MOLECULAR DYNAMICS SIMULATIONS ON THE EFFECTS OF MOISTURE ON THE INTERFACIAL ADHESION PROPERTIES OF GLASS FIBRE-EPOXY COMPOSITES

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Abstract

Molecular Dynamics (MD) simulations were used in investigating interface adhesion in glass fibre reinforced polymer composites. Novel contributions were made for; (i) determining the solubility limit of water in a crosslinked epoxy system, (ii) generating slab composite interfaces, (iii) determining the solubility limit of water in at composite interfaces, and (iv) quantifying interfacial adhesion in a slab composite for both dry and saturated systems.

Procedures were developed for uses in modelling crosslinked DGEBA/IPD epoxy systems. A new term was proposed, the reduced chemical potential $\tilde{\mu}$, and was applied in assessing the solubility of water in a polymeric system. DGEBA/IPD was found to have a moisture solubility of 3.50-3.75 wt.%. Experimentally, an average maximum water content was found as 2.66 wt.%. The average simulated elastic modulus for DGEBA/IPD saturated to 3.6 wt.% water was found as 4.11 GPa, a decrease of 16.5% from the dry system. An experimental value of 3.74 GPa was found, a decrease of 13.8%. The onset of the glass transition temperature was also considered, results indicate a significant decrease of 17.9% with an average value of 96.48 °C, while experimentally a decrease of 15.4% to a value of 91.54 °C was seen. The simulated system overestimates the maximum water content, and slightly overestimates the relative loss of properties due to the presence of absorbed moisture.

Ten thermodynamically equivalent slab composite interface structures (containing glass fibre, sizing, and epoxy) were generated. Novel procedures for saturating the system based in Grand Canonical Monte Carlo exchanges of noble water molecules were developed. An average solubility limit of 2.07 wt.% water was found, and calculated to correspond to 0.99 wt.% water in an equivalent full composite, an experimental value of 1.15 wt.% was found.

The work of adhesion was calculated for replicates of dry, moist, and fully saturated slab composites and compared to experimental tensile strength in unidirectional composites. The work of adhesion for the saturated SiO$_2$-sizing interface was found as 267.88 mJ m$^{-2}$, a 32% decrease. For the sizing-epoxy interface, a value of 191.01 mJ m$^{-2}$ was found, a decrease of 24%. The SiO$_2$-epoxy interface (representing an unsized fibre) a value of 148.61 mJ m$^{-2}$ was found, a 29% decrease. Results for both dry and saturated conditions indicated SiO$_2$-sizing as the critical interface for failure. Non-bonded and torsional terms make up the largest portion of adhesion, and that they consistently see the most significant relative decrease with increasing water content. This suggested that the loss of interface adhesion could be minimised through altering the fibre sizing system in a way such that the non-bonded and torsional terms are retained with increasing moisture content.

SEM analysis was undertaken on both dry and saturated samples after tensile failure. The results suggest more cohesive failures in the epoxy for the dry samples, while relatively clean fibre surfaces in the saturated samples indicate adhesive failure at the interface.
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Nomenclature

\( k_B \) Boltzmann constant
\( \mu \) Chemical potential
\( \lambda \) Coupling parameter
\( \rho \) Density
\( \mu_{ex} \) Excess chemical potential
\( T_g \) Glass transition temperature
\( \mathcal{H} \) Hamiltonian
\( K \) Kinetic energy
\( \mathcal{L} \) Lagrangian
\( E \) Modulus of elasticity
\( N \) Number of atoms in the system
\( n \) Number density
\( U \) Potential energy
\( \tilde{\mu} \) Reduced chemical potential
\( \gamma \) Surface energy
\( R \) Universal gas constant
\( W_{12} \) Work of adhesion

General Terminology

MC Monte Carlo
MD Molecular dynamics
NPT Isobaric-isothermal ensemble (constant number of atoms, pressure, and temperature)
NVT Canonical ensemble (constant number of atoms, volume, and temperature)
1 Introduction

Over the past several decades, composite materials, plastics, and ceramics have been dominant, emerging materials. Technological breakthroughs in material sciences have allowed composite materials to emerge as a perfectly viable alternative to more traditional material systems in many applications.

A composite material is formed by combining two or more dissimilar materials to form a new material. As an example, concrete is formed when aggregate is are combined with cement. Both the rock and the cement dictate the resulting properties of the concrete, though, inherently, the two are very different materials. While most physical, chemical, and processing-related properties can be enhanced purely by altering the combination of materials used. Most commonly, composites are made by combining strong fibres and a binding material. Carefully selecting the constituents, as well as altering the angle of the fibres and volume fraction can alter the physical, mechanical, and chemical properties of the resulting composite system. As a result, modern composites are frequently tailored for specific applications, and because of this are being used in ever-increasing roles in industry.

Today, composites are widely used across the aerospace, automotive, and energy industries. Take the aerospace industry for example; prior to the 1950s aircraft were constructed entirely out of metal, though around this same period fibreglass had been finding uses as part of boats and automobiles. The Boeing 707 premiered as the first commercial aircraft to incorporate the use of composite materials, comprising nearly 2% of the structure. Since then each generation of aircraft has seen an increase in composite usage, which has now culminated in the Boeing 787 that is comprised of 50% composite materials, primarily carbon fibre. This same trend of increased composite usage in seen across a range of industries, and is sure to continue as we develop and refine our understanding of composites [1].

Primary factors driving the use of composites are weight reduction, reduction in number of parts, and corrosion resistance. Weight reduction provides one of the more enticing motivations for the use of composite material systems, especially throughout the aerospace and transportation industries, where weight is paramount. Composites are lightweight, as both the fibres and matrix (commonly polymeric) have relatively low densities. Though more crucially, fibres have a very high specific strength and specific stiffness when compared to other materials. Additionally, since polymers can be moulded into complex shapes, a single composite part may be able to replace multiple, assembled metallic parts, while still attaining the same function [1].

Strong fibres cannot be used alone as the fibres are unable to sustain compressive or transverse loading, and so a binding or matrix material is therefore required to hold the fibres together and maintain their orientation. As the matrix surrounds the fibres, it also
1 INTRODUCTION

serves to protect the fibres from the environment. Therefore, the matrix is crucial for the overall corrosion resistance of the system. Polymer matrices have relatively good corrosion resistance, because of this, fibre reinforced polymer composites find many uses through chemical industries, replacing more conventional materials [1, 2].

Glass fibres are commonly one the cheapest and most-readily available reinforcement options. While, it should be noted that, the relative strength of the glass fibers is much lower than that of the stronger, lighter, and consequently much more expensive carbon fibre options. As a result, glass fibres find uses in industries where weight is not a primary design constraint. Take the wind energy industry, where the primary structure of wind turbine blades are traditionally made almost exclusively of unidirectional glass fibre reinforced composite systems. Marine energy is a renewable energy resource that involves harnessing the power in the moving ocean water (waves, ocean currents, tidal currents etc...). The sheer energy potential for marine energy is vast, but its predictability (and therefore reliability) is perhaps what makes it most attractive.

The marine energy industry remains relatively undeveloped for several reasons. The installation and maintenance costs are high as sites are obviously offshore, and inherently difficult to access. The wind industry has widely utilized epoxy glass composite systems as the primary turbine structure for quite some time. With the many parallels between the wind and marine industries it naturally seems appropriate to consider epoxy glass composites as a primary structural material for marine energy turbines. Understanding what operating environments the structures will need to endure and how to properly design for these kinds of environments becomes of utmost importance to long term viability of the industry.

Environmental concerns prove to be a primary design considerations in many applications, most notably where the composite system will be operating in water rich environments. Polymeric composite systems are known to absorb water during long-term exposure to water. More significantly, the overall composite system experiences a distinct loss in mechanical strength as a direct consequence of water absorption. Mechanical strength loss is further exacerbated when the structure is additionally subjected to a (more operationally representative) sustained tensile loading condition during the ageing process. In general, the presence of absorbed water held within a polymeric composite tends to increase the ductility and flexibility of system, while decreasing elastic modulus and strength.

The strength of fibre composites is directly derived from adhesion at the interface between the fibre and the matrix. A loss of strength in the system is therefore a direct results of adhesion loss at the interface. The specific driving mechanisms behind the loss of interfacial adhesion in polymeric composite systems due to the presence of absorbed water are not well understood. The important effect of the interface on the properties of glass fibre reinforced composites has led to efforts to understand, control, and even to modify the interfacial area.
The interface is complicated as it is buried within the composite structure, and is microscopic in nature. Due to the complicated nature of the interface there has been minimal work dedicated specifically to molecular interactions (and consequent adhesion loss) occurring directly at the fibre-matrix interface, let alone with the presence of absorbed water.

1.1 Thesis Statement

Adhesion at the interface, being so key to the overall composite performance, needs to be better understood to allow better design of fibre sizing, epoxy, and composite systems. Recently, Molecular Dynamics (MD) simulation has proven to be a powerful tool for investigating the structure, properties, and interactions of materials at an atomic level. The aim of this thesis is to investigate if MD simulations can be used to study the effects of absorbed water on adhesion at the fibre composite interface. To accomplish this, several specific research questions must be addressed. What are the strengths and limitations of MD as it relates to investigating fibre composite systems? Can MD be reasonably employed in generating fibre composite interfaces? How can MD be applied in determining the solubility limit of water at composite interfaces? Can MD simulation methods be used in quantifying interfacial adhesion at a composite interface?

