy of the atoms (which is also the momenta of the atoms as discussed in Section 2.1) within the system can be related to the temperature of the system through the equipartition theorem [105], where

$$\sum_{i=1}^{N_m} \frac{|\mathbf{p}_i|^2}{2m_i} = \frac{3}{2} N_m k_b T \quad (2.41)$$

From Equation 2.41, one can observe that the most obvious and fundamental way to achieve the desired temperature within an MD simulation is simply to rescale the atomic velocities repeatedly via a factor λ_T till the temperature fluctuates around the desired value, and the temperature change at each timestep becomes

$$\Delta T = (\lambda_T^2 - 1)T(t) \quad (2.42)$$

$$\lambda_T = \sqrt{\frac{T_0}{T(t)}} \quad (2.43)$$

where $T(t)$ is the temperature of the system at a certain time t , and T_0 is the desired temperature.

Another formulation of this approach is the Berendsen thermostat [165], where the temperature of the system is coupled to an external heat bath with the constant desired temperature. The rate of change of temperature is directly proportional to the difference in temperature between the heat bath and the system, such that

$$\frac{dT(t)}{dt} = \frac{1}{\tau}(T_0 - T(t)) \quad (2.44)$$

where τ denotes the strength of the coupling between the bath and the system. The temperature of the system will decay exponentially towards the temperature of the bath, where the change in temperature in each timestep and the scaling factor is

$$\Delta T = \frac{\delta t}{\tau}(T_0 - T(t)) \quad (2.45)$$

$$\lambda_T^2 = 1 + \frac{\delta t}{\tau} \left\{ \frac{T_0}{T\left(t - \frac{\delta t}{2}\right)} - 1 \right\} \quad (2.46)$$

The appearance of the term $T(t - \delta t/2)$ is due to the method of integrating the equations of motion, which will be explained in Section 2.4. δt refers to the timestep during the simulation. The value of τ has to be carefully chosen to prevent undesirable dynamics such as sudden changes in the temperature which can lead to atoms flying apart. The thermostat is switched off if τ approaches infinity, and the simulation is being sampled in the microcanonical ensemble. Strong coupling with small values of τ can lead to fluctuations that are too minuscule such that the desired temperature is either never obtained or takes too long computationally to achieve, and the simulation becomes unrealistic. If τ is taken

to be the same value as the timestep, then this thermostat reverts to the temperature scaling method of Equation 2.43. The major detractors from these scaling methods are that they will not reproduce statistically the correct velocity distributions in the canonical or microcanonical ensembles. They are merely simplistic ways to artificially bump the system into the correct temperature fluctuations without consideration for the statistical meaning behind the motions of the atoms within the system. In order to rectify this, the more rigorous approach in terms of statistical mechanics is to employ another thermostat known as the Nosé-Hoover thermostat [164].

The main idea behind the Nosé-Hoover thermostat is to perform the MD simulation in order to equilibrate the system to obtain temperature fluctuations that gives the correct average and canonical distribution of temperature. In this approach, the heat bath is coupled to the Hamiltonian through an additional degree of freedom, denoted by the coordinate s , such that it is an integrated part of the system. The timescale and coordinates in this new system is also extended by the factor s , such that

$$\delta t_s = s \delta t \quad (2.47)$$

The total Hamiltonian of the system is modified to be

$$H = \sum_i \frac{p_i^2}{2m_i s^2} + \frac{1}{2} \sum_{i \neq j} U(r_{ij}) + \frac{p_s^2}{2Q} + gkT \ln(s) \quad (2.48)$$

The additional two terms that are now included in the Hamiltonian refer to the kinetic and potential energy introduced by the coupled heat bath. The variable Q is a fictitious mass of the bath and g is the number of independent momentum degrees of freedom of the system.

2.4. Time Integration

Methods of solving the ordinary differential equations of motions in MD typically are the finite difference approach [105, 106]. In the most basic scheme, known as the “leap-frog” scheme, half steps of integration are used, such that

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}\left(t + \frac{1}{2} \delta t\right) \quad (2.49)$$

$$\mathbf{v}\left(t + \frac{1}{2} \delta t\right) = \mathbf{v}\left(t - \frac{1}{2} \delta t\right) + \delta t \mathbf{a}(t) \quad (2.50)$$

The current position $\mathbf{r}(t)$, acceleration $\mathbf{a}(t)$, and half-step velocities $\mathbf{v}(t-1/2\delta t)$ of each atom are stored. Firstly, Equation 2.50 is evaluated, determining the velocities of the next half-step $\mathbf{v}(t+1/2\delta t)$, effectively “leap-frogging” over the current coordinates to be evaluated. The current velocities will be re-evaluated by

$$\mathbf{v}(t) = \frac{1}{2} \left[\mathbf{v}\left(t + \frac{1}{2} \delta t\right) + \mathbf{v}\left(t - \frac{1}{2} \delta t\right) \right] \quad (2.51)$$

The current velocities are needed in order to evaluate any properties that require the current velocities and positions to be known, such as the current kinetic and potential energy at time t . The positions will once again “leap-frog” over the velocities through Equation 2.49 and the accelerations evaluated. However, such a method introduces a significant amount of rounding error. In order to minimize this error, the more advantageous velocity-Verlet algorithm is implemented in our studies. This method allows for the storage of positions, velocities, and accelerations at the same time t .

This will take the form

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2} \delta t^2 \mathbf{a}(t) \quad (2.52)$$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{1}{2} \delta t [\mathbf{a}(t) + \mathbf{a}(t + \delta t)] \quad (2.53)$$

The new positions at the next time step are calculated first through Equation 2.52. The half-step velocities are calculated through

$$\mathbf{v}\left(t + \frac{1}{2} \delta t\right) = \mathbf{v}(t) + \frac{1}{2} \mathbf{a}(t) \delta t \quad (2.53)$$

Subsequently, forces and accelerations in the next timestep are calculated together with the velocities

$$\mathbf{v}(t + \delta t) = \mathbf{v}\left(t + \frac{1}{2} \delta t\right) + \frac{1}{2} \delta t \mathbf{a}(t + \delta t) \quad (2.53)$$

2.5. Flow of MD Simulations

Overall, the entire flow of MD simulations is illustrated in Figure 2.2, consisting of initialization of all necessary parameters, equilibration of the system, and production of the quantities to be analyzed.

Figure 2.2. Flow chart of a generic run using MD simulation

In the initialization stage, the system geometry is generated, typically by placing atoms in a crystal lattice. All parameters are also specified, such as the ensemble of the simulation as discussed in Section 2.1 and the required interatomic interaction potentials, such as those

described in Section 2.2. Subsequently, a neighbor list for each atom is generated to describe which atoms are interacting with each other, and the initial interatomic potential energy and forces can be calculated, which can be minimized through schemes such as steepest-descent or conjugate gradient to prevent the system from diverging due to unexpected high energy interactions if atoms are packed too closely to each other.

Next, in the equilibration stage, the time integration process can begin, using the methods described in Section 2.4 together with the thermostats described in Section 2.3 to bring the system towards the desired ensemble. Convergence can be monitored through observation of the fluctuations of system variables such as the temperature and total energy. An example of convergence is depicted in Figure 2.3.

Figure 2.3. Illustration of a MD simulation's convergence through monitoring of a) the temperature and b) the total energy.

Finally the thermodynamic variables can be output and analyzed, typically through time-averaging of certain variables as explained in Section 2.1, such as the velocity autocorrelation function.

2.6. Thermal Conductivity Simulations

There are three possible methods to determine the thermal conductivity of materials using MD simulations. The first method is the equilibrium method, also known as the Green-Kubo (GK) method. Thermal transport coefficients can be found through a system's response to perturbations, by an integral involving the autocorrelation function of energy current [105, 131],

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty \langle j_z^e(t) j_z^e(0) \rangle dt \quad (2.54)$$

where the z -component of the energy current is defined as,

$$j_z^e = \frac{d}{dt} \sum_{i=1}^{N_m} z_i \frac{1}{2} \left(m_i v_i^2 + \sum_{j \neq i} U(r_{ij}) \right) \quad (2.55)$$

such that N_m is the number of particles in the system, m_i the mass of a particle i , z_i the z -component of the position vector of particle i , $v_i(t)$ the velocity of particle i at time t , $U(r_{ij})$ the system's governing potential function, and k_B the Boltzmann's constant. Typically, the GK method requires very long simulation times to achieve convergence, as noted by Sellan *et al.* [166].

The other two methods of simulating thermal properties are known as non-equilibrium methods. The direct NEMD method [167] involves the imposition of a temperature gradient through the maintenance of one hot and one cold reservoir at each end of the simulated system, as shown in Figure 2.4. This is achieved by adding and subtracting non-translational kinetic energy to the hot and cold reservoir respectively, such that the aggregate momentum is conserved.

Figure 2.4. Schematic for direct NEMD on a graphene strip, where energy is added to the hot reservoir (red) and subtracted in the cold reservoir (blue). (The arrow depicts the direction of the heat flux).

The heat flux is measured as the response of the system, similar to Equation 2.55 above.

The thermal conductivity is found through Fourier's Law, such that

$$\lambda = \frac{j^e}{dT / dx} \quad (2.56)$$

From Equation 2.56, another method can be deduced to determine the thermal conductivity, by imposing a heat flux and measuring the corresponding temperature gradient at equilibrium. This method is known as the reverse non-equilibrium molecular dynamics

(RNEMD) method [168]. A heat flux is imposed across the simulation cell in all three Cartesian axes separately to form a temperature gradient. This is done by dividing the simulation cell into an even number of slabs in the direction of heat transfer, and the first slab is designated the cold slab, while the middle slab is designated as the hot slab. A schematic of this is shown in Figure 2.5.

Figure 2.5. Schematic for Reverse Non-Equilibrium Molecular Dynamics (RNEMD) (arrows depict direction of heat flux). Dotted lines represent the periodic image of the cold slab.

These hot and cold conditions are enforced by selecting the atom with the highest kinetic energy (the “hottest” atom) within the cold slab, and swapping its energy with that of the atom with the lowest kinetic energy (the “coldest” atom) within the hot slab. This swap is repeated periodically, and over time would induce a temperature gradient in the system due to the flux from the hot slab to the cold one.

The flux can be written as

$$j^e = \frac{1}{2tA} \sum_{N_{\text{swap}}} \frac{m_i}{2} (v_{\text{hot}}^2 - v_{\text{cold}}^2) \quad (2.57)$$

where t is the total simulation time; A the cross-sectional area of the material studied, orthogonal to the direction of heat flux; N_{swap} the total number of swaps; m_i the atomic mass; and v_{hot} and v_{cold} the velocities of the hot and cold atom respectively.

After achieving steady state, the temperature profile of the system was sampled by computing the temperature of each slab through time averaging:

$$\frac{3N_{\text{slab}}k_B T_{\text{slab}}}{2} = \frac{1}{2} \left\langle \sum_i^{N_{\text{slab}}} m_i v_i^2 \right\rangle \quad (2.58)$$

where N_{slab} is the number of atoms in the slab; T_{slab} the temperature of the slab; and k_B the Boltzmann's constant. A typical temperature profile that could be obtained via RNEMD in steady state is shown in Figure 2.6.

Figure 2.6. Plot of a typical temperature distribution obtained through RNEMD.

The average temperature gradient was found by linear regression of the temperatures of the slabs that display linear variation of temperature with distance as shown in Figure 2.7. And finally, the thermal conductivity will again be determined by Fourier's Law in Equation 2.56.

Figure 2.7. Linear regression to obtain the average temperature gradient in the region showing linear response.

Chapter 3

Numerical Simulations of Atomic Structures

This chapter will detail the methods of simulating silica aerogels, graphene, and silicene that have been explored so far in this study, including simulations of their structures and the schemes for determining their thermal conductivities.

3.1. Silica Aerogels

Many simulations and models have been derived for silica aerogels with very varied purposes such as investigating the chemical kinetics, structural evolution and relaxation, coordination of the atoms, mechanical properties, and the kinetics during gelation. As the structure of aerogels can be exact and complete in a computational model, the relationships between the structure and material properties can be directly measured and analyzed. Many challenges remain in modelling the structures of aerogels as insufficient information at the atomic scale is provided through experimental characterizations due to their amorphous nature. Techniques to obtain the porous backbone of silica can be broadly classified into two categories, namely “mimetic” simulations, where dynamic simulations are employed to reproduce the aerogel’s experimental preparation, and reconstructions, where statistically accurate models are used to represent available experimental data. Typical structural and geometrical characterizations of the aerogel model include the pore size distributions, fractal dimensions, surface areas, and bond length and bond angle distribution [169].