1.2 Thesis Layout

This thesis will first provide a fundamental background on polymers, composites, epoxies, glass fibres, and fibre sizing systems. The fundamentals of molecular dynamics (MD) simulations are considered next, where the theory, applications, and limitations are discussed. Following, a comprehensive review of literature pertaining to the effects of water on glass fibre reinforced polymer composites is provided. Additionally, literature is reviewed and discussed regarding the applications of MD simulations to polymeric systems and interfaces. Next, specific MD simulation methods will be presented and validated for use in modelling crosslinked epoxy systems. These MD methods will then be expanded on to investigate specific interactions occurring between epoxy and water molecules. Simulation procedures for generating and saturating the full glass fibre composite interface are then presented. Finally, the interface adhesion at the interface under both dry and saturated conditions are investigated.
2 Fundamental Background

2.1 Polymers

Polymers are composed of hydrocarbons, specifically, polymers are made of carbon atoms which are bonded together to form long chains, forming what is called the backbone of the polymer. Due to the chemical nature of carbon, one or more other atoms can also be bonded to each carbon along the backbone. Polymers can contain only carbon and hydrogen atoms (e.g. Polyethylene, polypropylene, and polystyrene). Polyvinyl chloride (PVC) is an example of a polymer with chlorine attached to the carbon backbone, while Teflon has fluorine attached to the backbone [3]. Polymer systems can take many different structural characteristics. They can be linear (uninterrupted polymer chains), branched (individual branches off longer chains), or networked (many interconnected linear chains), Fig. 1.

![Figure 1: Characteristics of: (a) linear, (b) branched, and (c) networked polymers.](image)

Generally, polymer systems lack specific order, they are amorphous. By definition, a crystals have long range order. Controlling the polymerization and quenching process gives control over the degree of crystallinity of the polymer, Fig. 2. Most polymers will exhibit 40-70% crystallinity [4]. Crystallinity creates benefits for strength, stiffness, optical translucency, and chemical resistance [3, 5].

![Figure 2: Amorphous and crystalline polymer structure.](image)
There are several classifications of polymers, each with unique characteristics.

(i) Thermoplastics (plastics): linear, small degree of crosslinking. Can be melted and reused. Structurally, amorphous or semi-crystalline.

(ii) Elastomers (rubbers): Moderate crosslinking and easily recover elastic deformations.

(iii) Thermosets (epoxies): Highly crosslinked, rigid, and degrades on heating.

2.1.1 Viscoelasticity

Polymers exhibit both viscous and elastic characteristics when deformed. For viscous materials, the deformation response is heavily strain rate dependent, while elastic materials deform instantaneously with applied stress. Viscoelastic properties are commonly studied using Dynamic Mechanical Analysis (DMA), where a small oscillatory, usually sinusoidal, stress is applied and the resulting strain is measured.

For purely elastic materials the stress and strain response are in phase, meaning the strain occurs simultaneously to the applied stress. For purely viscous materials, the strain response will be completely out of phase with the applied stress, indicating a 90 degree phase lag, \( \delta \). Viscoelastic materials exhibit a behaviour between purely elastic and purely viscous materials, meaning viscoelastic materials will have some phase lag \( \delta \) for an applied oscillatory stress, Fig. 3.

\[
\sigma = \sigma_0 \sin(\omega t + \delta)
\]
\[
\epsilon = \epsilon_0 \sin(\omega t)
\]

(2.1)

Figure 3: Phase lag \( \delta \) between oscillatory stress and strain in viscoelastic materials.

For a viscoelastic material, the stress \( \sigma \) and strain \( \epsilon \) are given as follows,
where $\sigma_0$ and $\epsilon_0$ are the amplitudes of stress and strain respectively, $\omega$ is the angular frequency of oscillation, $t$ the time, and $\delta$ the phase lag ($0 < \delta < \frac{\pi}{2}$). Storage and Loss modulus are properties of viscoelastic materials that measure the stored energy (elastic portion), and the dissipated energy (viscous portion). The tensile storage modulus $E'$ and loss modulus $E''$ are,

\[
E' = \frac{\sigma_0}{\epsilon_0} \cos(\delta) \\
E'' = \frac{\sigma_0}{\epsilon_0} \sin(\delta)
\] (2.2)

Similarly, the shear storage $G'$ and loss moduli $G''$ can be found. Through taking the ratio between the loss and the storage moduli, an important term, the $\tan(\delta)$, is found,

\[
\frac{E''}{E'} = \frac{\sin(\delta)}{\cos(\delta)} = \tan(\delta)
\] (2.3)

The $\tan(\delta)$ is a dimensionless measure of energy lost in a viscoelastic system and represents mechanical damping and internal friction. A high $\tan(\delta)$ indicates a higher loss modulus, meaning a large non-elastic strain component, while a lower value indicates the system a more elastic strain response [6].

### 2.1.2 Glass Transition Temperature

The glass transition temperature $T_g$ is a transition in amorphous materials from a hard 'glassy' state at low temperature into a more viscous 'rubbery' state at higher temperature. This transition is fully reversible, where the reverse from a 'rubbery' state to a 'glassy' state is referred to as vitrification. It is important to note, the glass transition is not an instantaneous occurrence but rather a range over which the mobility of polymer chains is significantly increased. At temperatures above the $T_g$, the system is much more flexible, has a lower modulus, lower strength bearing capacity, and a higher coefficient of thermal expansion. Therefore, it is often advantageous to ensure the system operates well below the $T_g$.

The glass transition is not the same as the melting point of the material $T_m$, furthermore, the glass transition temperature is always lower. Melting is a transition that occurs in only the crystalline portion of the polymer, wherein the chains lose their ordered structure become amorphous. While, the glass transition is a transition that occurs in the only amorphous portion of the structure. A highly crystalline polymer can exhibit up to 70% crystallinity, indicating that, even in the most crystalline polymer, amorphous regions still constitute 30% of the system [4]. Therefore, polymers have both a melting point and a glass transition.

$T_g$ is commonly measured using DMA. This is done by applying a sinusoidal load to the
sample at a fixed frequency while concurrently heating the sample at a constant rate through the glass transition region. The storage modulus $E'$ (representing the elastic portion of the material stiffness) is then plotted against temperature, Fig. 4a. Several thermal transitions are easily seen. The main reduction in storage modulus occurs as the system passes through the $T_g$. $T_\beta$ represents a secondary transition in the system, many times related to toughness, though secondary transitions are not always present [6]. The melting point $T_m$ is seen when $E' = 0$. Note, purely crystalline (no amorphous) materials will not undergo a glass transition, and thermosets, such as epoxies, will not melt but rather will gradually burn off and degrade with increasing temperature.

Additionally, plotting both storage modulus and tan(δ) with temperature shows an important relationship, Fig. 4b. The tan(δ) is seen to prominently spike as the system passes through the glass transition region. While the onset of the glass transition can be taken from the storage modulus as the intersection of the two tangents of the portion before and during the transition. Commonly, $T_g$ is identified as the temperature at which tan(δ) is maximum.

2.2 Composite Materials

A composite material is formed through the combination of two or more dissimilar materials, where each constituent material has its own discrete set of physical and mechanical properties. It follows that by knowing the constituent properties a composite material may be tailored in attempts to achieve desired physical and mechanical properties. Commonly,
there are several different composite materials that are classified either by the type of matrix or the type and geometry of the reinforcement used. Composites classified by matrix type include: carbon/carbon composites, ceramic matrix composites, metal matrix composites and polymer matrix composites. The three primary types of reinforcements are particles, short, and fibres, which are illustrated in Fig. 5. Fibrous reinforcement is preferred as most materials are much stronger in fibre form than in their respective bulk form. This can be attributed to a sharp reduction in the number of material defects as the system is reduced from bulk to fibre [1].

2.2.1 Fibre Reinforced Polymer Composites

The most common advanced composite systems are those using polymer matrix compounds reinforced with continuous fibres, more commonly referred to as fibre reinforced polymer (FRP) composites. FRP composites offer more control over the resulting composite properties, primarily due to the continuous reinforcing fibres used. The fibres not being randomly arranged, as particles or short fibres may be, allows the manufacturer to better control the resulting composites properties. The fibres are generally stiff and strong in the direction of the fibre axis; as a result, the fibres carry most of the structural loads within the composite. In contrast, the matrix material typically has lower tensile strength and modulus of elasticity than the fibre. The matrix serves to keep the fibres properly aligned, distributes loads throughout the fibres, and carries most of the compressive loads, as fibres cannot tolerate compressive loading.

Fibre reinforced polymer composites are constituted of successive layers of thin laminae, commonly referred to as plies. Each ply has its own set of mechanical properties, which are directly dependent upon orientation of the fibres and fibre volume. It follows that multidirectional stiffness in laminates is achieved through the use of different fibre orientations, or by using textile weaves [1]. Figure 6 presents a series of scanning electron microscope (SEM) cross sections of a four-ply epoxy-glass laminate. First, at a magnification of ×15 four distinct plies are seen, where the arrangement of the fibre bundles that make up each ply
are clear. A clearer image of the individual fibres is seen ×50 magnification, while increasing to a magnification of ×200 shows how individual fibres are arranged within a fibre bundle.

2.2.2 Epoxy Systems

Epoxy resin systems are widely used because of their versatility, high mechanical properties, and high corrosion resistance. Epoxies tend to shrink less that other similar thermoset resin systems, which lends itself to excellent bonding characteristics when used in adhesives [1]. Most industrial applications of epoxy resins involve thermosetting, in which the epoxy reacts with crosslink hardening agent. The most common hardening classes are comprised of amines, anhydrides, and phenols. Thermosetting with amines deteriorates electrical properties, especially at elevated temperature and humidity. While, anhydrides require high energy consumption due to prolonged curing times at high temperature. Thermosetting by phenols leads to strong insulating characteristics, good adhesive properties, and chemical resistance [7].

2.2.3 Glass Fibre

Glass fibres are one the cheapest and most-readily available reinforcement options. They are readily produced from raw materials which are available in ample supply. When compared to carbon fibre, glass fibre is not nearly as strong or rigid, but is much cheaper and less brittle. Glass fibre is a more suitable reinforcement choice for applications where strength-weight ratio is not a primary design concern [1].