A wide range of time- and length-scales can be accessed through many different modelling techniques; the smallest scales can be treated very accurately using quantum-mechanical

methods on the order of picoseconds and just a few molecules, larger scales on the order of nanoseconds and nanometers with thousands of atoms can be dealt with through atomistic studies such as MD, and finally, beyond such scales, lies the way of coarse-graining through the representation of a small number of atoms as a simplified “particle”. The method most suitable to be employed depends on the relevant computational data desired, as well as limitations on the computational power and cost. Hybrids of these techniques also exist, through multi-scale models. We will be largely focused on atomistic studies in our review here, as we will be attempting to verify that certain atomistic models are capable of reproducing the thermal properties of silica aerogel.

One of the earliest and simplest atomistic methods of simulating silica aerogel’s percolated structure through MD was through the scheme of negative pressure rupturing by Kieffer and Angell [29]. In this method, from a sample of amorphous silica, stepwise expansion was employed to bring the sample down to the percolation threshold. At each expansion step, the existing bonds were stretched simultaneously and instantaneously to lengths that were 10 to 35% beyond their equilibrium, and subsequently equilibrated. The potential applied was two-body interaction potential of the Born-Mayer form.

Nakano *et al.* [30] used a similar method to simulate much larger systems of more than 40,000 atoms and used a more complex Vashishta potential [36] consisting of two- and three-body terms with a highly parallel algorithm. It was found that this method generated a porous structure with fractal dimensions that depended on the density of the sample. The study also noted that this dependence was not reflective of experimental processes as the porous glass at a certain density was derived from the expansion of a previous glass. The

neutron-scattering static structure factor, bond statistics, and pore size distribution was found to be quite similar to experimental data.

Pohl *et al.* [31] presented three different methods of modelling silica aerogels, to provide greater understanding of aerogel synthesis and the underlying pore structure through comparisons with experimental data. In the first method, spherical silica particles of varying diameters were packed into a cell and their surface area was determined. The second method was the same as negative pressure rupturing. The final method was the cluster-cluster aggregation of silica clusters which produces the structure of aerogels upon gelation. The first method showed reasonable agreement with theoretical curves as the porosity increased. The pore size distribution was determined for the second method, and they found that different expansion rates results in differing pore size distributions. The final method was found to be the most representative of experimental aerogels in terms of the characteristic size and the composition.

More advanced methods of simulating silica aerogels was performed by modeling the oligomerization and gelation process directly. This was done through simulating solutions consisting of water, silicic acid monomers, and silicic acid dimers, with potentials that were designed specifically for such problems [170-172]. These were subsequently improved upon by imposing a more realistic all-atom reactive approach which incorporates the transfer of charges [33, 34]. These models were mainly used to study the actual gelation process in the final stage of condensation. A very comprehensive review on the methods and results of quantum-mechanical, MD, and coarse-grained models for silica aerogels was given by Gelb [169].

One of the most recent schemes to reconstruct the porous silica aerogel backbone was proposed by Murillo *et al.* [35]. Using a two- and three-body MD potential termed the Vashishta potential [36], the samples were prepared firstly by expanding a crystalline lattice of β -cristobalite with 24,000 atoms to the density required. Next the entire system is heated up to 3,000K, allowed to become amorphous, and subsequently relaxed by cooling down at temperatures between 2,500 to 0K. Geometrical features such as the fractal dimension were found to be in agreement with experimental data. These features were characterized using pair distribution function and from simulated scattering experiments. The samples' Young's modulus and tensile strength scaled with density via a power-law, and their magnitudes were in the same range as experimental data. The exponents of the power-law variation with density for the elastic modulus and tensile strength were found to be 3.11 ± 0.21 and 2.53 ± 0.15 respectively.

3.1.1. Negative Pressure Rupturing

In our MD studies to obtain the porous aerogel structure, two different methods were explored. In the first method of negative pressure rupturing, following the work of Kieffer and Angell [29], aerogels with densities in the range of 2.17 (dense glass) to 0.32g/cm^3 were produced. The initial lattice configuration of ideal β -cristobalite [173] was used as it has the same density as amorphous silica, which is 2.17g/cm^3 . The initial configuration is displayed in Figure 3.1.

Figure 3.1. Initial silica configuration of ideal β -cristobalite. Large blue dots represent silica atoms, small black dots represent oxygen atoms.

This configuration was quenched by decreasing the temperature linearly from 6,000K to 300K over 500ps to generate a random configuration of amorphous silica. Subsequently, the system was uniformly expanded in successive steps, stretching the existing bonds instantaneously by a factor in the range of 1.1–1.3. After each expansion step, the system was brought to a local minimum-energy configuration by conjugate gradient minimization and thermalized at 300K for another 15ps. Figure 3.2 displays the expanded porous state at various densities.

Figure 3.2. Percolated structure of silica aerogel at three different densities of 2.17g/cm^3 , 0.50g/cm^3 and 0.32g/cm^3 from left to right respectively. Large blue dots represent silica atoms, small black dots represent oxygen atoms.

Using this scheme, the system was gradually expanded down to the percolation threshold, where the porous network of silica still spans the simulation box in all three directions. This corresponded to a density of approximately 0.32g/cm^3 . The thermal conductivity at each expanded configuration was then determined by RNEMD. A time step of 0.5fs was used. Periodic boundaries were imposed in all directions. The heat flux was imposed by swapping energies once every 0.025ps . This amount of swapping ensured a rapid convergence of the simulated temperature gradient, and produced a linear response within the simulation cell. The system was allowed to equilibrate for a further 500ps , and finally, the temperature gradient was averaged over another 500ps . These time intervals had been found to be necessary for ensuring that a fully linear response had been reached in the system. Finally, the total thermal conductivity was calculated by simple averaging of the sample's thermal conductivity in the x -, y - and z -directions.

3.1.2. Expanding, Heating, Quenching Scheme

In the second method explored, an expanding, heating, and quenching scheme is utilized to obtain the porous aerogel structure, following the work of Murillo *et al.* [35], producing aerogels in the density range of 0.3 to 1.0g/cm³. Using the same initial lattice configuration of ideal β -cristobalite, the configuration is instantaneously expanded to the desired density, heated, and quenched, from 3,000K to 300K over 350ps to generate the percolated network of silica. Subsequently, the system is brought to a local minimum-energy configuration by conjugate gradient minimization and thermalized at 300K for another 50ps. Figure 3.3 displays the expanded porous state at 0.3g/cm³ with simulation cell size of approximately 18nm on each side. The thermal conductivity at each density is then determined with RNEMD, as discussed above.

Figure 3.3. Percolated structure of silica aerogel using the re-paramterized Tersoff potential with 52,728 atoms at a density of 0.3g/cm³.

3.2. Graphene

Classical MD with the AIREBO potential [117], as administered on LAMMPS [123], is employed to describe the interactions between carbon-carbon bonds. For the thermal conductivity studies, two different samples of graphene nanoribbons (GNRs) are considered, namely, the zigzag graphene nanoribbon (ZGNR) and the armchair graphene nanoribbon (AGNR). The widths of the GNRs are identified according to the number of dimer lines across their widths as shown in Figure 3.4.

Figure 3.4. Number of dimer lines for zigzag graphene nanoribbons (ZGNR) and armchair graphene nanoribbons (AGNR), respectively.

This first study of aligned STW defects used samples consisting of 10-ZGNR and 19-AGNR, and both samples measure approximately 2.1nm wide and 10.0nm long. The STW defects were introduced, as shown in Figure 3.5, by rotating two adjacent atoms by 90° with respect to the midpoint of their bond. The pristine graphene's hexagonal shape is thus distorted into two heptagons and two pentagons. Double vacancies were introduced by removing the two adjacent atoms.

Figure 3.5. STW and double vacancy defects, on the left and right respectively. STW defects simulated by 90° rotations about the midpoint of a bond.

Heat flux is imposed across the simulation cell in the direction of the y -axis to form a temperature gradient, as shown in Figure 3.6.

Figure 3.6. Schematic for Reverse Non-Equilibrium Molecular Dynamics (RNEMD) (Arrows depict the direction of the heat flux).

A time step of 0.5fs was used. Periodic boundaries were imposed only in the direction of heat transfer, i.e. the y -direction, which is also along the length of the GNRs. The energy of the initial configuration was first minimized using the conjugate gradient minimization scheme. Subsequently, the system was well equilibrated at a temperature of 300K for 250ps. Following this, the heat flux was imposed by RNEMD, swapping energies once every 0.025ps. This amount of swapping ensured a rapid convergence of the simulated temperature gradient, and produced a linear response within the simulation cell. The system

was allowed to equilibrate for a further 500ps, and finally, the temperature gradient was averaged over another 500ps. These time intervals have been found to be necessary for ensuring that a fully linear response has been reached in the system. Also, the global angular momentum of the system was nulled by subtracting a rotational component from each atom every 0.5ps. This ensured that there was no spurious global rotation of the entire system [174] due to significant perturbations during the swapping of energies.

The cross-sectional thickness of the graphene sheet had been assumed to be 0.142nm [2-4, 61, 175-177], which corresponds to the carbon-carbon bond length. As the thermal conductivity for an isolated single-layered GNR is not a well-defined quantity, the cross-section of heat conduction can be chosen in quite a few ways. One option is to assume the thickness to be the bond distance between layers of 0.34nm [178], which is the value we will use for validating the model for graphene monolayers with no edge effects. In order to allow for comparisons under consistent conditions, especially with previous reported studies [2-4, 61, 175-177], the carbon-carbon bond length (0.142nm) was chosen for comparisons with silicene.

3.2.1. Activating Superlubricity to Exfoliate Graphene

For our studies on the exfoliation of graphite through the activation of superlubricity, circular graphite flakes are compressed between two slabs of hydrogen-terminated silicon at room temperature of 300K. These AB-stacked flakes are either two or three layers thick, with diameters ranging from 2 to 4nm. A schematic of the model is depicted in Figure 3.7.

Figure 3.7. Initial configuration of our MD model for exfoliation of a graphite flake with three layers and diameter of 3nm at 300K using (111) H-terminated silicon substrates.

Periodic boundaries are prescribed in all directions to simulate bulk silicon substrate properties. The lateral dimensions of the simulation box are made sufficiently large to prevent interactions between the graphene layers in the neighboring periodic cell, even in a hypothetical situation where all graphene layers are exfoliated and aligned in one particular direction. The simulation occurs in a vacuum, thus mimicking dry contact between the substrates and the graphite flake. The LJ parameters σ and ϵ are determined using the Lorentz-Berthelot mixing rules [105] discussed in Section 2.2.1. Using the LJ parameters for pure carbon, silicon, and hydrogen [117, 179], the LJ parameters for any two atoms of differing elements have been obtained to be $\sigma_{C-Si} = 2.80\text{\AA}$, $\sigma_{C-H} = 3.03\text{\AA}$, $\epsilon_{C-Si} = 0.00500\text{eV}$, and $\epsilon_{C-H} = 0.00206\text{eV}$.

A time step of 0.50fs is used. To begin the simulation, the entire system is equilibrated to the specified temperature over 25ps. During the equilibration, the linear momentum of the graphite flake's center of mass is nulled every 0.5ps, preventing the graphite flake from drifting due to random fluctuations. Thereafter, the graphite flake is slowly compressed by

the silicon substrates. This compression is achieved by displacing the top of the simulation box downwards along the z-axis at a constant rate of displacement of $20 \mu\text{\AA}/\text{ps}$. Slower rates of displacements have also been checked to ensure that results are independent of the rate of displacement. The unloading rates are chosen to be double those of the loading rates to reduce the computational expense; we have determined that the exfoliation phenomenon is independent of the rate of unloading. The initial distance between the surfaces of the substrates and the graphite flake is considered to be $5 \text{\AA}$. The minimum distance achieved between the surfaces of the top and bottom substrate in each compression is $4 \text{\AA}$, which is close to the theoretical thickness of a single layer of graphene. This approach ensures that sufficient compressive stress is achieved in the graphite flake during each compression.

The average compressive stress is determined by the summation of the stress in the z-direction of each atom in the graphite flake, divided by the total volume of the graphite flake. The volume of each layer of the graphite flake is determined as the volume of a cylinder, where the diameter is given by the diameter of the flake. The height is the equilibrium interlayer distance of graphite, given as $3.35 \text{\AA}$. The average stress in the silicon substrates is calculated similarly by the summation of the values of the stress per atom and divided by the volume of the silicon substrates in the unit cell.

Figure 3.8 shows the final configuration where a tri-layer graphite flake is compressed between H-terminated silicon substrates, and the substrates are separated again. The exfoliation mechanism in this simulation can be explained using several data outputs, as shown in Figure 3.9.

Figure 3.8. Final configuration of our MD model for exfoliation of a graphite flake with three layers and diameter of 3nm at 300K using (111) H-terminated silicon substrates.

Figure 3.9. Molecular dynamics outputs calculated during compression of the 30 Å-diameter tri-layer graphite flake using H-terminated (111) silicon substrates.