There are two categories of glass fibres, general purpose low cost fibres and special purpose fibres. Most glass fibres fall in the low cost, general purpose category and are known by the designation E-glass. The remaining, special purpose fibres have separate designations. Table 1 gives the common designation codes, while the compositions of several common glass fibres are given in Table 2.
Table 1: Common glass fibre designation codes [8]

<table>
<thead>
<tr>
<th>Designation</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, electrical</td>
<td>Low electrical conductivity</td>
</tr>
<tr>
<td>S, R, Te, strength</td>
<td>High strength</td>
</tr>
<tr>
<td>C, chemical</td>
<td>High chemical resistance</td>
</tr>
<tr>
<td>M, modulus</td>
<td>High stiffness</td>
</tr>
<tr>
<td>A, alkali</td>
<td>High alkali (soda lime) glass</td>
</tr>
<tr>
<td>D, dielectric</td>
<td>Low dielectric constant</td>
</tr>
</tbody>
</table>

Table 2: Compositions of commercial glass fibres [9, 10]

<table>
<thead>
<tr>
<th>Fibre</th>
<th>SiO$_2$</th>
<th>B$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>ZnO</th>
<th>TiO$_2$</th>
<th>ZrO$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Li$_2$O</th>
<th>Fe$_2$O$_3$</th>
<th>F$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-glass</td>
<td>52-56</td>
<td>4-6</td>
<td>12-15</td>
<td>21-23</td>
<td>0.4-4</td>
<td>-</td>
<td>0.2-0.5</td>
<td>-</td>
<td>0.1</td>
<td>trace</td>
<td>0.2-0.4</td>
<td>0.2-0.7</td>
<td></td>
</tr>
<tr>
<td>Boron-free E-glass</td>
<td>59.0</td>
<td>-</td>
<td>12.1</td>
<td>22.6</td>
<td>3.4</td>
<td>1.5</td>
<td>-</td>
<td>0.9</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>ECR-glass</td>
<td>58.2</td>
<td>-</td>
<td>11.6</td>
<td>21.7</td>
<td>2.0</td>
<td>2.9</td>
<td>2.5</td>
<td>-</td>
<td>1.0</td>
<td>0.2</td>
<td>1.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>D-glass</td>
<td>74.5</td>
<td>22.0</td>
<td>0.3</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>S-, R-, and Te-glass</td>
<td>60-65.5</td>
<td>-</td>
<td>25-25</td>
<td>0.9</td>
<td>6-11</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0-0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silica quartz</td>
<td>99.999</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A glass is an amorphous solid that is obtained by cooling a melt sufficiently fast as to not allow crystallisation to occur. On the manufacturing of glass fibres, Fig. 7 provides a generalised layout of a glass fibre furnace. Initially, individual components are weighed and delivered into a batch mixing station where the ingredients are thoroughly mixed prior to entering the furnace. Then, a glass melt is made in the furnace by fusing silica with various minerals containing oxide compounds required to form a desired end composition. This glass melt is then passed through the refiner and then through platinum/rhodium alloy brushings in the forehearth into small diameter fibres. On exiting the brushings, the glass is rapidly quenched and attenuated to prevent crystallisation. Typically, end glass fibre diameters range from 5 to 20 $\mu m$. The temperatures throughout the process are different for each type of glass being processed [9].

E-glass is the most common glass fibre system and comes in two general variants, boron containing and boron-free E-glass. Boron free E-glass is a more recent development because of environmental concerns and regulations on emission gasses from boron contains melts. The ASTM standard on E-glass [11] distinguishes E-glass by end application, where compositions containing 5-10 wt.% boron oxide are certified for uses in aerospace applications and in printed circuit boards. Conversely, 0-10 wt.% are certified for general class applications.

Special purpose glass fibres (not designated E-glass) find uses throughout industry. C-glass is designed to have much higher chemical and corrosion resistance than E-glass, while D-glass has a much lower dielectric constant, making D-glass attractive for printed circuit
Figure 7: A generalised layout of a furnace used in glass fibre manufacturing. Temperatures are given as examples, but will vary with every glass composition [9].

board laminates. S-glass, R-glass, and Te-glass are the classes of glass fibres classed for higher strength applications. These class of fibres can offer 15%+ increase in strength when compared with traditional E-glass, and additionally are generally able to withstand much higher operational temperatures (up to 815 °C). Commonly, S- R- and Te-glasses find military and aerospace applications. Processing is more difficult, requiring higher melt temperature, more overall processing energy, and more costly brushing alloys [9].

Similarly, pure silica/quartz glasses can be used in applications requiring higher operational temperatures. High silica fibres (95% SiO$_2$) are amorphous glass fibres that are manufactured through an acid leaching process on E-glass fibres, and are frequently used as insulators at temperatures in excess of 1000 °C. Pure silica fibres (99% SiO$_2$) are manufactured using a dry spinning process and can be used as insulators up to 1100 °C. Ultrapure silica fibres (99.99% SiO$_2$) have excellent high temperature performance and a high degree of transparency to ultraviolet light and long wavelength radiation [8].

2.2.4 Fibre Sizing

Fibre sizing systems are essential to the overall performance of glass fibre reinforced composite systems. Sizing is applied primarily for two reasons (i) to improve the adhesion between the epoxy system and glass fibre reinforcement and (ii) to improve handling and processing characteristics [1]. Fibre sizing is applied as an aqueous solution immediately following the forming and cooling of the glass fibre structure (Fig. 8). The solutions are usually very dilute (between 0.01 to 2 wt.%) as a means of ensuring that the sizing molecules do not react with one another.

Glass fibre sizing is not one single compound, and manufactures are commonly hesitant
to reveal the precise details of sizing applied to their fibres, as sizing is what distinguishes products between competitors. Generally, a sizing system will be composed to film forming materials and a coupling agent. The film former serves two primary functions within the system; the film former is designed to (i) protect and hold the fibres in the correct place/orientation prior to composite manufacture and (ii) improve separation of the fibres during composite manufacture to promote wetout of as many filaments as possible. Ideally, film formers are designed such that they are chemically similar to the resin system being used [12]. Summarising, the film forming compound primarily serves to better handling and processing characteristics of glass fibres, but do provide much performance increase to the end composite.

The coupling agent portion of the sizing system serves the primary function of establishing covalent bonds across the interface, which can drastically improve the performance and properties of the composite [13]. Silane is a specific class of coupling agent that is used to promote bonding between inorganic surfaces and organic polymer molecules (i.e. Glass fibre to epoxy matrices). At one end of the Silane molecule an alkoxy group reacts with fibre surface, while the opposite end has functional groups that directly bond with the reactive sites in the epoxy matrix [14]. Figure 9 provides the generalised molecular bonding structure of a glass fibre interface sized with γ-Aminopropyltriethoxysilane (AMPTES) silane coupling agent, where R represents the functional aminopropyl group.

Furthermore, some sizing systems may also include additional components that may serve specialised purposes, lubricating or antistatic agents, for example. Altogether, a sizing formulation may contain ten or more separate components. Interactions between each of the sizing components, the fibre surface, and the resin system become rather complex.
2.3 Micromechanics

Micromechanics of composites involves the study of specific interactions taking place between constituent materials. This gives the ability to represent a heterogenous material as an equivalent, generally anisotropic, homogenous material, Fig. 10. Broadly, micromechanics can be applied to predict composite stiffness and strength [1].

2.3.1 Volume Fractions

When designing composite material systems the relative amount of fibre and matrix are altered as a means to achieve desired material properties. The relative amount of fibre and matrix are commonly expressed in terms of a *volume fraction*. The fibre volume fraction $V_f$ and matrix volume fraction $V_m$ are given as,

$$V_f = \frac{\text{volume of fibre}}{\text{total volume}}$$
$$V_m = \frac{\text{volume of matrix}}{\text{total volume}}$$

(2.4)
The total volume is the sum of fibre volume and matrix volume,

\[ V_f + V_m = 1 \]  \hspace{1cm} (2.5)

Similarly, the amount of fibre and matrix by weight are known as the mass fractions,

\[ W_f = \frac{\text{weight of fibre}}{\text{total weight}} \]
\[ W_m = \frac{\text{weight of matrix}}{\text{total weight}} \]  \hspace{1cm} (2.6)

The total weight is the sum of fibre and matrix weights,

\[ W_f + W_m = 1 \]  \hspace{1cm} (2.7)

The total mass of a material is equal to the product of density \( \times \) volume. Therefore, the density of a composite, \( \rho_c \), can be found through knowing the density and volume fraction of each constituent,

\[ \rho_c = \rho_f V_f + \rho_m V_m \]  \hspace{1cm} (2.8)

The total volume is found by dividing mass by density, therefore the density of a composite can also be found through knowing the density and weight of each constituent,

\[ \frac{1}{\rho_c} = \frac{W_f}{\rho_f} + \frac{W_m}{\rho_m} \]  \hspace{1cm} (2.9)

When designing composites, the volume fraction is commonly used directly in the calculation of stiffness and strength. While, mass fractions are applied more during processing and manufacturing as it is much easier to weigh components rather than measuring their volume. Regardless, it is simple to convert from one to the other,

\[ W_f = \frac{\rho_f}{\rho_c} V_f \]
\[ W_m = \frac{\rho_m}{\rho_c} V_m \]  \hspace{1cm} (2.10)

### 2.3.2 Stiffness

Independently, both glass fibres and matrix are assumed to behave as isotropic materials. It is worth noting that other reinforcement types, such as carbon and natural fibres, behave as anisotropic materials, greatly complicating the calculation of mechanical properties of the resulting laminate [15–17]. The present work is concerned with glass fibre reinforce compos-
Figure 11: The micromechanics of uniform longitudinal loading

ites, and as such all following derivations assume isotropic reinforcing fibres. The stiffness for an isotropic material is fully represented by two properties: the modulus of elasticity $E$ and Poisson’s ratio $\nu$. Through applying micromechanics, the combination of two isotropic materials (fibre and matrix) is represented an equivalent, generally anisotropic, homogenous material (Fig. 10). Under the assumption of continuous, parallel aligned fibres which are perfectly bonded to the matrix, the stiffness of this equivalent homogenous material is described by five elastic properties:

$E_1$: modulus of elasticity in the fibre direction
$E_2$: modulus of elasticity in the direction perpendicular to the fibres
$G_{12}$: in-plane shear modulus
$G_{23}$: out of plane shear modulus
$\nu_{12}$: in-plane Poisson’s ratio

### 2.3.3 Longitudinal Modulus

The modulus of elasticity in the fibre direction (1-direction) can be predicted quite well through application of the rule of mixtures (ROM). This method makes a key assumption in that the strains in the direction of the fibres are the same for both the matrix and the fibre, essentially indicating a perfect bond between fibre and matrix. In other words, when the material is stressed in the fibre direction ($\sigma_1$), the fibre and matrix will undergo the same

```
\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure11.png}
\caption{The micromechanics of uniform longitudinal loading}
\end{figure}
```
The stress $\sigma_1$ acts across the entire cross sectional area $A$,

$$ P = \sigma_1 A = \sigma_f A_f + \sigma_m A_m $$  \hfill (2.12)\

Bearing in mind $V_f = A_f/A$ and $V_m = A_m/A$, solving for $\sigma_1$ gives,

$$ \sigma_1 = \epsilon_1 (E_f V_f + E_m V_m) $$  \hfill (2.13)\

For the equivalent homogeneous material $\sigma_1 = \epsilon_1 E_1$, therefore the rule of mixtures is as follows,

$$ E_1 = E_f V_f + E_m V_m $$  \hfill (2.14)\

In nearly all cases the modulus of the fibre is much larger than that of the matrix ($E_f \gg E_m$), indicating that the longitudinal modulus $E_1$ is a fibre dominated property.
2.3.4 Transverse Modulus

For the prediction of transverse modulus the primary assumption made is that the stress is the same for both the fibre and matrix, indicating a perfect fibre-matrix bond. Note, for simplicity, the cylindrical shape of the fibre is not perfectly captured in this formulation, but rather has been replaced with a rectangular profile, Fig. 12.

As the fibre and matrix are assumed to be linear elastic materials, the strains for this case in the fibre and matrix are

$$\epsilon_f = \frac{\sigma_2}{E_f}$$

$$\epsilon_m = \frac{\sigma_2}{E_m}$$

(2.15)

Since the stress is assumed to be the same for the fibre and matrix ($\sigma_f = \sigma_m = \sigma_2$), the total strain in the 2 direction for this system becomes,

$$\epsilon_2 = \frac{\sigma_2}{E_f}V_f + \frac{\sigma_2}{E_m}V_m$$

(2.16)

Then through applying Hooke’s Law for an equivalent homogenous system ($\sigma_2 = E_2\epsilon_2$),

$$\frac{1}{E_2} = \frac{V_f}{E_f} + \frac{V_m}{E_m}$$

(2.17)

This is often referred to as the inverse rule of mixtures. It is apparent that the fibres do not make significant contributions to the transverse stiffness, unless $V_f$ is extremely high. Therefore, transverse stiffness $E_2$ is a matrix dominated property. This formulation is rather simple and is good for quick checks of material properties, but generally tends to underestimate. A more accurate prediction can be made using the semi-empirical Halpin-Tsai formulation [18],

$$E_2 = E_m\left(\frac{1 + \zeta\eta V_f}{1 - \eta V_f}\right)$$

$$\eta = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \zeta}$$

(2.18)

where $\zeta$ is an empirical parameter determined through curve fitting. A value of $\zeta = 2$ generally produces a reasonable fit for the case of circular or square fibres.

2.3.5 Poisson’s Ratio

Following the rule of mixtures a prediction for in-plan Poisson’s ratio can be made,

$$\nu_{12} = \nu_f V_f + \nu_m V_m$$

(2.19)
2 FUNDAMENTAL BACKGROUND

Figure 13: Difference between (a) In-plane shear and (b) Interlaminar shear.

In the context of composite design, an approximate prediction for the Poisson’s ratio is generally suitable. This is primarily due to the Poisson’s ratios for the fibre and matrix being similar, meaning Eqn. (2.19) will further predict a similar value for the composite [1].

2.3.6 In-plane and Interlaminar Shear Modulus

In-plane shear stress deforms the laminate as in Fig. 13a. From a strength of materials approach, an inverse rule of mixtures for the in-plane shear modulus, $G_{12}$, gives the following,

$$\frac{1}{G_{12}} = \frac{V_f}{G_f} + \frac{V_m}{G_m}$$

$$G_{12} = \frac{G_m}{V_m + V_f G_m / G_f}$$

Assuming stiff reinforcing fibres ($G_m << G_f$), the in-plane shear modulus can be shown to be a matrix-dominated property,

$$G_{12} = \frac{G_m}{1 - V_f}$$

As previous, the inverse rule of mixtures provides a relatively simple approximation of the in-plane shear modulus. A more accurate representation is given by the cylindrical assemblage model (CAM)[19],

$$G_{12} = G_m \left[ \frac{(1 + V_f) + (1 - V_f)G_m / G_f}{(1 - V_f) + (1 + V_f)G_m / G_f} \right] \quad (2.22)$$
Again assuming stiff fibres \((G_m << G_f)\), this can be represented as,

\[
G_{12} = G_m \left(1 + \frac{V_f}{1 - V_f}\right) \tag{2.23}
\]

The interlaminar shear stress, \(\sigma_4\), across the thickness of the composite is illustrated in Fig. 13b. The interlaminar shear modulus can be calculated through application of the stress partitioning parameter technique \([20]\),

\[
G_{23} = G_m \frac{V_f + \eta_4(1 - V_f)}{\eta_4(1 - V_f) + V_f G_m/G_f} \\
\eta_4 = \frac{3 - 4\nu_m + G_m/G_f}{4(1 - \nu_m)} \tag{2.24}
\]

2.4 Ply Mechanics

This section will present the constitutive equations of a single, arbitrarily oriented composite ply. There are two coordinate systems used in composite design. The material coordinates \((1, 2, 3)\) axes; where the 1-axis is the fibre direction, the 2-axis is perpendicular to the 1-axis, and 3-axis is perpendicular to the surface and to the 1- and 2-axis. The laminate coordinates \((x, y, z)\) axes are common to all laminae in the composite, and is generally chosen for convenience \([1]\).

2.4.1 Stress

To begin, consider the \(6 \times 6\) stress matrix in the material \((1, 2, 3)\) coordinate system. Where for each component of the stress tensor, the first subscript indicates the direction normal to the face where the stress vector was computed, and the second indicates the direction of the stress vector. Assuming the stress tensor is symmetric \((\sigma_{ij} = \sigma_{ji})\), the stress matrix can be re-written composed of only six independent stress components,

\[
\sigma = \begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{bmatrix} \tag{2.25}
\]

For convenience, each tensorial stress component can be written in a reduced notation,
2.4.2 Strain

The strain tensor is also shown to be symmetric \((\epsilon_{ij} = \epsilon_{ji})\), and given in the material coordinate system,

\[
\epsilon = \begin{bmatrix}
\epsilon_{11} & \gamma_{12}/2 & \gamma_{13}/2 \\
\gamma_{12}/2 & \epsilon_{22} & \gamma_{23}/2 \\
\gamma_{13}/2 & \gamma_{23}/2 & \epsilon_{33}
\end{bmatrix}
\] (2.26)

Each of the tensorial strain components can again be rewritten in a reduced notation,

\[
\begin{array}{c|c}
\text{Tensorial} & \text{Reduced} \\
\hline
\epsilon_{11} & \epsilon_1 \\
\epsilon_{22} & \epsilon_2 \\
\epsilon_{33} & \epsilon_3 \\
\gamma_{23} & \gamma_4 \\
\gamma_{13} & \gamma_5 \\
\gamma_{12} & \gamma_6 \\
\end{array}
\]

2.4.3 Stress-Strain Relations

Generally, composites are used in the form of thin plates, where length and width are much greater than thickness. In this case of plane stress, it is reasonable to assume that the transverse stress is approximately 0 \((\sigma_3 = 0)\). The stress-strain equations for a single lamina are easily experimentally derived as follows. First, a tensile stress is applied in only the fibre direction (1-axis) and the strain is calculated,

\[
\epsilon_1 = \frac{\sigma_1}{E_1}
\] (2.27)
Then, the system is stressed in the 2-direction by $\sigma_2$. The strain in the fibre direction is again calculated through applying Poisson’s Ratio ($\nu_{ij} = -\varepsilon_j/\varepsilon_i$),

$$\varepsilon_1 = -\nu_{21}\varepsilon_2 = -\nu_{21}\frac{\sigma_2}{E_2} \quad (2.28)$$

The total strain in the fibre (1-direction) becomes the sum of the two components,

$$\varepsilon_1 = \frac{\sigma_1}{E_1} - \frac{\sigma_2\nu_{21}}{E_2} \quad (2.29)$$

This is repeated in the transverse fibre direction (2-direction),

$$\varepsilon_2 = -\frac{\sigma_1\nu_{12}}{E_1} + \frac{\sigma_2}{E_2} \quad (2.30)$$

Then, Hooke’s Law for shear stresses is used in calculating shear terms,

$$\sigma_6 = G_{12}\gamma_6$$

$$\sigma_4 = G_{23}\gamma_4$$

$$\sigma_5 = G_{13}\gamma_5 = G_{12}\gamma_5 \quad (2.31)$$

Take note, $G_{13} = G_{12}$ as the 2- and 3- directions are the same, this is a traverse isotropic material. The compliance equations are now given,

$$\begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \gamma_6 \end{bmatrix} = \begin{bmatrix} 1/E_1 & -\nu_{21}/E_2 & 0 \\ -\nu_{12}/E_1 & 1/E_2 & 0 \\ 0 & 0 & 1/G_{12} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_6 \end{bmatrix} \quad (2.32)$$

$$\begin{bmatrix} \gamma_4 \\ \gamma_5 \end{bmatrix} = \begin{bmatrix} 1/G_{23} & 0 \\ 0 & 1/G_{13} \end{bmatrix} \begin{bmatrix} \sigma_4 \\ \sigma_5 \end{bmatrix}$$