With reference to the initial configuration shown in Figure 3.6, the labels for plotting the data of each layer in Figure 3.9 are as follows: the lowest, middle, and topmost layers have been numbered as layers 1, 2, and 3, respectively. Figure 3.9a shows the distances between the centers of mass of adjacent layers. The circular shape of the layers allows us to easily observe the exfoliation phenomenon through this plot which, in this example of tri-layer graphite, consists of a two stages. The first exfoliation, occurring around the 430,000th timestep, is the most significant exfoliation. The increase in the layers' center-to-center distance is approximately each layer's nominal diameter. A partial second exfoliation occurred around the 600,000th timestep.

Figures 3.9b and 3.9c show the changes in the relative inter-layer in-plane velocities, and the relative inter-layer angular velocities respectively. These results have been calculated using the velocities of the centers of mass of the individual layers and their angular velocities. As observed in Figure 3.9b, an initial infinitesimal sliding motion exists between the layers which can be attributed to the atomistic thermal vibrations. Upon exfoliation, the magnitudes of the inter-layer in-plane velocities suddenly increase. These changes in the inter-layer velocities are accompanied by sudden changes in the inter-layer angular velocities, demonstrating that during exfoliation, the layers not only slide with respect to each other, but they also rotate. Figure 3.9d shows the total resultant torque on each layer. As observed, during compression and particularly upon exfoliation of the layers, the magnitudes of the torques applied on the layers increase. This can explain the rotating motion of the layers with respect to each other.

Figure 3.9e shows the changes in the total potential energy of the carbon atoms in each layer. The gap between the energy levels of layer 2 and those of layers 1 and 3 is due to the

AB structure of the layers in the finite-sized graphite flake. Figures 3.9f and 3.9g respectively show the average compressive stress experienced by the graphene layers and the silicon substrate. Figure 3.9e shows an initial drop in energies of the layers, between approximately 0 and 400,000 timesteps, which can be attributed to the adhesion of the graphite flake to the substrates prior to the compression. Subsequently, as the compression comes into effect and increases, strain energy is stored in the layers, and the energies of the layers increase. Next, during exfoliation, some of the stored energies in the layers are released, and the layers reach a new, but somewhat higher, minimum state of energy. With reference to Figures 3.9b and 3.9c, it appears that these amounts of energies are converted to the kinetic energies required for the layers to slide and rotate.

During exfoliation, compressive stresses drop due to thinning. However, as observed in Figures 3.9f and 3.9g, after the two-stage partial and complete exfoliation, further compression does not lead to further exfoliation of the layers. The maximum average compressive stress required to initiate the exfoliation, as experienced by the graphite flake and the silicon substrates, have been observed to be 17.4kbar and 0.4kbar, respectively. The latter can be assumed to be equal to the theoretical average external load required to initiate this thinning phenomenon.

Figure 3.9h shows the standard deviation of the z-coordinate positions of the atoms in each of the graphene layers as a measurement of the layers' flatness during the compression. It is observed that prior to the occurrence of any exfoliation, the layers involved in the exfoliation are brought into atomically flat configurations. Keeping this information in mind, and by considering the fact that inter-layer rotations are involved as observed in Figure 3.9c, it can be concluded that the observed exfoliation of the layers are initiated by activating the

superlubricity regime between the layers. However, during exfoliation, the standard deviations of the out-of-plane deflections of the layers increase as observed in Figure 3.9e. These out-of-plane deformations serve as topographical roughness which tends to inhibit superlubricity, causing partial of the layers, as observed in Figure 3.9a, particularly for the second stage exfoliation.

In order to obtain better understanding of the superlubricity mechanism involved in the exfoliation of graphite flakes under compression using H-terminated silicon substrates, the effects of different parameters in the MD simulations were studied. The parameters varied were the diameters of the graphite flakes, number of the graphene layers in the flake, and the crystalline orientation of the substrate surfaces. Table 3.1 summarizes the values of the parameters considered for the different sets of studies.

Table 3.1. Parameter sets considered for studies of the factors affecting compressive exfoliation.

Case Study Number	1	2	3	4	5	6
Number of Layers	2	2	2	3	3	2
Flake size (Å)	30	30	20	30	40	40
Substrate	(111)	(110)	(111)	(111)	(111)	(111)

Each of the six sets of conditions was repeated four times by re-assigning the initial random Gaussian velocity distributions of the atoms in each run. Twenty-four simulations were conducted in total. In reporting the results of the compression of the graphite flakes, we consider an increase of the center-to-center distance of any two adjacent layers to at least

70% of the flake’s diameter as a “major” exfoliation. Any increase less than 10% is not considered as exfoliation. Other cases in between are considered to be “partial” exfoliation. In the majority of simulations carried out, i.e. 19 out of 24, at least one major exfoliation is observed. For the tri-layer cases studied, partial exfoliations are also observed in addition to a major exfoliation. In all of these cases with major exfoliations, it is observed that single graphene layers have been exfoliated as a result of compression. In cases 1 to 5, exfoliation behavior is observed to occur frequently. Also, major exfoliations are observed in at least three of the four repetitions of the simulation. In Figure 3.10, the maximum average compressive stress in the graphene flake that is required to initiate the exfoliation is compared across the five cases.

Figure 3.10. The maximum average compressive stress, together with their errorbars, required by the graphite layers for activating the exfoliation under five of the different sets of conditions specified in Table 3.1. Each set was repeated four times and the errorbars represent the standard deviation.

Previous studies of the spontaneous rotation of sliding graphite flakes on crystalline substrates may help to explain the thinning phenomenon that is observed here. It was reported by Filippov *et al.* [56] that the sliding and rotation of moving finite-sized graphite flakes on crystalline substrates are coupled due to anisotropic friction. Due to this coupling, torque is experienced by the flakes in addition to friction, causing them to undergo spontaneous rotations. With these rotations, the graphite flakes tend to reorient from one potentially favorable state to another while sliding on the crystalline substrates.

A comparison between the compressive stresses observed in simulation cases 1 and 2 reveals little difference. In these two sets of studies, a bi-layer graphite flake of the same size is compressed using substrates with different crystalline surfaces. It can be established that the effect of incommensurate contact of the graphene layers and the substrates by itself is not significant in initiating the superlubricity behavior which results the exfoliation of graphene layers. This mechanism could possibly be an effect of the commensurate AB structure of the graphite flakes instead, which is constant in these two sets of studies.

The AB crystalline structure of graphite possesses in-plane shear thermal modes [180]. In these modes, the graphene layers perform in-plane vibration with respect to each other. Figure 3.9c confirms the existence of such modes since, even prior to the initiation of the exfoliation, the magnitude of the in-plane velocities of the layers relative to each other is not zero on average, and thus an infinitesimal sliding motion exists between the layers. Due to the infinitesimal inter-layer sliding motions, a very similar phenomenon to that reported by Filippov *et al.* [56] appears to be occurring during the compression of the finite-sized graphite flake in our study. By applying compression, interlayer friction arises due to the atomistic surface energy corrugation of the layers. With the emergence of these inter-layer

frictions, the shear modes of the layers are affected and the inter-layer sliding motion of the layers becomes coupled with inter-layer rotations. As a result of these interlayer rotations, the superlubricity regime is activated and the inter-layer frictions significantly decrease. This allows the graphene layers to move almost freely and become exfoliated. As discussed earlier in this chapter, out-of-plane deformations may also appear in the layers during exfoliation, and this tends to take the layers out of the superlubricity regime and prevent exfoliation. However, in the majority of the cases studied, the exfoliation phenomenon dominates, and the result is that these out-of-plane deformations do not generally prevent the exfoliations.

On the other hand, in extreme cases, when the graphite flakes are sufficiently large and thin, as in case 6 in Table 3.1, the out-of-plane deformations prevent any exfoliation from occurring at all. Figure 3.11 shows the outputs from one such case. It can be seen from Figure 3.11a that exfoliation has not occurred, even though the compressive stress applied to the graphene layers, shown in Figure 3.11b, is much larger than in the other cases studied where exfoliation is observed (Figure 3.10). It is observed in Figure 3.11c that in this case, the out-of-plane deformations which appear at the start of thinning persist, stopping the superlubricity regime and preventing exfoliation. From Figure 3.10, it is generally observed that as the size of the graphene layers decreases or as the number of layers increases, the compressive stress required for initiating the exfoliation decreases. This can be observed by comparing the stresses corresponding to cases 1 and 3, 1 and 4, as well as 4 and 5, with each other.

Figure 3.11. Molecular dynamics outputs calculated during compression of a non-exfoliating case of bi-layer 40 Å graphite flake using (111) H-terminated substrates.

Out-of-plane deformations of the layers are significant in preventing the exfoliation phenomenon for the extreme case of bi-layer 40 Å graphite flake studied in Figure 3.11. By comparing how dominant the out-of-plane deformations of the layers are expected to be during the exfoliation of the graphite flakes as reported in Figure 3.10, the difference between the values of the average compressive stresses required for initiating the thinning can also possibly be explained. It is expected that when the graphite flakes become more “slender”, implying decrease in the number of the layers or increase in the diameter of the flakes, the out-of-plane deformations of the layers become more dominant. Hence, larger compression should be applied to suppress these out-of-plane deformations and to bring the layers to the flat configuration required for initiating the superlubricity regime. On the other hand, when the graphite flakes become less “slender”, implying increase in the number of the layers or decrease in the diameter of the flakes, the out-of-plane deformations of the layers become less dominant and can be suppressed with less compression.

Finally, it is worth comparing the outcomes of compressing the flakes in cases 5 and 6. For sufficiently large flakes of 40Å in diameter, exfoliation is not observed to occur for the bi-layer cases, while it is observed to occur for the tri-layer cases. This result implies that if the graphite flakes are sufficiently thick, the thinning is expected to happen for sizes which are relevant for graphene device manufacturing. Moreover, the superlubricity behavior in the graphite layers, which has been shown here to be necessary for the thinning phenomenon to happen, was experimentally observed for graphite flakes, up to micrometer sizes and at ambient conditions [54]. All these suggest the necessity for further experimental studies on compression of graphite flakes using passivated crystalline substrates. This type of process may open new routes in producing graphene on clean passivated substrates.

3.3. Silicene

For the comparison studies between graphene and silicene monolayers, the respective parameterization of the Tersoff potential for carbon [103] or silicon [156, 157], is employed. Monolayered silicene possesses the same honeycomb structure as graphene. The structure of silicene was obtained in our study simply by placing silicon atoms within the hexagonal lattice positions and minimizing the entire structure with the Tersoff potential using conjugate gradient minimization.

The cross-sectional thickness of the graphene sheet has been similarly assumed to be 0.142nm, as explained in Section 3.2. In the same vein, the silicene thickness was chosen to be 0.23nm, which is the nearest neighbor bond length determined through the radial distribution function after the honeycomb structure was fully relaxed using conjugate

gradient minimization. This length is close to the bond length of 0.224nm and 0.232nm found in previous theoretical studies [87, 181] using density functional theory.

Strip sizes are approximately 5nm in width and varied between 50-2000nm in length. Periodic boundaries were imposed in all directions to simulate bulk properties, and the ends of the strips in the y-direction were fixed. The energy of the initial configuration was first minimized using the conjugate gradient minimization scheme. Next, the system was equilibrated to the canonical ensemble at a temperature of 300K.

Thereafter, heat flux was introduced into the system in the microcanonical ensemble. The amount of energy added and subtracted from the strips has to be scaled according to the length of the strips, in order to achieve proper convergence. Essentially, shorter monolayers would require greater rate of change in energy in order for the temperature gradient to be fully linear, consistent with the findings of Cao [178]. With too low a rate, the temperature gradient will take too long to converge, and too high a rate will cause the temperature gradient to be non-linear regardless of the length of time of the simulation. In the present study, the rate of energy addition and subtraction decreased from 1.0 to 0.1eV/ps, as the length of the strips increased. These were chosen by iteratively observing which rates were able to generate a linear temperature for a given length, and yet did not require simulation times to be too lengthy to achieve linearity.

Chapter 4

Solid Thermal Conductivity of Silica Aerogels

The results for the solid thermal conductivity of silica aerogels are presented in this chapter. These results are obtained from the simulation methods laid out in Section 3.1. This study is first validated using the thermal conductivity of dense amorphous silica using the BKS potential, by comparison with previous theoretical studies. Subsequently, porous silica aerogels is obtained using negative pressure rupturing and results of their thermal conductivity are laid out and discussed. The deficiencies of this model is discussed and analyzed through the comparison of the phonon density of states of amorphous silica for both the BKS and the re-parameterized Tersoff potential. An enhanced model is devised using the Tersoff potential together with a heating, expanding, and quenching scheme.