The compliance matrix, Eqn. (2.32), must be symmetric in that $\nu_{21}/E_2 = \nu_{12}/E_1$. Therefore, under plane stress conditions there are only four properties needed to solve ($E_1$, $E_2$, $G_{12}$, and $\nu_{12}$). The compliance equations can be written in a more concise notation [1],

$$\begin{bmatrix} \epsilon \\ \sigma \end{bmatrix} = [S] \begin{bmatrix} \sigma \\ \tau \end{bmatrix} \quad (2.33)$$

where $\epsilon$ are all the in plane strains, $\sigma$ are in-plane stresses, $\gamma$ are shear strains, and $\tau$ are interlaminar stresses. Again, $[S]$ is the compliance matrix for the system, while $[S^*]$ is the interlaminar compliance.
Inversion of \([S]\) and \([S^*]\) gives the reduced stiffness matrices, \([Q]\) and \([Q^*]\),

\[
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_6
\end{bmatrix} =
\begin{bmatrix}
E_1 \Delta & \nu_{12} E_2 / \Delta & 0 \\
\nu_{12} E_2 / \Delta & E_2 / \Delta & 0 \\
0 & 0 & G_{12}
\end{bmatrix}
\begin{bmatrix}
\epsilon_1 \\
\epsilon_2 \\
\gamma_6
\end{bmatrix}
\]

\[
\begin{bmatrix}
\sigma_4 \\
\sigma_5
\end{bmatrix} =
\begin{bmatrix}
G_{23} & 0 \\
0 & G_{13}
\end{bmatrix}
\begin{bmatrix}
\gamma_4 \\
\gamma_5
\end{bmatrix}
\]

(2.34)

where, \(\Delta = 1 - \nu_{12} \nu_{21} = 1 - \nu_{12}^2 E_2 / E_1\). Finally, the compliance equations for a single lamina in the final, reduced form,

\[
\begin{bmatrix}
\sigma \\
\tau
\end{bmatrix} =
\begin{bmatrix}
Q \\
Q^*
\end{bmatrix}
\begin{bmatrix}
\epsilon \\
\gamma
\end{bmatrix}
\]

(2.35)

The components of the \(3 \times 3 [Q]\) and \(2 \times 2 [Q^*]\) matrices are,

\[
Q_{11} = \frac{E_1}{\Delta}
\]

\[
Q_{12} = Q_{21} = \nu_{12} \frac{E_2}{\Delta}
\]

\[
Q_{22} = \frac{E_2}{\Delta}
\]

\[
Q_{66} = G_{12}
\]

\[
Q_{44} = G_{23}
\]

\[
Q_{55} = G_{13}
\]

(2.36)

2.4.4 Transformations

To this point, all the stress-strain relations have assumed the case of only having loading in the material direction. In practice, it is necessary to transform these relationships for uses in the global, laminate coordinate system. This is done through the following,

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_{xy}
\end{bmatrix} =
\begin{bmatrix}
Q_{11} & Q_{12} & Q_{16} \\
Q_{12} & Q_{22} & Q_{26} \\
Q_{16} & Q_{26} & Q_{66}
\end{bmatrix}
\begin{bmatrix}
\epsilon_x \\
\epsilon_y \\
\gamma_{xy}
\end{bmatrix}
\]

\[
\begin{bmatrix}
\sigma_y \\
\sigma_{xz}
\end{bmatrix} =
\begin{bmatrix}
Q^*_{44} & Q^*_{45} \\
Q^*_{45} & Q^*_{55}
\end{bmatrix}
\begin{bmatrix}
\gamma_{yz} \\
\gamma_{xz}
\end{bmatrix}
\]

(2.37)

where \(Q_{ij}\) and \(Q^*_{ij}\) are each components of the transformed stiffness matrices. Sparing some of the derivational details (see \([1]\)) , the final forms for each component of the transformed
[Q] and [Q∗] matrices in terms of the components of [Q] and [Q∗] and the angle between laminate and material coordinates θ are,

\[
\begin{align*}
\bar{Q}_{11} &= Q_{11} \cos^4 \theta + 2(Q_{12} + 2Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{22} \sin^4 \theta \\
\bar{Q}_{12} &= (Q_{11} + Q_{22} - 4Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{12}(\sin^4 \theta + \cos^4 \theta) \\
\bar{Q}_{22} &= Q_{11} \sin^4 \theta + 2(Q_{12} + 2Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{22} \cos^4 \theta \\
\bar{Q}_{16} &= (Q_{11} - Q_{12} - 2Q_{66}) \sin \theta \cos^3 \theta + (Q_{12} - Q_{22} - 2Q_{66}) \sin^3 \theta \cos \theta \\
\bar{Q}_{26} &= (Q_{11} - Q_{12} - 2Q_{66}) \sin^3 \theta \cos \theta + (Q_{12} - Q_{22} - 2Q_{66}) \sin \theta \cos^3 \theta \\
\bar{Q}_{66} &= (Q_{11} + Q_{22} - 2Q_{12} - 2Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{66}(\sin^4 \theta + \cos^4 \theta) \\
\bar{Q}^{∗}_{44} &= Q^{∗}_{55} \cos^2 \theta + Q^{∗}_{55} \sin^2 \theta \\
\bar{Q}^{∗}_{55} &= Q^{∗}_{44} \sin^2 \theta + Q^{∗}_{55} \cos^2 \theta \\
\bar{Q}^{∗}_{45} &= (Q^{∗}_{55} - Q^{∗}_{44}) \sin \theta \cos \theta
\end{align*}
\] (2.38)

2.5 Diffusion

Commonly, Fickian diffusion laws are used to mathematically describe the diffusion process. Fick’s first law of diffusion states the given flux of a component will move from an area of high concentration to an area of low concentration, mathematically this is given in Eqn. (2.39). The negative sign in this relationship indicates mass diffuses in a downward gradient direction (i.e. from areas of high concentration to low concentration). Fick’s second law of diffusion, Eqn. (2.40), is derived from Fick’s first law and the principle of mass conservation, and is for determining how concentration changes with time [21].

\[
J_i = -D_{ij} \frac{\partial C}{\partial x_j} \quad (2.39)
\]

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) \quad (2.40)
\]

where, \(J_i\) is a flux term (kg s\(^{-1}\) m\(^{-2}\)), \(D_{ij}\) is the mass diffusivity tensor (m\(^2\)s\(^{-1}\)), \(C\) is concentration, \(x_j\) is the spatial coordinate of interest (m), and \(t\) is time (s).

Mass diffusion into a Fickian material is driven completely by a concentration gradient. Hence, mass diffusion will no longer occur once an equilibrium state has been achieved. Experimentally, this phenomenon is investigated through tracking weight changes in a sample and plotting this against time. The resulting curve will exhibit several characteristics that all Fickian materials share. A Fickian mass diffusion plot will exhibit an initially linear period of mass uptake into the system. As the equilibrium state is reached (mass concentration...
Figure 14: A generalised Fickian diffusion curve.

gradient tending towards zero) the rate at which mass diffuses into the system drops off, eventually reaching an equilibrium point where no further mass enters the system, Fig. 14.
3 Molecular Dynamics Fundamentals

Molecular Dynamics (MD) simulation has proven to be a useful tool in exploring the structure and properties of materials at an atomic level. Mathematically, MD is a computational method which calculates time dependent behaviour of molecular systems. Commonly, MD serves as a compliment to conventional experiments, a bridge between theory and experimental work. Additionally, the simulation provides microscale details in addition to macroscale level details gained through experimental work. Frequently, MD simulations are carried out to verify results found experimentally; though MD may also be carried out to simulate difficult or impossible experimental conditions (for example, extremes of temperature and pressure).

Initially finding roots in theoretical physics, MD found uses throughout materials sciences, biophysics, and biochemistry. Notably, MD simulations have proven to be an invaluable tool in understanding the dynamics of proteins and nucleic acids. MD techniques are regularly used to investigate the structure, thermodynamics, and interactions of complex bio-molecular systems, leading to applications in simulating the protein folding process. Overall, MD simulations find applications in areas where experimental investigations are difficult to undertake and, with proper dynamics, are often able to provide insight into the system [22].

3.1 Equations of Motion

Fundamentally, Molecular Dynamics is a numerical simulation method rooted in Newton’s second law, $F = ma$, where $F$ is the force on the atom, $m$ is the atom mass and $a$ its acceleration. Through knowing the force applied to and mass of each atom, it becomes possible to determine acceleration for every atom in the system. Further integrating the equations of motion then yields a system trajectory that describes all atom positions, velocities, and accelerations each as a function of time. Newton’s second law is given as follows,

$$F_i = m_i a_i = m_i \frac{d v_i}{d t} = m_i \frac{d^2 r_i}{d t^2}$$

where $F_i$ is the force exerted on atom $i$, $m_i$ is the mass of atom $i$, and $a_i$ is its acceleration. Acceleration can also be expressed as the first derivative of the atom velocity $v_i$; furthermore, acceleration is also represented as the second derivative of the atom position $r_i$. From this point a shorthand notation will be used in describing atom position ($r_i$), velocity ($\dot{r_i}$), and acceleration ($\ddot{r_i}$).

For a purely conservative system, the force acting on the atom can also be expressed as the gradient of potential energy $U$, yielding an important relationship between the potential
energy of the system and atom position as a function of time,

\[ F_i = m_i \ddot{r}_i = -\frac{\partial U(r_i)}{\partial r_i} \]

### 3.1.1 Lagrangian and Hamiltonian Formulations

At the most fundamental level of classical mechanics is the Lagrangian formulation. The Lagrangian, \( \mathcal{L} \) for a system is defined as the difference between the kinetic and potential energies and is expressed as a function of atom positions and velocities,

\[ \mathcal{L}(r_i, \dot{r}_i) = K - U = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{r}_i^2 - U(r_i) \]  

(3.1)

Furthermore, the Lagrangian equation of motion is given through the Euler-Lagrangian relation\[22],

\[ \frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \right) - \frac{\partial \mathcal{L}}{\partial r_i} = 0 \]  

(3.2)

This is shown to be completely equivalent to Newton’s second law,

\[ \frac{\partial \mathcal{L}}{\partial r_i} = m \dot{r}_i \quad \frac{\partial \mathcal{L}}{\partial \dot{r}_i} = -\frac{\partial U(r_i)}{\partial r_i} \]  

(3.3)

\[ \frac{d}{dt}(m \dot{r}_i) - \left( -\frac{\partial U(r_i)}{\partial r_i} \right) = 0 \]

\[ \Rightarrow F_i = m_i \ddot{r}_i = -\frac{\partial U(r_i)}{\partial r_i} \]  

(3.4)

Therefore, using the Lagrangian equation, we can solve for the motion of atoms in a system using kinetic and potential energies without the need for solving for an acceleration term (as \( \mathcal{L} \) is a function of only atom position \( r_i \) and velocity \( \dot{r}_i \)). Consider change of the Lagrangian \( d\mathcal{L} \),

\[ d\mathcal{L} = \sum_i \frac{\partial \mathcal{L}}{\partial r_i} dr_i + \frac{\partial \mathcal{L}}{\partial \dot{r}_i} d\dot{r}_i \]

\[ \frac{d\mathcal{L}}{dt} = \sum_i \frac{\partial \mathcal{L}}{\partial r_i} \frac{dr_i}{dt} + \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \frac{d\dot{r}_i}{dt} \]

\[ = \sum_i \frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \right) \dot{r}_i + \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \frac{d}{dt} (\dot{r}_i) \]

\[ = \frac{d}{dt} \sum_i \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \dot{r}_i \]  

(3.5)

indicating that the Lagrangian \( \mathcal{L} \) is not conserved with time. Rearranging, and introducing
a new variable, the Hamiltonian $\mathcal{H}$,

$$
0 = \frac{d}{dt} \left( \sum_i \frac{\partial L}{\partial \dot{r}_i} \dot{r}_i - \mathcal{L} \right)
$$

$$
\mathcal{H} = \sum_i \frac{\partial L}{\partial \dot{r}_i} \dot{r}_i - \mathcal{L}
$$

$$
\Rightarrow \frac{d\mathcal{H}}{dt} = 0
$$

(3.6)

Importantly, it is seen that the Hamiltonian $\mathcal{H}$ is a conserved quantity for the system. $\mathcal{H}$ can be further refined through using the definition of momentum on atom $r_i$. We know momentum $p_i$ is defined as mass$\times$velocity ($m_i \dot{r}_i$), this was given in relation to $\mathcal{L}$ earlier in Eqn. (3.3), this is referred to as the conjugate momenta,

$$
p_i = m_i \dot{r}_i = \frac{\partial L}{\partial \dot{r}_i}
$$

(3.7)

On substitution of the conjugate momenta $p_i$ into the Lagrangian equation of motion (Eqn. 3.2),

$$
\frac{\partial L}{\partial r_i} = \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{r}_i} \right) = \frac{d}{dt} p_i = \dot{p}_i
$$

(3.8)

we are left with the following,

$$
p_i = \frac{\partial L}{\partial \dot{r}_i} \quad \dot{p}_i = \frac{\partial L}{\partial r_i}
$$

(3.9)

Substituting this into Eqn. (3.6) yields,

$$
d\mathcal{L} = \sum_i \frac{\partial L}{\partial r_i} dr_i + \frac{\partial L}{\partial \dot{r}_i} d\dot{r}_i = \sum_i \dot{p}_i dr_i + p_i d\dot{r}_i
$$

$$
\frac{d\mathcal{L}}{dt} = \sum_i \dot{p}_i \frac{dr_i}{dt} + p_i \frac{d\dot{r}_i}{dt} = \sum_i \frac{dp_i}{dt} \dot{r}_i + p_i \frac{d\dot{r}_i}{dt}
$$

$$
= \frac{d}{dt} \sum_i p_i \dot{r}_i
$$

$$
0 = \frac{d}{dt} \left( \sum_i p_i \dot{r}_i - \mathcal{L} \right)
$$

(3.10)
Therefore, the Hamiltonian can be shown to take the final form,

\[
\mathcal{H} = \sum_i p_i \dot{r}_i - \mathcal{L} = \sum_i (m_i \dot{r}_i)(\dot{r}_i) - \left(\frac{1}{2} \sum_i m_i \dot{r}_i^2 - U(r_i)\right) \tag{3.11}
\]

\Rightarrow H = K + U

The Hamiltonian equations of motion for the system are then defined as,

\[
\dot{r}_i = \frac{\partial \mathcal{H}}{\partial p_i} \quad \quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial r_i} \tag{3.12}
\]

This transformation from the Lagrangian \( \mathcal{L} \) to the Hamiltonian \( \mathcal{H} \) is known as the Legendre transform.

In summary,

1. The Lagrangian is defined as the difference between the kinetic and potential energies of the system, and is a function of atom positions \( r_i \) and velocities \( \dot{r}_i \):
   \[
   \mathcal{L}(r_i, \dot{r}_i) = K - U
   \]
2. The Lagrangian equations of motion are given by:
   \[
   m_i \ddot{r}_i = \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \quad -\frac{\partial U(r_i)}{\partial r_i} = \frac{\partial \mathcal{L}}{\partial r_i}
   \]
3. The conjugate momenta are defined as \( p_i = \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \)
4. The Hamiltonian is calculated as the kinetic plus the potential energy and is a function of atom position \( r_i \) and momentum \( p_i \): \( \mathcal{H}(r_i, p_i) = K + U \)
5. The hamiltonian equations of motion are given by:
   \[
   \dot{r}_i = \frac{\partial \mathcal{H}}{\partial p_i} \quad \quad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial r_i}
   \]
6. \( d\mathcal{H}/dt = 0 \) indicates conservation of energy

Molecular Dynamics theory is rooted in this relationship between the system energy and atom positions. Where, through explicitly defining an energy potential function for the system, atom trajectories can be numerically determined. Through knowing atom trajectories, the average values for several material properties can be determined. MD is a deterministic method; as once the positions and velocities of each atom are known, the state of the entire system can be predicted for all time steps (forward and backward).

Due to the numerical nature of the solution methods, MD can be both time consuming and computationally intensive. Most commonly, simulations are calculated within the
nanosecond time scale, simulations into the millisecond range are rarely seen. An outline of the numerical MD process is provided in Fig. 15.

3.2 Force Fields and The Energy Potential Function

Fundamentally, the energy potential function is a parametrised mathematical description of how atoms interact with one another throughout the simulation; within Chemistry and Biology this is referred to as a force field. The force field functions and parameter set used therein can be derived both experimentally, using Nuclear Magnetic Resonance techniques, and through high order ab-initio quantum mechanics calculations. The functional form of a force field sees contributions from both bonded (covalent bonds) and non-bonded (electrostatic and Van der Waals) terms. The covalent terms are bonded interactions which include bond stretch, bond angle bending, and dihedral angle torsion; commonly the bonded terms are represented as harmonic oscillators that explicitly do not account for bond breaking (Fig. 16). The non-bonded terms consist of electrostatic terms and Van der Waals, in which the electrostatic portion is calculated using Coulomb’s Law and Van der Waals are found through the application of the Lennard-Jones potential[22–24]. The most generalised representative form for a force field can be given as the following,

\[
U_{total} = U_{bonded} + U_{nonbonded}
\]

\[
U_{bonded} = U_{bond} + U_{angle} + U_{dihedral}
\]

\[
U_{nonbonded} = U_{electrostatic} + U_{Van der Waals}
\]

A reduced, parametrised form of the CHARMM as presented by Brooks et al. [25] is provided as an example of a force field function, demonstrating atomic quantities typically required to fully define the function. First, the potential energy contributions from bonded
interactions are defined as follows,

\[ U = \sum_b K_b (b - b_0)^2 + \sum_\theta K_\theta (\theta - \theta_0)^2 + \sum_\phi K_\phi (1 + d \cos(n\phi)) \]

where \( K_b, K_\theta, \) and \( K_\phi \) are force (spring) constants, \( b_0, \theta_0, \) and \( \phi \) are equilibrium bond length, bond angle, and dihedral angle, respectively; \( b \) and \( \theta \) are bond length and bond angle. The CHARMM force field provides the equilibrium and force constants for each given species in the simulation. It is noted that the potential energy of the system has significant contributions from non-bonded interactions. The Lennard-Jones (Van der Waal) potential and Coulombic (electrostatic) pairwise interactions are calculated for all atoms \( i,j \).

\[ U_{LJ} = \sum_{i\neq j} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]

\[ U_{el} = \sum_{i\neq j} \frac{Cq_iq_j}{\epsilon_0 r_{ij}} \]

respectively, where, \( \epsilon_{ij} \) defines how strongly the atoms attract each other and \( \sigma_{ij} \) is the cut-off distance at which the intermolecular potential between atoms \( i \) and \( j \) is zero. \( C \) is an energy-conversion constant, \( q_i \) and \( q_j \) are the charges for atoms \( i \) and \( j \), \( \epsilon_0 \) is the permittivity of free space, and \( r_{ij} \) is the distance between the atoms. The CHARMM force field provides the parameters for each pair of atoms in the system.

### 3.3 Numerical Solution Methods

Potential energy is a function of the position of all atoms in the system. This function is inherently complicated and analytical solution do not exist; therefore, the functions must be numerically solved. There are several algorithms that have been developed for integrating the equations of motion; each algorithm carries certain advantages and disadvantages. When
selecting an algorithm one should primarily consider the degree of accuracy desired and the computational resources available.

All integration algorithms assume acceleration, velocity, and position can all be approximated through using a Taylor series expansion,

\[
\begin{align*}
    r(t + \delta t) &= r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 + \cdots \\
    v(t + \delta t) &= v(t) + a(t)\delta t + \frac{1}{2}b(t)\delta t^2 + \cdots \\
    a(t + \delta t) &= a(t) + b(t) + \cdots
\end{align*}
\]

### 3.3.1 Verlet-Stoermer Algorithm

One of the most commonly applied algorithms is the Verlet-Stoermer algorithm [22, 23, 26],

\[
\begin{align*}
    r(t + \delta t) &= r(t) + v(t)\delta t + \frac{1}{2}a(t)\delta t^2 \\
    r(t - \delta t) &= r(t) - v(t)\delta t + \frac{1}{2}a(t)\delta t^2
\end{align*}
\]

Summing these two equations the atom position at a future time step \( t + \delta t \) is found,

\[
r(t + \delta t) = 2r(t) - r(t - \delta t) + a(t)\delta t^2
\]

The Verlet-Stoermer algorithm uses position and acceleration at time \( t \) and position at time \( t - \delta t \) to calculate the new atom position at time \( t + \delta t \). It should also be noted that there are no explicit velocity terms needed. The Verlet-Stoermer algorithm is a straightforward example of an integration algorithm with moderately accurate solution outputs while only requiring modest computational resources. Overall the algorithm provides excellent numerical stability, time-reversibility, and full energy conservation.