4.1. Thermal conductivity of dense amorphous silica with the BKS potential

This study begins with the validation of the current MD simulation scheme through determining the thermal conductivity of dense amorphous silica. Firstly, a system of 648 atoms (216 silicon atoms and 432 oxygen atoms) of amorphous silica was simulated by quenching to a temperature of 300K. This number of atoms corresponds to a system volume of $(21.5 \times 21.5 \times 21.5) \text{\AA}^3$ (corresponding to the length, width, and height of the simulation box respectively) at a density of 2.17g/cm^3 . Results from RNEMD indicated a thermal conductivity of approximately $1.20 \pm 0.07 \text{W/(m K)}$. This was in good agreement with previous results reported by Jund and Jullien [128] and Coquil *et al.* [132] for systems of similar dimensions and number of atoms.

Figure 4.1. Thermal conductivity for amorphous silica systems of various lengths at 300K compared with results of previously reported studies of Huang *et al.* [182] and Coquil *et al.* [132]. S is the cross-sectional area of the simulated samples in angstroms.

Next, a larger system of 3,000 atoms (1,000 silicon atoms and 2,000 oxygen atoms) was simulated, corresponding to a system volume of $(35.8 \times 35.8 \times 35.8)\text{\AA}^3$ at a density of 2.17g/cm^3 . The thermal conductivity was found to be 1.39W/(m K) at 300K. This was in good correlation with the findings by both Huang *et al.* [182] and Coquil *et al.* [132], who found an increasing trend in the thermal conductivity as the length of the simulation cell increases, and that this increasing trend was largely independent of the cross-section. Moreover, this result is close to the experimental thermal conductivity of silica which is approximately 1.40W/(m K) [183]. These results are consolidated in Table 4.1 and plotted in Figure 4.1 for comparison. Furthermore, Coquil *et al.* [132] noted that due to size effects, thermal conductivity will be over-estimated as system size gradually increases, such that

the predicted thermal conductivity will reach a plateau at around 2.1W/(m K) at room temperature for system sizes exceeding 110Å.

Table 4.1. Thermal conductivity for amorphous silica systems of various lengths at 300K compared with results of previously reported studies of Huang *et al.* [182] and Coquil *et al.* [132].

	Cross-sectional Area, Å ²	Length, Å	Thermal Conductivity, W/(m K)
Huang <i>et al.</i> [182]	21.4 × 21.4	21.4	1.32
Huang <i>et al.</i> [182]	21.4 × 21.4	43.0	1.70
Huang <i>et al.</i> [182]	21.4 × 21.4	64.0	1.94
Coquil <i>et al.</i> [132]	23.4 × 22.5	23.4	1.20
Coquil <i>et al.</i> [132]	23.4 × 22.5	45.0	1.60
Coquil <i>et al.</i> [132]	23.4 × 22.5	70.0	1.85
Coquil <i>et al.</i> [132]	31.3 × 27.1	45.0	1.58
Present Study	21.5 × 21.5	21.5	1.20 ± 0.07
Present Study	35.8 × 35.8	35.8	1.39 ± 0.11

4.2. Structural correlations of porous silica aerogel with the BKS potential

The porous network of the silica aerogel was simulated next, using negative pressure rupturing on a system of 3,000 atoms. Such a system size was found to be necessary in order to produce an aerogel sample that was sufficiently porous and yet retained connectivity along all three axes. The fractal dimension was found after each expansion step, at densities of 0.99, 0.57, 0.50, 0.43, 0.37, 0.32g/cm³. The total radial distributions for each density were calculated using the Interactive Structure Analysis of Amorphous and Crystalline Systems (ISAACS) [184], and power-law decays are superimposed on the peak structures to determine the fractal dimension of the resulting samples, using the method described by Kieffer *et al.* [29]. The present results are compared with that study as well, as shown in Figure 4.2 and tabulated in Table 4.2.

Table 4.2. Values of fractal dimension with increasing density, in comparison with Kieffer *et al.* [29].

	Density, g/cm ³	Fractal Dimension, d_f
Kieffer <i>et al.</i> [29]	0.10	1.70
Kieffer <i>et al.</i> [29]	0.20	1.90
Kieffer <i>et al.</i> [29]	0.40	2.17
Kieffer <i>et al.</i> [29]	0.70	2.54
Kieffer <i>et al.</i> [29]	1.10	2.90
Present Study	0.32	1.87

Present Study	0.37	1.94
Present Study	0.43	2.02
Present Study	0.50	2.09
Present Study	0.57	2.29
Present Study	0.99	2.86

Figure 4.2. Variation of fractal dimension with increasing density, in comparison with Kieffer *et al.* [29].

We can see that the variation of the fractal dimension, d_f , with density is close to that by Kieffer *et al.* [29]. The minor differences are likely to be due to the different potentials used. Experimentally, aerogel fractal dimensions were found to vary with processing conditions, where it is approximately 1.8 under basic processing conditions, and about 2.2 to 2.4 in both acidic and neutral conditions [185].

4.3. Thermal conductivity of porous silica aerogel with the BKS potential

Next, the thermal conductivity was found after each expansion step, using the method of RNEMD described in Section 2.4. The data obtained are shown in Figure 4.3 and Table 4.3. The curve of a power-law fit of the data is also plotted in the figure.

Table 4.3. Values of the solid thermal conductivity of the simulated aerogel samples with increasing density.

Density, g/cm ³	Thermal Conductivity, W/(m K)
0.32	0.12 ±0.06
0.37	0.15 ±0.05
0.43	0.17 ±0.05
0.50	0.20 ±0.05
0.57	0.20 ±0.05
0.99	0.41 ±0.04

Figure 4.3. Power law fit of the variation of the solid thermal conductivity of the simulated aerogel samples with density.

We can see that the variation of thermal conductivity with density is almost linear, where it decreased as the density decreased. This shows that the method of negative pressure rupturing is able to reproduce the significant decrease in thermal conductivities observed in silica aerogels experimentally, where the thermal conductivity at a density of 0.32g/cm³ decreases by almost an order of magnitude to $0.13 \pm 0.06 \text{ W/(m K)}$, compared with dense amorphous silica.

Experimental data showed that a power law fit of the variation between thermal conductivity and density would produce an ζ value of 1.6 in the density range of 0.3 to 1.0g/cm³ [28]. This study found a ζ value of 1.01 in the density range of 0.32 to 0.99g/cm³. The very low density of experimental aerogel was not achievable considering the relatively small system size of this study in comparison to bulk aerogel, as the sample would fragment into totally disconnected parts, hence the thermal conductivity variation could not be

determined. Moreover, at the density range of around 0.3g/cm^3 , the experimental value was of the order of $0.01\text{W}/(\text{m K})$ [28], which is one order of magnitude smaller than the value of $0.13 \pm 0.06\text{W}/(\text{m K})$ as determined by this study.

However, it was noted by Jain *et al.* [186] that the thermal conductivity of aerogels were very much dependent on the processing conditions that produced the aerogel. Their experiments have found that after sintering their aerogel sample, a power law fit obtained an ζ value of 1.04 for a density range of $0.4 - 1.6\text{g/cm}^3$ with a prefactor C_λ of 0.58. This correlates very well with the present results our study found as shown in Figure 4.3, and can be explained by the fact that the method of negative pressure rupturing was not able to fully reproduce various defects that would account for the extremely low thermal conductivity of as-prepared bulk aerogel, as it cannot reproduce the exact conditions during the sol-gel process. These defects include micro-cracks, very broad pore size distribution resulting in micro-porosity, impurities, and hanging/loose-ended silica chains. All these would significantly scatter phonons and result in a very limited mean free path. Negative pressure rupturing is only able to produce structural correlations such as the fractal dimensions and pore size distributions in the nano-scale [29, 30]. This implies that larger micro to macro scale features will not be represented adequately, especially considering the small size of our simulation relative to bulk aerogel.

Experimentally, this was verified by Jain *et al.* [186], where the power law relationship exponent for as-prepared bulk aerogel was 1.65 and thermal conductivity was on the same order of magnitude as determined by Fricke [28]. Sintering the aerogel effectively removed a large portion of the defects, healing the microstructure of the aerogel. The phonon mean free path was found to be $5.6\text{\AA}$ for dense silica at room temperature [186]. This is similar

to the size of the micropores present in as-prepared bulk aerogel, thus these micropores cause the most significant phonon scattering [186]. Since the method of negative pressure rupturing was not able to reproduce defects and was only able to produce nanopores, the present results obtained from this method were largely correlated with sintered bulk aerogels rather than as-prepared bulk aerogels, down to the order of magnitude of the thermal conductivity.

Figure 4.4. Comparisons of the power law fit of the results from the present study with experimental studies by Jain *et al.* [186] and Fricke [28].

This can clearly be seen in Figure 4.4, where the power law curves are plotted together for comparison. This is even more apparent when we consider the pore size distribution of our simulated aerogel, as calculated using PSDsolv [187] which determines the relative probability of finding pores of different sizes, in a procedure described as follows.

A possible definition of a pore's size within a model structure for a given point is a sphere. Such a sphere should be sufficiently large so as to contain the given point, yet it does not overlap with its neighboring atoms. An estimation of the distribution of pore sizes can be made by constructing a grid of the entire space of the model and determining, at each grid point, the biggest possible diameter of a sphere, D . This information is used to construct a cumulative histogram, $H(D)$. This histogram is representative of the probability of encountering a point with pore size equal to or greater than the diameter, D .

Figure 4.5. Determination of pore sizes within a cavity, depicted in 2D for simplicity.

- a) The cavity is in the middle, surrounded by atoms which are depicted as orange circles. P is the point where the pore size will be measured. D is the diameter of any sphere that encloses the cavity. b) For any given largest sphere enclosed by atoms within the cavity, R_L is the radius, C_L the center, S_i the distance between C_L to the center of the i -th atom, and r the radius of an atom.

Consequently, the pore size distribution can be given as

$$P(D) = -\frac{dH(D)}{dD} \quad (4.1)$$

Figure 4.5 is a schematic depicting how $P(D)$ can be determined. Since R_L is a function of C_L , such that

$$R_L(C_L) = \text{MIN}(S_i) - r, \quad i = 1, \dots, n \quad (4.2)$$

C_L needs to be determined such that R_L is maximum, in order to find the largest sphere radius possible. This is constrained by the fact that the point P should be within the sphere, such that

$$d_p \leq R_L(C_L) \quad (4.3)$$

Constrained nonlinear optimization is used in PSDsolv to determine the pore size distribution by solving for the largest sphere diameter D that encompasses a given point P , which is an optimization problem setup as

$$\text{MAXIMIZE } R_L(C_L) = \text{MIN}(S_i) - r, \quad d_p - R_L(C_L) \leq 0 \quad (4.4)$$

Figure 4.6. Pore size distribution of simulated aerogel at the lowest density of 0.32g/cm^3 .

As seen in Figure 4.6, where the pore size distribution for the lowest density of 0.32g/cm^3

was plotted, the largest pore size that could be found has a pore diameter in the order of

less than $30\text{\AA}$.

Additionally, it was noted in Section 4.1 that the predicted thermal conductivity of amorphous silica had a tendency to increase as the system size increases. Similarly, finite size effects may have played a significant role in the larger than expected values of thermal conductivity of the aerogel obtained in this study for the very low density aerogels. This problem is exacerbated further by the fact that the BKS potential may not have been the best choice of potential for modeling the thermal properties of amorphous silica.

These are the possible explanations for the discrepancy noted between predicted results in this study and those from experiments. In order to address these issues, an enhanced model is devised and validated, using an expanding, heating, and quenching scheme as discussed

in Section 3.1. This is implemented together with the Tersoff potential which was re-parameterized to handle the interatomic interactions for silicon and oxygen, as discussed in Section 2.2.4. We will demonstrate that such an approach is superior to the model discussed above, giving us a better representation of the experimental and theoretical thermal properties of bulk experimental silica aerogel.

4.4. Thermal conductivity of dense amorphous silica with the Tersoff potential

To validate our MD scheme, we compared the thermal conductivity of much larger slabs of amorphous silica with experimental results. Increasing lengths of amorphous silica were generated by quenching from 5,000K to 300K, their thermal conductivities were determined through RNEMD, and the results were plotted in Figure 4.7 with their respective error bars.

Note that the error bars for the results from the Tersoff potential are significantly smaller than the marker size, implying that the variations between simulations are very small in comparison with the BKS potential. Table 4.4 lists down all the results obtained. The results from previous theoretical studies [132, 182] were also furnished for comparison.

Figure 4.7. Comparisons of the variation of the thermal conductivity for amorphous silica systems of various lengths at 300K with results of previously reported studies from Huang *et al.* [182] and Coquil *et al.* [132]. S is the cross-sectional area of the simulated samples.

Table 4.4. Values of the thermal conductivity for amorphous silica systems of various lengths at 300K with results of previously reported studies from Huang *et al.* [182] and Coquil *et al.* [132].

	Cross-sectional Area, Å ²	Length, Å	Thermal Conductivity, W/(m K)
Huang <i>et al.</i> [182]	21.4 × 21.4	21.4	1.32
Huang <i>et al.</i> [182]	21.4 × 21.4	43.0	1.70
Huang <i>et al.</i> [182]	21.4 × 21.4	64.0	1.94
Huang <i>et al.</i> [182]	21.4 × 21.4	85.0	1.85
Coquil <i>et al.</i> [132]	23.4 × 22.5	23.4	1.20

Coquil <i>et al.</i> [132]	23.4 × 22.5	45.0	1.60
Coquil <i>et al.</i> [132]	23.4 × 22.5	67.0	1.85
Coquil <i>et al.</i> [132]	23.4 × 22.5	90.0	2.00
Coquil <i>et al.</i> [132]	23.4 × 22.5	115.0	2.10
Present Study, BKS Potential	50.2 × 50.2	64.5	1.20 ± 0.09
Present Study, BKS Potential	50.2 × 50.2	107.5	1.60 ± 0.05
Present Study, BKS Potential	50.2 × 50.2	150.5	1.82 ± 0.07
Present Study, BKS Potential	50.2 × 50.2	193.5	1.92 ± 0.09
Present Study, BKS Potential	50.2 × 50.2	236.5	1.94 ± 0.12
Present Study, Tersoff Potential	50.2 × 50.2	64.5	0.93 ± 0.02
Present Study, Tersoff Potential	50.2 × 50.2	107.5	1.02 ± 0.002
Present Study, Tersoff Potential	50.2 × 50.2	150.5	1.05 ± 0.007
Present Study, Tersoff Potential	50.2 × 50.2	193.5	1.10 ± 0.01
Present Study, Tersoff Potential	50.2 × 50.2	236.5	1.10 ± 0.008

We can clearly see an increasing trend as the system length increases. The BKS potential has a tendency to overshoot the thermal conductivity of bulk amorphous silica, which typically lies between $1.37 - 1.4 \text{ W}/(\text{m K})$ [183]. At our largest length scale, the BKS potential produced a thermal conductivity which plateaus approximately at values between $1.89 \pm 0.12 \text{ W}/(\text{m K})$ and $1.94 \pm 0.0912 \text{ W}/(\text{m K})$. Huang *et al.* [182] and Coquil *et al.* [132] reported significantly higher values at shorter length scales and smaller cross-sectional areas, as seen in Figure 4.6. We can deduce that finite size effects can be caused by a limited length scale as well as drastic changes in the cross-sectional areas. In contrast, the Tersoff potential underestimates the thermal conductivity, plateauing at $1.10 \pm 0.01 \text{ W}/(\text{m K})$, and displaying an almost linear dependence with increasing length scales.

In fact, if we were to extrapolate the results to an infinite length scale to obtain a better representation of bulk amorphous silica, we would find that the Tersoff potential provides a significantly better estimation of bulk thermal properties. In Figure 4.8, we plot the inverse of the thermal conductivities versus the inverse of the lengths ($1/\lambda_s$ vs $1/L$), and extrapolated the results. Table 4.5 displays all the numerical results.

Table 4.5. Values of the inverse thermal conductivities for amorphous silica systems using the BKS and Tersoff potentials.

Interatomic Potential Used	Inverse Length, $1/\text{\AA}$	Inverse Thermal Conductivity, $(\text{m K})/\text{W}$
BKS	0.004	0.529
BKS	0.005	0.514
BKS	0.007	0.522

BKS	0.009	0.550
BKS	0.016	0.627
Tersoff	0.004	0.908
Tersoff	0.005	0.908
Tersoff	0.007	0.948
Tersoff	0.009	0.984
Tersoff	0.016	1.077

Figure 4.8. Linear extrapolation of the thermal conductivities for amorphous silica systems using the BKS and Tersoff potentials.

From the linear extrapolation and applying the inverse of the x -intercepts of each curve, we obtained values of 2.13W/(m K) for the BKS potential, and 1.19W/(m K) for the Tersoff potential, at bulk length scales. This gives an error of 55% overestimation for the former, and 13% underestimation for the latter, thus clearly showing that the re-parameterized Tersoff is much more capable of reproducing bulk thermal properties than the BKS potential can.

Further analysis of these potentials is possible by examining the vibrational density of states (vDOS) of each potential, in Figure 4.9. The vDOS, which shows the different phonon frequencies excitable in each material and are dependent on the interatomic potential used, can be found through the Fourier transform of the velocity autocorrelation function (VACF), as described in texts on lattice dynamics or statistical mechanics [188]. The velocities of each atom are output at regular intervals, determined based on the sampling frequency desired. In our study, we used a sampling frequency of 5THz. This is done throughout an MD run at a given temperature (taken as 300K in the present study) in the microcanonical ensemble, such that we obtain, for the initial and each subsequent n -th time step for a given time step of Δt , respectively

$$\mathbf{v}_i(t_0) = (v_{ix}(t_0), v_{iy}(t_0), v_{iz}(t_0)) \quad (4.5)$$

$$\mathbf{v}_i(t_0 + n\Delta t) = (v_{ix}(t_0 + n\Delta t), v_{iy}(t_0 + n\Delta t), v_{iz}(t_0 + n\Delta t)) \quad (4.6)$$

Once the requisite numbers of samples are acquired, the VACF can be found by time-averaging,

$$\begin{aligned}
 C_v(t) &= \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle \\
 &= \frac{1}{N} \sum_{i=1}^N \frac{1}{t} \sum_{n=1}^t (\mathbf{v}_i(t_0) \cdot \mathbf{v}_i(t_0 + n\Delta t))
 \end{aligned}
 \tag{4.7}$$

where N is the total number of atoms, and t the total number of time steps. An example of the VACF variation over 5ps is shown in Figure 4.9. The full vibrational spectrum can only be captured when damped oscillations have approximately converged to zero, through observation of Figure 4.9.

Figure 4.9. Decay of the VACF with time.

Finally, the vibrational spectrum can be determined by the Fourier transform of the VACF and the resulting data smoothed using a smoothing filter as the amount of random noise in

the system can be quite significant. In all our studies where the calculation of the vDOS is necessary, we have used the Savitzky–Golay smoothing filter [189].

Figure 4.10. Vibrational density of states of amorphous silica based on a) the BKS potential and b) the Tersoff potential.

From previous experimental and theoretical results by Laughlin *et al.* [163], the vDOS of amorphous silica showed three significant peaks near the frequencies of 10.5THz, 24.0THz and 36.0THz. These peaks are clearly shown in the current results based on the Tersoff potential in Figure 4.10b. Moreover, the distribution of the frequencies is in good correlation with the distribution obtained by Laughlin *et al.* [163].

In sharp contrast, the corresponding results based on the BKS potential was largely smeared in the lower frequency range as observed in Figure 4.10a, showing no apparent peaks below the 30THz region, and only clearly reproducing the peak near 36.0THz. The low frequency content below the 30THz region is the likely cause of the overestimation of the bulk thermal properties of amorphous silica, as the amplitudes over-represents those found in experiments on amorphous silica.

Thus, from all the numerical data presented, we can conclude that the re-parameterized Tersoff potential is a far superior alternative in the thermal characterization of bulk amorphous silica than the BKS potential.

4.5. Structural correlations of porous silica aerogel with the Tersoff potential

The porous network of the silica aerogel was simulated next, using the heating, expanding, and quenching scheme discussed in Section 3.1, on a cubic system of 52,728 atoms, with densities ranging from 0.3 to 1g/cm³. The fractal dimension was found at each density, using the same method, discussed in Section 4.2, proposed by Kieffer *et al.* [29], where the total radial distributions for each density were calculated, and power-law decays are superimposed on the peak structures to determine the fractal dimensions. These results are plotted in Figure 4.11 with their error bars and tabulated in Table 4.6, as well as data from

previous theoretical studies by Nakano *et al.* [30] and Murillo *et al.* [35]. Note that some of the error bars are significantly smaller than the corresponding marker size.

Table 4.6. Values of fractal dimension with increasing density, in comparison with results from Murillo *et al.* [35] and Nakano *et al.* [30].

	Density, g/cm ³	Fractal Dimension, d_f
Nakano <i>et al.</i> [30]	0.1	1.8
Nakano <i>et al.</i> [30]	0.2	2.1
Nakano <i>et al.</i> [30]	0.4	2.4
Nakano <i>et al.</i> [30]	0.8	2.7
Nakano <i>et al.</i> [30]	1.5	2.9
Murillo <i>et al.</i> [35]	0.23	2.13
Murillo <i>et al.</i> [35]	0.28	2.13
Murillo <i>et al.</i> [35]	0.35	2.25
Murillo <i>et al.</i> [35]	0.45	2.38
Murillo <i>et al.</i> [35]	0.58	2.56
Murillo <i>et al.</i> [35]	0.77	2.63
Murillo <i>et al.</i> [35]	1.05	2.88
Murillo <i>et al.</i> [35]	1.48	3.00
Present Study	0.3	2.13 ± 0.09

Present Study	0.4	2.27 ± 0.01
Present Study	0.5	2.44 ± 0.01
Present Study	0.6	2.59 ± 0.004
Present Study	0.7	2.71 ± 0.007
Present Study	0.8	2.53 ± 0.01
Present Study	0.9	2.75 ± 0.01
Present Study	1.0	2.77 ± 0.02

Figure 4.11. Variation of fractal dimension with increasing density, in comparison with results from Murillo *et al.* [35] and Nakano *et al.* [30].

It is obvious that the variation of the fractal dimension, d_f , with density is in good agreement with those found in previous studies using different methods and/or potentials. Experimentally, aerogel fractal dimensions were found to vary with processing conditions,

where it is approximately 1.8 under basic processing conditions, and about 2.2 to 2.4 in both acidic and neutral conditions [48].

4.6. Thermal conductivity of porous silica aerogel with the Tersoff potential

The thermal conductivity was found at each density using RNEMD. The data obtained are shown as a log-scale plot in Figure 4.12 with their corresponding error bars, along with the power-law fit of the data. The corresponding results are tabulated in Table 4.7. Comparisons with results obtained from the BKS potential and from previous experimental studies are also included for comparison [1, 28].

From our current results, thermal conductivity is found to decrease as density decreases, in a non-linear fashion. This is in sharp contrast with our previous study with the BKS potential [1], where thermal conductivity decreased in an almost linear manner. At the lowest density of 0.3g/cm^3 , the thermal conductivity also reached its lowest value of $0.05 \pm 0.003\text{W/(m K)}$, a value that is almost 3 times lower than the $0.13 \pm 0.06\text{W/(m K)}$ at 0.32g/cm^3 obtained previously.

Figure 4.12. Power-law fit of the variation of thermal conductivity of the simulated aerogel samples with density, together with experimental results from Fricke [28].

Table 4.7. Values of the thermal conductivity of the simulated aerogel samples with density, using the Tersoff potential.

Density, g/cm ³	Thermal Conductivity, W/(m K)
0.3	0.05 ± 0.003
0.4	0.09 ± 0.004
0.5	0.13 ± 0.008
0.6	0.18 ± 0.003
0.7	0.22 ± 0.007
0.8	0.23 ± 0.007
0.9	0.30 ± 0.030
1.0	0.40 ± 0.025

Moreover, experimental bulk aerogel displayed a power-law variation between thermal conductivity and density, such that the power-law exponent, ζ , would have a value of 1.6 in the density range of 0.3 to 1.0g/cm³ [28]. The present study indicates a ζ value of 1.61 in exactly the same density range, displaying extremely good correlation with experimental results. This also represents a marked improvement over the ζ value of 1.01 obtained previously with the BKS potential [1]. Another significant advantage of the current model is that the very low density of experimental aerogel was achievable, possibly going far below densities of 0.1g/cm³, without any adverse phenomenon.

However, there is a downside to the current model: at densities of 0.3g/cm^3 , the experimental value was of the order of $0.01\text{W}/(\text{m K})$ [28], which is approximately 5 times lower than the value of $0.05 \pm 0.003\text{W}/(\text{m K})$, as determined by this study. Overall, the thermal conductivities at each density had approximately 5-fold larger magnitudes than those observed experimentally. While this could be explained by the fact that the present MD model is clearly unable to reproduce actual aerogel defects, including micro-cracks, impurities, and hanging/loose-ended silica chains, we believe that the more significant reason is that the pore size distribution of the current model is unable to breach porous regimes beyond 5nm in diameter.

We can gain a better understanding of this by analyzing the pore size distribution of samples of increasing length scales, as shown in Figure 4.13, calculated using PSDsolv [187] which determines the relative probability of finding pores of different sizes. At the density of 0.3g/cm^3 , we generated three different samples with system lengths of $69\text{\AA}$, $180\text{\AA}$ (our current system length at 0.3g/cm^3), and $277\text{\AA}$. It is observed that as the system length scales increases, the largest pore sizes accessible in our simulations increases as well, growing from $20.75\text{\AA}$ to $32\text{\AA}$ in diameter.