Note, the velocities are not explicitly defined but are often required for the calculation of many physical quantities of the system, such as kinetic energy. This introduces challenges for applications in MD simulations, where temperatures and kinetic energy for the system at some time \( t \) cannot be calculated until all atom positions are known at \( t + \delta t \). Fundamentally, this can be handled through estimating atom velocity using atom positions at \( t + \delta t \) and \( t - \delta t \) and applying the mean value theorem [21],

\[
v(t) = \frac{r(t + \delta t) - r(t - \delta t)}{2\delta t}
\]

This velocity term is calculated at a timestep behind \( t \) the currently calculated position.
term $(t + \delta t)$. To further address the issue the *Leap-frog* or *Velocity Verlet* algorithms can be applied.

### 3.3.2 Leap-frog Algorithm

The *Leap-frog* algorithm [27] first calculates velocities at time $t + 1/2\delta t$; these velocities are then used to calculate atom position $r$ at time $t + \delta t$. This process continues such that the velocities leap over the positions with each iteration.

$$r(t + \delta t) = r(t) + v(t + \frac{1}{2}\delta t)$$

$$v(t + \frac{1}{2}\delta t) = v(t - \frac{1}{2}\delta t) + a(t)\delta t$$

The *Leap-frog* algorithm has advantages in that the velocities are calculated explicitly, however they are not calculated at the same time step as the position, meaning approximations are still required. An approximation of the velocity at time $t$ is given by,

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

This algorithm finds two primary strengths. First, the *Leap-frog* algorithm is fully time reversible, meaning that after integrating forward $n$ timesteps it is always possible to then reverse the direction of integration backwards $n$ timesteps to arrive at the initial starting position. Secondly, it fully conserves the energy of a dynamic system [26].

### 3.3.3 Velocity Verlet Algorithm

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

$$v(t + \delta t) = v(t) + \frac{1}{2} \left[ a(t) + a(t + \delta t) \right] \delta t$$

The *Velocity Verlet* algorithm is similar to the *Leap-frog* algorithm, except that the velocities and positions are calculated at the same time value. This algorithm is not necessarily more computationally intensive than the basic *Verlet* algorithm, as the velocity does not need to be tracked with every timestep.
Initially proposed in 1976, Beeman’s algorithm [28] is yet another variant on the classic Verlet algorithm. The advantage of the Beeman’s algorithm is that it incorporates higher order integration terms, yielding a more accurate expression for the system trajectory and leading to better overall energy conservation. However, as the simulation must track atom position, velocity, acceleration, and acceleration from the previous timestep, this complex expression comes with relatively high computational costs.

3.4 Statistical Mechanics

Molecular dynamics simulations allow us to generate detailed structural information at the atomic level, including atom positions and velocities. Therefore, the integration of Newton’s equations of motion provides the basis for simulating kinetic properties of molecular systems. The connection between the properties of microscopic simulations and experimentally observable macroscopic properties, such as pressure and temperature, is made through statistical mechanics (Fig. 17). Fundamentally, statistical mechanics provides mathematical relationships that connect the macroscopic properties to the position and motion of microscopic atoms in a N-body system. With this, MD simulations can be used as a means of studying not only time dependent kinetic properties but also thermodynamic properties of a system.

3.4.1 Ensembles

An ensemble is defined as a collection of all possible systems that vary microscopically but have identical macroscopic and thermodynamic states [22]. Figure 18 illustrates this concept,
Figure 18: The same macroscopic, thermodynamic state represented as many different microscopic configurations $C_i$

where each copy $C_i$ represents a possible microscopic state some macroscopic system may take under thermodynamic constraints (N,P,T,V).

For most applications, precise control over the simulation system is required to better mimic real life experimental conditions. Where maintaining certain extensive system properties at a constant value is paramount to accurately capturing the thermodynamics occurring in the system. The macroscopic system becomes defined in terms of extensive variables which are held constant, this essentially manifests itself in the microscopic system as boundary conditions, or restraints. As an example, take the NVT ensemble, here the number of atoms $N$, volume $V$, and temperature $T$ of the macroscopic system are held constant. There are several different ensembles available, each with distinct characteristics useful for simulating a wide variety of conditions [24].

- **Microcanonical (NVE) Ensemble**
  
  Assuming all forces are directly related to the energy potential of the system then the total energy of the system, $E$, is conserved with each timestep. If the total number of atoms in the system, $N$, and the volume of the simulation cell, $V$, have additionally been held constant then the MD simulation has been undertaken in the microcanonical (NVE) ensemble. The NVE ensemble represents molecular dynamics simulations in the purest form, where the dynamics of the system is completely undisturbed. This corresponds to an isolated system. Fundamentally, the microcanonical ensemble can be viewed as a constant exchange of potential and kinetic energies, where the total
energy of the system is always conserved.

Care must be taken when choosing to run a simulation under a microcanonical ensemble, especially when looking to reach equilibrium conditions in the system. Without the energy flow of the system facilitated by a temperature control method (thermostatting) the temperature of the simulation can drastically fluctuate, making reaching equilibrium nearly impossible. Though, with a sufficiently large simulation system the microcanonical ensemble may be viewed as a representative canonical (NVT) ensemble, as the magnitude of temperature fluctuations reduces with the size of the system [22, 24].

- **Canonical (NVT) Ensemble**
  Fundamentally, the canonical ensemble represents a fixed number of atoms $N$, a fixed volume $V$, and a fixed temperature $T$. The Canonical ensemble represents all possible states of a system in thermal equilibrium with an external heat bath. A system under canonical ensemble conditions constantly undergoes energy exchange with the coupled heat sink, in the form of heat transfer, indicating that all states of the system will differ in total energy. The fact that the system energy is not held constant represents the most significant difference from the microcanonical (NVE) ensemble.

- **Isobaric-Isothermal (NPT) Ensemble**
  A system under isobaric-isothermal (NPT) ensemble conditions maintains a constant number of atoms $N$, a fixed pressure $P$, and a fixed system temperature $T$. The volume cannot be restrained as pressure is modulated through changing the volume of the simulation system. This ensemble can be used in situations where a constant pressure is important in capturing the correct dynamics in the system. Commonly, the NPT ensemble is used when reaching the equilibrium density for the system before switching to the canonical or microcanonical ensembles for data collection.

- **Isenthalpic (NPH) Ensemble**
  The isenthalpic-isobaric (NPH) ensemble maintains a fixed number of atoms $N$, a fixed pressure $P$, and a fixed system enthalpy $H$. The system enthalpy is given by $H = E + PV$, where $E$ is the energy of the system, $P$ the pressure, and $V$ the volume. With the pressure being held constant, a constant $H$ for the system also maintained, even without thermostatting.

- **Grand Canonical ($\mu$VT) Ensemble**
  The grand canonical ensemble is used in representing all possible states of a system that is maintained in thermodynamic equilibrium (both thermal and chemical) with
Figure 19: The average of property $A$ over microscopic states $C$. The average is not merely taken over the three states as usual, but rather includes probability factors, $\rho$, representing how likely the given state is to occur.

The system is able to exchange energy and atoms with the reservoir, but the volume and system temperature are held constant. There is a fixed chemical potential $\mu$, a fixed volume $V$, and a fixed system temperature $T$. The $\mu VT$ ensemble applies to systems of any size, with the only assumption that the coupled external reservoir is much larger than the system of interest.

### 3.4.2 Calculation of System Properties

The ensemble used defines the thermodynamic constraints placed on the macroscopic system (constant temperature, volume, number of atoms, etc...). The behaviour of each corresponding microscopic system directly relates to the macroscopic conditions specified. To properly calculate macroscopic properties from microscopic information the distribution of microscopic states must be known. Therefore, it is never suitable to take a single measurement from one microscopic state and directly relate it to a macroscopic property for the system. Rather, a property is taken as an average over all possible microscopic states that represent the desired macroscopic condition [22–24]. Averaging, in this case, needs to be carefully approached. The specific distribution of microscopic states must be considered, where some states are inherently more likely to occur than others. Therefore, the averaging must include probability factors for each state, see Fig. 19.

Recall that a microscopic state is fundamentally described by atom positions, $r$, and momenta $p$. This indicates that the system property of interest (take some arbitrary property $A$ as a general example) is a function of $r$ and $p$. An ensemble average, $\langle A \rangle$ of property $A$ is calculated through integrating over all considered microscopic states of the represented macrostate,

$$\langle A \rangle = \int \int A(r,p)\rho(r,p)d\mathbf{r}d\mathbf{p}$$  \hspace{1cm} (3.13)

where $A(r,p)$ is a property of one considered microstate, and $\rho(r,p)$ is the probability weight-
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The probability density function given by,

\[ \rho(r, p) = \frac{1}{Q} \exp \left( \frac{-\mathcal{H}(r, p)}{k_B T} \right) \]  

where \( \mathcal{H} \) is the Hamiltonian, \( T \) the temperature, and \( k_B \) the Boltzmann constant. \( Q \) is known as the partition function and is given by,

\[ Q = \int \int \exp \left( \frac{-\mathcal{H}(r, p)}{k_B T} \right) d^2r d^2p \]  

The integral needed to derive \( Q \) is functionally nearly impossible to calculate as it requires the calculation of all possible microscopic state of the macroscopic system of interest, to calculate \( \rho \).