Figure 4.13. Pore size distribution of simulated aerogel at the lowest density of 0.3g/cm^3 , at three different system length scales of a) $69\text{\AA}$, b) $180\text{\AA}$, and c) $277\text{\AA}$.

But clearly, the pore size regime is nowhere near the large hundred- to thousand-nanometre diameters that could be observed in bulk experimental silica aerogels. Moreover, the maximum pore size accessible increases at a decreasing rate, such that a four-fold increase in the system length only led to a corresponding increase of approximately 50% in the largest pore diameters.

Accessing the experimental pore size regime would require more than 1,000 to 10,000 times larger system sizes, corresponding to simulations of tens of millions atoms. Such an endeavor is currently not practically feasible through a pure MD simulation. However, coupling the current model to multiscale modelling techniques could be viable to having more accurate resemblances to bulk thermal properties, and utilizing the current model to thermally characterize silica aerogels in the nanoporous regime. Such could be the next frontier of future numerical studies for this problem.

Chapter 5

Thermal conductivity of Graphene, Defective Graphene, and Silicene

Using RNEMD, the thermal conductivity of both pristine and defective graphene nanoribbons is determined and compared. The MD scheme is first validated with previous research, by comparing the thermal conductivity of pristine graphene nanoribbons. Next, the variation of the conductivity due to increasing aligned STW defects is presented. Subsequently, high densities of dispersed STW defects and double vacancies are introduced, and the differences in the trends in the conductivity are analyzed and discussed. Finally, contrasts are made between the conductivities of infinitely wide graphene and silicene monolayers of increasing length, determined through direct NEMD. The differences in the thermal conductivities were discussed through the analysis of the vibrational density of states and phonon dispersion curves of each material.

5.1. Thermal conductivity of pristine graphene

We begin the study by determining the thermal conductivities of the pristine graphene samples. The thermal conductivity of each pristine or defective sample was averaged over five independent simulations, and the thermal conductivities and their corresponding error bars are plotted in Figure 5.1. The corresponding results are given in detail in Table 5.1.

Table 5.1. Thermal conductivities of 10-ZGNR and 19-AGNR at 300K with increasing numbers of aligned STW defects.

Number of Defects	10-ZGNR, W/(m K)	19-AGNR, W/(m K)
0	78.03 ± 2.50	53.67 ± 1.95
2	74.39 ± 1.72	49.42 ± 1.58
4	52.04 ± 1.61	39.92 ± 1.32
6	39.75 ± 0.63	32.82 ± 0.82
8	35.65 ± 1.13	30.63 ± 0.94
10	38.52 ± 1.66	32.13 ± 0.87

Figure 5.1. Variation of thermal conductivity of 10-ZGNR and 19-AGNR at 300K with increasing numbers of aligned STW defects.

The thermal conductivity of pristine 10-ZGNR was found to be $78.0\text{W}/(\text{m K})$, whereas the thermal conductivity of pristine 19-AGNR was found to be significantly lower at $53.6\text{W}/(\text{m K})$. These values are much lower than the reported experimental values of $2500\text{--}5300\text{W}/(\text{m K})$ [42, 64, 190] as the lengths of GNRs modeled in this study are significantly lower than the phonon mean free path of single atomic carbon material. This phenomenon had been extensively observed by other reported studies as well [61, 63, 65]. However, the absolute magnitudes of the thermal conductivities are of lesser interest in this study as we are focusing on the relative effects on thermal conductivity, with respect to pristine graphene, that STW defects could pose. Also, the small size of the simulation model is beneficial as it allows us to easily and rapidly populate the GNRs with very high densities of defects, and observe the corresponding changes in the thermal conductivities.

The thermal conductivities obtained in this study also varies significantly from previous computational studies, and this can be attributed to the different potentials used, different sample sizes, different boundary conditions as well as differing methods of imposing heat flux or temperature gradients, among many other variations in modeling techniques. This can be clearly observed, by removing the torsional and Lennard-Jones terms in the AIREBO potential, thus reducing to the second-generation REBO potential. Our results obtained from the REBO potential, with the same sample size and methods of modeling, indicated thermal conductivities of $95.0\text{W}/(\text{m K})$ and $74.6\text{W}/(\text{m K})$ for 10-ZGNR and 19-AGNR, respectively. These values are clearly different from that obtained from the AIREBO potential. Similarly, many other variations in the methods of modeling graphene have significant impact on the final result obtained. In particular, the thermal conductivity has been found to increase as sample size increases [61], as the sample size approaches the phonon mean free path of graphene.

A comprehensive review of the many variations and results reported in the literature have been reviewed by Nika *et al.* [102]. For instance, Koblinski *et al.* [65] found thermal conductivities upwards of 8,000W/(m K) using the Tersoff potential together with equilibrium MD for square graphene sheets with edges larger than 2nm, whereas Hu *et al.* [62] employed the Brenner potential and the direct NEMD method on 5nm long graphene nanoribbons and found thermal conductivities less than 1,500W/(m K). Clearly such large variations between previous studies as well as our current study render severe difficulties in being able to make concrete and definite conclusions on the absolute best combination of potentials, methods and sample sizes to obtain the closest match to experimental results. Moreover, the accuracy of experimental results are as yet unknown as seen in the wide spread of reported thermal conductivity data.

The thermal conductivity of pristine 19-AGNR in our study was 31.3% lower than 10-ZGNR for samples of the same length and width. Such large differences in thermal conductivity between ZGNR and AGNR have also been observed in previous works. Guo *et al.* [61] found a difference of 53.8%, Hu *et al.* [63] observed a difference of 21.2%, Koblinski *et al.* [65] determined a 15% difference, and Zhong *et al.* [67] reported a difference of 43%. Once again, such large variations in the results obtained can be attributed to the very diverse manners with which graphene and its thermal conductivity had been determined. More important is the fact that graphene's chirality has a significant impact on the thermal conductivity, with AGNR having significantly lower thermal conductivity, and this study reflected these as well.

5.2. Effects of aligned STW defects

Next we introduced increasing numbers of STW defects into the pristine GNR samples. Beginning from the center of the sample, the number of defects was increased by the rotation of 2, 4, 6, 8, and 10 pairs of atoms, where each rotated pair constituted one STW defect. The final configuration of 10 STW defects is shown in Figure 5.2. Each defective GNR's thermal conductivity was found using the same methods discussed above, with no variations.

Figure 5.2. A 10-ZGNR sample containing 10 aligned pairs of rotated bonds.

From the results shown in Figure 5.1, it can be observed that both 10-ZGNR and 19-AGNR experienced a decrease in thermal conductivity as the number of pairs of defects increased, at a temperature of 300K. There was a sharp decrease initially as the number of pairs of rotated atoms increased from 2 to 6 pairs. Thereafter, the decrease slowly tapered off, and showed only slight fluctuations as the number of defects increased to 10. Moreover, 10-ZGNR displayed a more significant decrease in thermal conductivity than 19-AGNR, where the decrease was 54% for the former and 43% for the latter. This seemed to imply that there was significant phonon scattering occurring due to the presence of STW defects. The effects of these defects on AGNR might have been somewhat less due to the presence of edge effects, which already posed significant phonon scattering [63]. This is in qualitative agreement with previous studies which identified decreases in thermal conductivity due to other defects such as vacancies [63, 191].

Figure 5.3. Variation of thermal conductivity of 10-ZGNR with temperature.

Figure 5.4. Dependence of thermal conductivity of 19-AGNR with temperature.

The variation of thermal conductivity with increasing temperature was also investigated. This study modeled both 10-ZGNR and 19-AGNR in the temperature range of 100K to 600K. From both Figures 5.3 and 5.4, and from Table 5.2, it can be observed that the variation of thermal conductivity with temperature decreased with an increase in STW defects. The thermal conductivity in pristine GNRs of either chirality showed significant variations in thermal conductivity, with increasing trend from 100K to 300K, and decreasing trend from 300K to 600K. In comparison, the thermal conductivity in defective GNRs displayed less variation, as shown by a largely flat curve, with only very slight increases as temperature increased. This indicates that GNRs displaying high densities of STW defects could in fact be beneficial in terms of the predictability of the thermal conductivity across a large range of temperatures, especially when used as a thermal device undergoing large variations in temperature.

Table 5.2. Dependence of thermal conductivity of both 10-ZGNR and 19-AGNR with temperature.

Temperature, K	Number of Defects	Thermal Conductivity of 10-ZGNR, W/(m K)	Thermal Conductivity of 19-AGNR, W/(m K)
100	0	69.20 ± 1.84	51.78 ± 1.92
100	2	68.20 ± 1.57	42.27 ± 1.18
100	4	42.81 ± 1.41	32.01 ± 1.52
100	6	31.83 ± 1.84	27.12 ± 0.90
100	8	29.91 ± 0.87	24.96 ± 0.78
100	10	33.91 ± 1.02	27.48 ± 0.32

200	0	76.84 ± 2.14	51.15 ± 0.94
200	2	71.19 ± 4.41	48.97 ± 2.72
200	4	49.31 ± 2.49	36.84 ± 0.70
200	6	38.03 ± 2.10	31.52 ± 1.20
200	8	33.32 ± 0.88	29.10 ± 1.05
200	10	37.34 ± 1.34	31.00 ± 0.98
300	0	78.03 ± 2.50	53.67 ± 1.95
300	2	74.29 ± 1.72	49.42 ± 1.58
300	4	52.00 ± 1.60	39.92 ± 1.33
300	6	39.75 ± 0.63	32.82 ± 0.82
300	8	35.65 ± 1.13	30.63 ± 0.94
300	10	38.52 ± 1.66	32.13 ± 0.87
400	0	76.27 ± 3.91	55.02 ± 1.05
400	2	76.67 ± 2.60	51.03 ± 0.55
400	4	52.54 ± 2.26	40.48 ± 1.88
400	6	39.54 ± 0.99	33.77 ± 0.65
400	8	34.98 ± 1.52	31.35 ± 1.08
400	10	38.81 ± 0.95	32.05 ± 1.15

500	0	75.28 ± 4.15	53.83 ± 1.37
500	2	70.16 ± 1.86	53.32 ± 2.06
500	4	53.15 ± 1.18	41.06 ± 1.08
500	6	39.73 ± 0.91	34.39 ± 0.86
500	8	34.84 ± 1.67	31.45 ± 1.27
500	10	39.26 ± 1.78	33.89 ± 0.34
600	0	71.88 ± 1.29	53.97 ± 3.15
600	2	69.79 ± 2.05	52.24 ± 2.25
600	4	51.13 ± 1.16	41.67 ± 1.43
600	6	39.92 ± 0.84	35.16 ± 1.16
600	8	35.22 ± 0.93	31.96 ± 0.63
600	10	39.32 ± 1.01	33.03 ± 0.68

It can also be observed by a comparison of Figures 5.3 and 5.4 that the thermal conductivity of AGNR is always lower than that of ZGNR, regardless of the number of defects present. This is likely due to the combination of the effects of both the edge and the STW defect phonon scattering being concurrently present in AGNR. Also, as the number of defects increase from 6 to 10, the thermal conductivity of both chiralities across all temperatures no longer show significant decreases. For example, for 10-ZGNR at 100K, the change in thermal conductivity, as the number of defects increased to 6, was about 54%. Thereafter, as the defects increased to 10, the thermal conductivity only decreased by a further 6%. This seems to imply that across

all temperatures, there is an upper limit to which increasing the STW defect densities could significantly affect the thermal conductivities of GNRs.

5.3. Effects of randomly dispersed STW defects and double vacancies

Next, we randomly introduced increasing numbers of STW and double vacancy defects into the pristine GNR samples. Due to the high density of defects introduced into the nanoribbons as compared to that in Section 5.2, we need to define the percentage coverage of defects, determined as the ratio of the number of defective atoms and the total number of atoms. For example, 40 STW defects in 10-ZGNR will give a percentage coverage of approximately 9.8%. Each defective GNR's thermal conductivity was found using the same numerical approach discussed in Section 3.2, with no variations.

Figure 5.5. Variation of thermal conductivity of both 10-ZGNR and 19-AGNR at 300K with increasing number of defects, with error bars.

From the results shown in Figure 5.5 and Table 5.3 and 5.4, it can be observed that both 10-ZGNR and 19-AGNR experience a decrease in thermal conductivity as the number of pairs of defects increase. There is a sharp decrease initially, but thereafter, the decrease slowly tapers off, and shows only slight fluctuations as the defect density increased. Moreover, 10-ZGNR displays a more significant decrease in thermal conductivity than 19-AGNR, where the decrease at the highest number of defects, at 300K, is 82.1% for the former and 69.6% for the latter, for STW defects. For double vacancy defects, the corresponding decreases are 87.5% and 70.1% respectively. These trends are also similar at both low and high temperatures of 100K and 600K, as seen in Figure 5.6.

Figure 5.6. Variation of thermal conductivity of both 10-ZGNR and 19-AGNR, at temperatures of a) 100K and b) 600K from top to bottom, with increasing numbers of both STW and double vacancy defects, and their respective error bars.

This implies that the larger decrease in thermal conductivity is due to the chirality rather than any temperature effects. Overall, it is observed that 10-ZGNR with double vacancies displays the sharpest decline in thermal conductivity. There is significantly less variation in the trend of decreasing thermal conductivity in 19-AGNR, where the thermal conductivities were approximately the same at each defect density. For example, at 8.8% coverage and a temperature of 300K, the 19-AGNR with STW defects has a thermal conductivity of $16.3 \pm 0.6 \text{ W/(m K)}$, while with double vacancies, the thermal conductivity is $16.1 \pm 0.7 \text{ W/(m K)}$. Again, this observation is true at both low and high temperatures of 100K and 600K.

Such a trend was further verified by investigating the variation of thermal conductivity with increasing temperature. This study modeled both 10-ZGNR and 19-AGNR through the temperature range of 100K to 600K, at 100K intervals. Figure 5.7 shows that the variation of thermal conductivity of 19-AGNR across the entire temperature range was largely similar for both STW and double vacancy defects. In contrast, the dip in thermal conductivity for 10-ZGNR was greater when the defects were double vacancies, and this was independent of the temperature simulated. This larger decrease due to double vacancies can be very clearly observed through Figures 5.5 and 5.6 at temperatures of 100K, 300K, and 600K. The likely reason for greater decreases experienced by nanoribbons with double vacancies than STW defects is that there is greater phonon scattering in the absence of bonded atoms in the vicinity.

10-ZGNR with STW defects

10-ZGNR with Double Vacancy defects

Figure 5.7. Variation of thermal conductivity of both 10-ZGNR and 19-AGNR with increasing numbers of both STW and vacancy defects, and their respective error bars. Temperature range investigated was 100 – 600K. The points are fitted with a cubic-interpolated surface mesh to better observe the variations between each plot.

Table 5.3. Thermal conductivity of 10-ZGNR with increasing numbers of both STW and vacancy defects.

Temperature, K	Number of Defects	Thermal Conductivity with STW Defects, W/(m K)	Thermal Conductivity with Double Vacancies, W/(m K)
100	0	69.66 ± 1.41	69.66 ± 1.41
100	8	23.10 ± 4.91	23.10 ± 4.91
100	16	15.87 ± 1.81	15.87 ± 1.81
100	24	12.30 ± 1.08	12.30 ± 1.08
100	32	9.81 ± 0.12	9.81 ± 0.12
100	40	8.93 ± 0.99	8.93 ± 0.99
200	0	76.27 ± 2.86	76.27 ± 2.86
200	8	25.27 ± 4.97	25.27 ± 4.97
200	16	16.92 ± 1.46	16.92 ± 1.46
200	24	13.34 ± 1.08	13.34 ± 1.08
200	32	10.72 ± 0.31	10.72 ± 0.31
200	40	9.47 ± 1.03	9.47 ± 1.03
300	0	78.03 ± 2.50	78.03 ± 2.50
300	8	26.43 ± 5.30	26.43 ± 5.30

300	16	17.86 ± 2.00	17.86 ± 2.00
300	24	13.53 ± 1.05	13.53 ± 1.05
300	32	11.06 ± 0.18	11.06 ± 0.18
300	40	9.75 ± 0.85	9.75 ± 0.85
400	0	77.86 ± 3.54	77.86 ± 3.54
400	8	27.32 ± 5.69	27.32 ± 5.69
400	16	18.04 ± 1.91	18.04 ± 1.91
400	24	13.68 ± 0.86	13.68 ± 0.86
400	32	11.25 ± 0.25	11.25 ± 0.25
400	40	10.08 ± 0.97	10.08 ± 0.97
500	0	76.89 ± 2.79	76.89 ± 2.79
500	8	27.82 ± 5.17	27.82 ± 5.17
500	16	18.39 ± 1.60	18.39 ± 1.60
500	24	13.97 ± 1.20	13.97 ± 1.20
500	32	11.53 ± 0.46	11.53 ± 0.46
500	40	10.18 ± 0.70	10.18 ± 0.70
600	0	72.70 ± 1.87	72.70 ± 1.87
600	8	27.93 ± 5.13	27.93 ± 5.13

600	16	18.32 ± 1.58	18.32 ± 1.58
600	24	14.09 ± 1.17	14.09 ± 1.17
600	32	11.47 ± 0.13	11.47 ± 0.13
600	40	10.35 ± 0.52	10.35 ± 0.52

Table 5.4. Thermal conductivity of 19-AGNR with increasing numbers of both STW and vacancy defects.

Temperature, K	Number of Defects	Thermal Conductivity with STW Defects, W/(m K)	Thermal Conductivity with Double Vacancies, W/(m K)
100	0	51.78 ± 1.92	51.78 ± 1.92
100	8	25.41 ± 3.66	26.70 ± 2.02
100	16	19.85 ± 1.59	20.88 ± 2.49
100	24	16.52 ± 1.11	17.85 ± 1.90
100	32	14.81 ± 0.68	16.62 ± 0.56
100	40	13.83 ± 0.45	14.97 ± 0.93
200	0	51.15 ± 0.94	51.15 ± 0.94
200	8	29.18 ± 3.70	29.32 ± 2.09
200	16	22.90 ± 2.03	23.02 ± 2.65

200	24	19.27 ± 1.31	19.09 ± 2.09
200	32	16.70 ± 0.40	17.61 ± 0.80
200	40	15.35 ± 0.59	15.51 ± 0.89
300	0	53.67 ± 1.95	53.67 ± 1.95
300	8	30.84 ± 3.40	30.27 ± 1.33
300	16	24.42 ± 2.00	23.94 ± 2.66
300	24	20.28 ± 1.14	19.99 ± 2.33
300	32	17.84 ± 0.61	18.16 ± 1.00
300	40	16.31 ± 0.65	16.06 ± 0.71
400	0	55.02 ± 1.05	55.02 ± 1.05
400	8	31.88 ± 3.92	31.63 ± 1.58
400	16	25.60 ± 1.39	24.58 ± 2.07
400	24	21.07 ± 1.19	20.30 ± 1.85
400	32	18.53 ± 0.59	18.36 ± 0.77
400	40	16.76 ± 0.55	16.10 ± 0.72
500	0	53.83 ± 1.37	53.83 ± 1.37
500	8	33.09 ± 4.23	32.01 ± 1.65
500	16	26.34 ± 1.95	24.90 ± 2.56

500	24	21.95 ± 1.49	20.37 ± 2.00
500	32	18.69 ± 0.89	18.26 ± 0.79
500	40	17.32 ± 0.72	16.00 ± 0.63
600	0	53.97 ± 3.15	53.97 ± 3.15
600	8	33.81 ± 3.41	31.70 ± 1.55
600	16	26.92 ± 2.12	24.88 ± 2.73
600	24	22.09 ± 1.32	20.49 ± 2.29
600	32	19.28 ± 1.03	18.48 ± 1.26
600	40	17.62 ± 0.71	15.88 ± 0.56

From Figure 5.7, it can also be observed that the variation of thermal conductivity with temperature decreased with an increase in both kinds of defects. The thermal conductivity generally shows an increasing trend from 100K to 300K, and a decreasing trend from 300K to 600K. In comparison, the thermal conductivity in defective GNRs has less variation, as shown by a largely flat curve, becoming virtually invariant as the density coverage reached the maximum. This indicates that GNRs displaying high densities of defects could in fact be beneficial in terms of the predictability of the thermal conductivity across a large range of temperatures, especially when used as a thermal device undergoing large variations in temperature.

In several earlier theoretical studies [192-194], it was shown that there are several factors that could account for the decrease in thermal conductivity due to defects in graphene. One factor

is the localization of long-wavelength phonon modes around the defects, reducing the ability of the nanoribbon to transmit thermal energy. Another factor identified is the broadening of the phonon mode peaks as defect density increased, observed from the phonon density of states, leading to a reduction in the mean free path. Increases in the density of states of low frequency modes also result in a decrease in the mean free path.

5.4. Thermal Conductivity of Silicene

The present MD simulations predicted very similar structural properties in both graphene and silicene. From Figure 5.8, we can see that the characteristic waviness of suspended graphene is also theoretically found in suspended silicene at 300K. However, from the out-of-plane mean square displacement of both silicene and graphene plotted in Figure 5.9, the characteristic waviness of graphene shows a much larger displacement than silicene.

Figure 5.8. Side view of a) graphene, and b) silicene, showing similar corrugated structures.

Figure 5.9. Out-of-plane mean square displacement of both silicene and graphene.

To validate the present MD model for thermal conductivity analysis, we performed direct NEMD on graphene and silicene samples, and determined the variation of the thermal conductivity with respect to width size. The thermal conductivity of each sample was averaged over three independent simulations.

It is observed in Figure 5.10, and Tables 5.5 and 5.6, that as the width increased, the thermal conductivity did not display any significant varying trends for the corresponding errorbars for zigzag graphene and silicene. This is consistent with the findings of Cao *et al.* [178] for graphene with fully periodic boundary conditions along the width, for simulating infinitely wide graphene.

Table 5.5. Changes in the thermal conductivity of zigzag graphene as monolayer width increases (monolayer length ~ 50 nm).

Strip Width, nm	Thermal Conductivity, W/(m K)
5.2	730.60 ± 47.76
10.4	540.23 ± 37.19
15.5	632.75 ± 79.54
20.7	638.62 ± 18.19

Table 5.6. Changes in the thermal conductivity of zigzag silicene as monolayer width increases (monolayer length ~ 50 nm).

Strip Width, nm	Thermal Conductivity, W/(m K)
5.5	62.70 ± 4.77
11.1	68.75 ± 4.79
16.6	60.48 ± 5.60
22.1	67.72 ± 16.76

Figure 5.10. Changes in the thermal conductivity of zigzag a) graphene, and b) silicene as monolayer width increases (monolayer length ~ 50 nm).

This invariance would not be true for non-periodic widths, as free edge effects could have very significant impact on the thermal conductivity of graphene [2, 3, 102], with remarkable differences in thermal conductivity between zigzag and armchair edges. The reason for this is that one can imagine free edges in a GNR to be extended defects running along both sides of the ribbon. In an infinitely wide monolayer with no edges, phonons are free to travel in all directions along the monolayer. However, in GNRs with free edges acting as defects, phonons experience very strong scattering at the boundaries, leading to dramatic reductions in the thermal conductivity [102]. This is exactly the same effect as having STW and vacancies, as shown in our results in Section 5.2 and 5.3.

The thermal conductivity of both graphene and silicene showed a fluctuation around a mean value as the width increased. In order to minimize the computational cost, we have chosen the smallest width in all present simulations. Also, the invariance of the thermal conductivity with changes in the width is crucial to us here, as we wish to isolate the behavior of the thermal conductivity due to increasing strip lengths.

Next, we gradually increased the lengths of the monolayers and determined the thermal conductivity with direct NEMD. The thermal conductivities, and the corresponding error bars, at a temperature of 300K are plotted in Figure 5.11. The present data shows good agreement with the data determined by Cao *et al.* [178] within errorbars, as shown in Figure 5.11a. The corresponding results are displayed in Table 5.7. The thermal conductivities of both graphene and silicene are highly dependent on their lengths, displaying elevated thermal conductivities as the strip length increased.

In the case of graphene, this was in agreement with previous theoretical [178] and experimental studies [102]. From previous reported experimental values, for graphene of 2-5 μm in length, the thermal conductivities were between 2500-5300W/(m K) [42, 64, 190], increasing as monolayer length increased. The present results also show minimal variations in the thermal conductivity between armchair and zigzag chiralities in graphene, in stark contrast to the marked difference found in our previous MD studies with free edges [2, 3]. This shows that edge effects would be a significant factor in the determination of the thermal conductivity as well.

Figure 5.11. Changes in thermal conductivity with increase in lengths of a) graphene in comparison with results from Cao *et al.* [178] , and b) silicene, of both zigzag and armchair chiralities.

Table 5.7. Changes in thermal conductivity with increase in lengths of graphene in comparison with results from Cao *et al.* [178] , and silicene, of both zigzag and armchair chiralities.

Chirality and Material	Monolayer Thickness, nm	Monolayer Width, nm	Thermal Conductivity, W/(m K)
Zigzag Graphene	0.34	51	772.75 $\pm$ 94.86
Zigzag Graphene	0.34	102	878.81 $\pm$ 133.43
Zigzag Graphene	0.34	508	1669.62 $\pm$ 128.02
Zigzag Graphene	0.34	1015	1994.98 $\pm$ 32.93
Zigzag Graphene	0.142	51	1850.24 $\pm$ 227.13
Zigzag Graphene	0.142	102	2104.19 $\pm$ 319.48
Zigzag Graphene	0.142	508	3997.68 $\pm$ 306.53
Zigzag Graphene	0.142	1015	4776.72 $\pm$ 78.84
Armchair Graphene	0.34	51	787.53 $\pm$ 22.52
Armchair Graphene	0.34	102	871.78 $\pm$ 86.26
Armchair Graphene	0.34	509	1791.57 $\pm$ 89.96
Armchair Graphene	0.34	1019	2143.90 $\pm$ 101.27
Armchair Graphene	0.142	51	1885.63 $\pm$ 53.91
Armchair Graphene	0.142	102	2087.37 $\pm$ 206.53

Armchair Graphene	0.142	509	4289.68 $\pm$ 215.39
Armchair Graphene	0.142	1019	5133.29 $\pm$ 242.48
Zigzag Graphene (Cao <i>et al.</i> [178])	0.34	45	500
Zigzag Graphene (Cao <i>et al.</i> [178])	0.34	90	750
Zigzag Graphene (Cao <i>et al.</i> [178])	0.34	180	1050
Zigzag Graphene (Cao <i>et al.</i> [178])	0.34	360	1375
Zigzag Graphene (Cao <i>et al.</i> [178])	0.34	720	1800
Zigzag Graphene (Cao <i>et al.</i> [178])	0.34	1440	2000
Armchair Graphene (Cao <i>et al.</i> [178])	0.34	45	500
Armchair Graphene (Cao <i>et al.</i> [178])	0.34	90	750
Armchair Graphene (Cao <i>et al.</i> [178])	0.34	180	1050

Armchair Graphene (Cao <i>et al.</i> [178])	0.34	360	1450
Armchair Graphene (Cao <i>et al.</i> [178])	0.34	720	1800
Armchair Graphene (Cao <i>et al.</i> [178])	0.34	1440	2100
Zigzag Silicene	0.23	52	62.70 ± 4.77
Zigzag Silicene	0.23	103	78.67 ± 2.08
Zigzag Silicene	0.23	515	87.29 ± 9.53
Zigzag Silicene	0.23	1030	115.63 ± 4.89
Armchair Silicene	0.23	50	67.56 ± 2.55
Armchair Silicene	0.23	100	76.75 ± 5.22
Armchair Silicene	0.23	498	94.33 ± 7.93
Armchair Silicene	0.23	995	111.08 ± 3.25

From Figure 5.11b, the present data establishes that the thermal conductivity of silicene possesses the same length dependence, but with a much milder rate of increase compared with that of graphene. The thermal conductivity of silicene of both chiralities increased by more than 60%. On the other hand, graphene of both chiralities experienced more than 150% increases in the thermal conductivities. This observation clearly indicates that graphene possess a much higher mean free path than silicene [166]. Moreover, it can be observed for silicene

that, similar to graphene, there are no significant differences (within error bars) in the thermal conductivity between zigzag and armchair chiralities, and this is to be expected due to the hexagonal symmetry. This gives further validation with regards to the reliability of our results.

From the present results, it can be reasonably concluded that freely suspended silicene will very likely possess much lower thermal conductivities across all lengths and chiralities than graphene. We will now determine the vibrational density of states (vDOS) for both materials to obtain further insights on this phenomenon. The method of determining the vDOS is discussed in Section 4.4. By examining the vDOS as shown in Figure 5.12, we observe remarkable differences that would account for the vast disparity in the thermal conductivities of graphene and silicene. From Figure 5.12a, we see that the vDOS obtained from the optimized Tersoff potential for graphene is in good agreement with previous studies [175, 192, 193], displaying the very prominent G-peak of graphene at approximately 50THz. However, it is slightly different from various features in the vDOS of graphene determined from mathematical models [195] and density functional perturbation theory [69], such as the low frequency peaks being not as prominent. This is likely to be a disparity due to finite temperatures in our MD studies. Nevertheless, it is clear in comparison with the vDOS of silicene, that the vibrational frequencies excitable in silicene are severely limited.

Furthermore, through qualitative observation of the acoustic phonon dispersion curves of both graphene and silicene in Figure 5.13, we can clearly deduce that the group velocities of the dominant acoustic phonons are far higher in graphene than in silicene. The phonon dispersion curve is a plot of how phonon frequencies vary with wave vectors.

Figure 5.12. Vibrational density of states of a) graphene, and b) silicene, for both zigzag and armchair chiralities.

Figure 5.13. Phonon dispersion curves of the acoustic modes of both graphene and silicene in the major symmetry directions. The phonon frequencies, ω , have been normalized by $2\pi/a$, where a is the lattice constants for either graphene or silicene.

The acoustic phonon group velocities are the slopes of the acoustic phonon dispersion curves [188], and the slopes of the dispersion curves for graphene are significantly steeper than those of silicene, especially near the Γ -point. The phonon dispersion was determined at a temperature of 300K, through the post-processing of the dynamical matrix constructed by observing the displacements of atoms during the MD simulation together with the fluctuation-dissipation theory [196].

Another possibility for the large disparity in the thermal conductivity is that the Tersoff potential has not been optimized to adequately represent the vibrational properties of the

silicene, unlike that which has been done for graphene [103]. Another observation that can be made from Figure 5.12 is the minimal difference in the vDOS between the zigzag and armchair chiralities for both materials, implying good agreement with the fact that the thermal conductivities for these chiralities also displays little variation, even as the monolayers' lengths increased.

Chapter 6

Summary and Future Work

The methods, results and discussions of all the simulations done in this study are summarized in this chapter. Future researches that can be derived and continued from our work are also presented.

6.1. Summary

- 1) In our study, an exfoliation mechanism of graphite flakes was discovered. In our simulations, we verified that, as a result of compression using hydrogen-terminated silicon substrates, major and partial exfoliations of graphene layers can occur, due to activation an inter-layer superlubricity regime. Superlubricity was shown to be activated by spontaneous rotations occurring due to coupling between the inter-layer rotations and sliding due to shear thermal modes in the graphite flakes during compression. The dependence of exfoliation behavior on flake diameter, number of graphitic layers, and crystalline orientation of the substrates was studied by comparing the compressive stress required for initiating exfoliation. It was verified to only occur when the ratio of diameter to thickness of the graphite flakes is sufficiently small. Out-of-plane deformations of the layers tend to impede superlubricity.
- 2) Predictions of the solid thermal conductivity of porous silica aerogel in the density range of 2.17g/cm^3 (dense glass) to 0.32g/cm^3 were presented, using negative pressure rupturing to produce the percolated silica backbone, and reverse non-equilibrium molecular dynamics simulations. A '24-6' LJ potential was used to augment the widely used BKS potential in modeling the interatomic interactions in silica. The procedure was validated via

comparison with previously reported studies for non-porous amorphous silica. This method of producing silica aerogels was shown to be reasonably adequate in reproducing the thermal properties of bulk sintered aerogel. The variation of thermal conductivity with density correlated very well with sintered bulk aerogel, and the values are of the same order of magnitude.

- 3) In comparison, as-prepared bulk aerogel had thermal conductivities that were lower by one order of magnitude. This can be explained by the distinct absence of defects such as micro-cracks and pores much larger than those that can be represented in the present simulation models. It was verified that the pore sizes in this model could not exceed 3nm. These defects account very significantly for the reduction in thermal conductivity through increased phonon scattering, thereby severely restricting the mean free path in as-prepared bulk aerogel. The predicted thermal conductivity of amorphous silica also tends to increase with increases in the system size, implying that finite size effects play an important role. Moreover, the BKS potential was shown to be unable to reproduce the thermal properties of bulk dense amorphous silica.
- 4) These issues raised were addressed through an enhanced model using an expanding, heating, and quenching scheme together with the Tersoff potential, re-parameterized to handle the interatomic interactions for silicon and oxygen. For both the BKS and Tersoff potentials, it was determined that there exists an increasing trend in the thermal conductivity as the system length increased. The BKS potential significantly overestimated the thermal conductivity of bulk amorphous silica, whereas the Tersoff potential slightly underestimated it. Through extrapolation of the results to an infinite length scale, thus giving a better representation of bulk amorphous silica, the Tersoff potential provided a

significantly better estimation of bulk thermal properties, giving an error of only 13% as compared to the error of 55% for the BKS potential. That the Tersoff potential was more potent in estimating the thermal properties of bulk amorphous silica was further verified in an analysis of the vDOS generated by each potential. The vDOS from the Tersoff potential was more representative of the vibrational spectra in comparison with both theoretical and experimental results.

- 5) Using this enhanced scheme, aerogels with densities ranging from 0.3 to 1g/cm³ were generated. Fractal dimension analysis indicates good agreements with experimental results. Thermal conductivities of this model were found to decrease as density decreased, in a non-linear fashion, in contrast with the linear variation in our previous model. The power-law variation agreed very well with experimental results. The magnitudes of our simulated results were still five times higher than experimental results. The most likely reason is the inability of this model to breach much larger pore sizes. This was verified through an analysis of the pore sizes as the system length increased. It was found that the pore sizes that can be represented increased in tandem with the increase in system size but it is still nowhere near being larger than the nanometer scale. This could possibly be resolved by application of multiscale modeling methods.
- 6) For graphene simulations, this report revealed that even well-scattered STW defects caused large decreases in thermal conductivity, an effect that was similar to that produced by other defects such as edge roughness and vacancies. Defects causing major deviations from the pristine crystalline structure of graphene have significant and profound effects on the thermal conductivity of graphene; likewise in GNRs with STW defects, despite the fact that the total number of carbon atoms and sample size are similar in both pristine and non-

pristine cases. Phonons could possibly be strongly scattered simply by directional changes in the carbon-carbon bonds. Conceivably, the direction of carbon-carbon bonds can be altered experimentally to tailor the thermal properties of GNRs.

- 7) This report also established that the variation of thermal conductivity with changes in temperature was less significant in the presence of larger numbers of STW defects. This implies that defective graphene could actually result in more stable thermal properties than pristine graphene in applications as thermal devices. Moreover, the thermal conductivity of AGNR was always lower than that of ZGNR, regardless of how many defects were present. Intuitively, it may be clear that any changes to the crystalline structure of graphene will negatively impact its thermal conductivity. However, what is surprising here is the very large extent of the decrease in thermal conductivity, and that the decrease was also heavily dependent on chirality. Comparisons between the effects of STW defects and double vacancies on the thermal conductivity of graphene showed that at all temperatures studied, the sharpest decline in thermal conductivity were found in 10-ZGNR with double vacancies. Thermal conductivity in 19-AGNR showed significantly less variation, being approximately the same at each defect density.
- 8) The thermal conductivity between large monolayers of pristine graphene and silicene were also compared. Geometrical analysis showed similar ripples in silicene as in graphene. Thermal conductivity of silicene was found to be drastically lower than that of graphene. Both materials displayed increasing thermal conductivity as the length of the monolayers increased, where the rate of increase was significantly higher in graphene than in silicene. Analysis of the vDOS and the phonon dispersions of both materials verified that the reason

for this significant difference was due to the superior group velocities of the dominant acoustic phonons in graphene.

6.2. Future Work

Many pertinent issues regarding the MD simulation of silica aerogel remain to be resolved. Finite size effects evidently have very significant effects in thermal conductivity simulations, and to resolve this, further studies have to be performed to determine methods that can adequately represent the properties of bulk aerogel. To achieve this, it is likely that multiscale methods of simulation needs to be looked into, to determine whether very large systems sizes, upwards of $1\mu\text{m}$ length scales, can be adequately represented. Extending the length scales may help to minimize finite size effects, allowing the extrapolation of results to infinite length scales. Possibly, the enhanced model may be applied to extremely large scale MD simulations of more than 1,000,000 atoms to simulate systems that are as close to bulk aerogels as possible. Also, such a model will need to be extensively tested to ensure that it can represent geometrical, mechanical as well as thermal properties of silica aerogels. Furthermore, the possibility of extending these methods to other aerogels, such as opacified silica aerogel, carbon aerogel and other possible constituents, can be investigated.

More detailed analytical and computational calculations should be performed on graphene to give precise and definite explanations with regards to the physics behind the impact on thermal conductivity of numerous coupling of various parameters such as the width, chirality, and temperature. The MD simulation of graphene can be further extended to determine the effects of many other defects on few-layer graphene, as well as investigating whether the relative arrangements of the defects have any kind of impact on the thermal conductivities. The thermal conductivity of polycrystalline graphene can also be determined and analyzed for comparison.

Further investigations can also be made to find out whether the thermal properties of graphene and other two-dimensional materials can be predicted more accurately. Also, experimental verification of the superlubricity activation of graphite can lead to many possible applications, especially in the realm of exfoliating many different categories of similar layered materials. With regards to the density of defect sites and the degree of STW defect formation, while defects can be introduced through methods such as ion and electron irradiation, perfect control of these parameters are as yet not achievable. This would also require further research to attain.

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