In terms of MD simulations, each microscopic representation is sampled sequentially with time. Therefore, to calculate the ensemble average corresponding to a given set of thermodynamic constraints, the system must pass through all possible microscopic states. This realisation leads to a cornerstone in statistical mechanics, the Ergodic hypothesis, stating that the time average is precisely equal to the ensemble average for a dynamic system [24],

\[ \langle A \rangle_{\text{Time}} = \langle A \rangle_{\text{Ensemble}} \]  

For MD simulations, this means that, over a suitably long time scale, the set of microscopic states generated (one with each timestep of integration on the equations of motion) inherently generates a properly distributed set of microscopic states. Assuming \( M \) timesteps of simulation time (and therefore \( M \) microscopic states), the time average is given by,

\[ \langle A \rangle_{\text{Time}} = \frac{1}{M} \sum_{i=1}^{M} A_i(r, p) = \langle A \rangle_{\text{Ensemble}} \]  

Theoretically, if the system is allowed to dynamically evolve indefinitely it will eventually pass through every possible microscopic state. Obviously, there are computational constraints that restrict just how long a simulation can reasonably be run. Therefore, it is paramount that an MD simulation is run for a suitable number of timesteps, and generate enough microscopic representations as to properly satisfy the equality. With suitably long simulation times accurate, and experimentally relevant, thermodynamic and structural properties can be extracted from MD simulation output data.
3.5 Thermostats

When running an MD simulation in the NVT ensemble, as an example, a thermostat is applied to the simulation to effectively modulate the temperature of the system. The goal of a thermostat is not to hold all atoms at a constant temperature, but rather to ensure that the average temperature of the entire simulation system is equal to the desired value.

When discussing temperature modulation in MD simulations it is important to note that the instantaneous temperature of the simulation is directly related to the kinetic energy of the system, \( K \), via the momentum of the atoms in the system,

\[
K = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} = \frac{1}{2}N_{df}k_B T \implies T = \frac{1}{N_{df}k_B} \sum_{i=1}^{N} \frac{p_i^2}{m_i} \tag{3.18}
\]

where, \( p_i \) is the linear momentum of atom \( i \), and \( N_{df} \) is the total number of degrees of freedom in the system. If there are \( N \) atoms and \( N_i \) constraints, then \( N_{df} = 3N - N_i \) [24]. A variety of thermostating techniques are available. The following subsections will discuss the Gaussian, the Berendsen, the Nosé-Hoover, and the Langevin thermostating techniques.

3.5.1 Gaussian Thermostat: Velocity Scaling

The simplest method of thermostating a system can be accomplished by scaling atom velocities. Assume that all atom velocities are scaled by a factor \( \lambda \), then the corresponding temperature change between two timesteps, \( \Delta T \), of the simulation system can be calculated through the following relationship,

\[
\Delta T = \frac{1}{2} \sum_{i=1}^{N} \frac{m_i(\lambda v_i)^2}{N_{df}k_B} - \frac{1}{2} \sum_{i=1}^{N} \frac{m_i v_i^2}{N_{df}k_B} \tag{3.19}
\]

If the temperature at time \( t \) is denoted as \( T \), and \( T_0 \) is the desired system temperature, then this can be shown to reduce to the following,

\[
\Delta T = (\lambda^2 - 1)T = T - T_0 \\
\lambda = \sqrt{T_0/T} \tag{3.20}
\]

This demonstrates the fundamental method of scaling atom velocities in a simulation system. Essentially, to maintain the system temperature at \( T_0 \) each atom has its velocity scaled at every timestep by the factor \( \lambda = \sqrt{T_0/T} \), where \( T \) is the current system temperature as calculated from the kinetic energy (Eqn. 3.18) [29].

The Gaussian thermostating method is the most straightforward technique used for
modulating the temperature in molecular simulations. Though it is not without drawbacks, primarily it does not permit any kind of fluctuations in temperature (i.e. energy) which are characteristically present in the canonical ensemble. Effectively, velocity rescaling directly interferes with the natural dynamics of the simulation system, as it is artificially interrupting the equations of motion.

### 3.5.2 Berendsen Thermostat

The Berendsen thermostat [30] attempts to overcome the limitations of the Gaussian thermostat through introducing a weak coupling method to an external bath. Fundamentally, this is a velocity scaling technique with an additional coupling parameter.

To modulate the temperature, the system is coupled with an externally maintained heat bath at temperature $T_0$. At each time step, the velocities are scaled so that the rate of change of the system temperature is directly proportional to the temperature difference

$$\frac{dT}{dt} = \frac{1}{\tau} (T_0 - T) \quad (3.21)$$

where $\tau$ a coupling parameter which describes how tightly or loosely the external bath and the system are coupled. This formulation yields an exponential decay of the system temperature towards the desired temperature. Therefore, the coupling parameter $\tau$ directly determines the time scale over which it takes for the system to reach the specified temperature $T_0$. Manipulating Eqn. (3.21) yields the following relationship,

$$\Delta T = \frac{\delta t}{\tau} (T_0 - T) \quad (3.22)$$

Furthermore, as previously, the velocity scaling factor $\lambda$ can be found,

$$\lambda = \sqrt{1 + \frac{\delta t}{\tau} \left[ \frac{T_0}{T} - 1 \right]} \quad (3.23)$$

In practice, the coupling parameter $\tau$ must be carefully selected. As $\tau \to \infty$ the Berendsen thermostat becomes inactive and the simulation is then effectively being run under microcanonical (NVE) ensemble conditions. As such, the temperature fluctuations in the simulation will continue without any amount of modulation. Conversely, as $\tau \to 0$ will result in unrealistically small temperature fluctuations. Finally, if $\tau$ is set to the same value as the simulation timestep $\delta t$, then the Berendsen thermostat will then merely do basic velocity scaling, as described previously. While the Berendsen thermostatting technique is efficient at bringing a system to target temperature it is still not a pure canonical ensemble, as energy
fluctuations are not permitted.

### 3.5.3 Nosé Thermostat

Both the Gaussian and Berendsen thermostats are unable to fully simulate the conditions present in the canonical ensemble, as neither captures the proper energy fluctuations. The Nosé thermostat [31] was originally developed in 1984 by Nosé and further improved by Hoover in 1985. It is an algorithm for effectively simulating the canonical ensemble during MD simulations. Nosé first devised a technique that involves extending the Lagrangian for the system, where the extended Lagrangian contains additional, fictitious coordinates and velocities. The idea is to introduce an artificial reservoir of mass $Q$, at position $\tilde{s}$, and velocity $\dot{\tilde{s}}$. The artificial variable $\tilde{s}$ behaves as a time scaling parameter, where in the extended system the time scale is stretched by the factor $\tilde{s}$. The introduced variables are related to the real variables as follows,

\[
\tilde{r} = r \quad \tilde{p} = p\tilde{s} \quad d\tilde{t} = \tilde{s}dt \tag{3.24}
\]

With this, Nosé proposes that the extended Lagrangian for the system becomes,

\[
\mathcal{L}_{\text{Nose}} = \sum_{i=1}^{N} \frac{m_i}{2} \tilde{s}^2 \ddot{r}_i^2 - U(\tilde{r}) + \frac{1}{2}Q\dot{s}^2 - 3(N_{df} + 1)k_B T \ln(\tilde{s}) \tag{3.25}
\]

The first two terms of the Lagrangian represent the kinetic minus the potential energy for the real portion of the system. The third term is the kinetic energy of $\tilde{s}$, while the final term represents the potential energy. This final potential energy term is carefully chosen, where the $\ln(\tilde{s})$ term ensures that the algorithm properly simulates a canonical ensemble. This now leads to the modified Nosé Lagrangian equations of motion in the extended system,

\[
\ddot{\tilde{r}}_i = \frac{\tilde{f}_i}{m_i\tilde{s}^2} - \frac{2\dot{\tilde{s}}\dot{\tilde{r}}_i}{\tilde{s}} \tag{3.26}
\]

\[
\dot{\tilde{s}} = \frac{1}{Q\tilde{s}} \left( \sum_{i=1}^{N} m_i \dot{s}^2 \ddot{r}_i^2 - (N_{df} + 1)k_B T \right) \tag{3.27}
\]

Fundamentally, these equations sample a microcanonical (NVE) ensemble in the extended system, but importantly the energy in the real portion of the system does not remain constant. Heat transfer between the fictitious temperature bath occurs with fluctuations of $\tilde{s}$, this regulates the temperature of the simulation system. This thermostat samples a canonical (NVT) ensemble in the real system [24].

The stretched time scale introduced with $\tilde{s}$ is not completely intuitive. However, the Nosé
equations can be reformulated in the terms of the real system variables using the following transformation mapping,

\[
\begin{align*}
  s &= \tilde{s} \\
  \dot{s} &= \tilde{s} \dot{\tilde{s}} \\
  \ddot{s} &= \tilde{s}^2 \ddot{\tilde{s}} + \tilde{s} \dot{\tilde{s}}^2
\end{align*}
\]

and with defining

\[
\dot{\eta} = \frac{\dot{s}}{s}
\]

Nosé arrive at the Lagrangian equations of motion in terms of the real system parameters,

\[
\begin{align*}
  \ddot{r}_i &= f_i \frac{m_i}{N_{df}} - \eta r_i \\
  \dot{\eta} &= -\frac{k_B N_{df}}{Q} T(t) \left(\frac{(N_{df} + 1) T_0}{N_{df} T(t)} - 1\right)
\end{align*}
\]

The Nosé algorithm proves to be time-reversible, deterministic, and smooth, though it is not without drawbacks. The nature of the time scaling introduced with \( \tilde{s} \), being described as a second order equation, may lead to the overall heat flow of the system oscillating about the desired temperature, resembling periodic temperature conditions. The magnitude of the mass \( Q \) directly determines how strong the coupling is between the reservoir and the real system and therefore influences the overall temperature fluctuations. As \( Q \to \infty \) (loose coupling) essentially simulates the system in the microcanonical (NVE) ensemble, though in principle, any positive, finite mass assigned to \( Q \) will ensure the generation of the canonical ensemble (albeit, if \( Q \) is too large the canonical ensemble will only be obtained at long simulation times). Conversely, as \( Q \to 0 \) (tight coupling) the system may devolve into relatively high frequency temperature oscillation about the desired temperature.

The effective relaxation time \( \tau_{\text{Nose}} \) for the simulation system with a specified mass \( Q \) can be derived as follows,

\[
\begin{align*}
  \dot{\eta} &= \frac{1}{\tau_{\text{Nose}}} \left(\frac{3(N_{df} + 1) T_0}{N_{df} T(t)} - 1\right) \\
  \tau_{\text{Nose}} &= \sqrt{\frac{Q}{N_{df} k_B T_0}}
\end{align*}
\]

### 3.5.4 Nosé-Hoover Thermostat

The Nosé-Hoover thermostat [32] was developed by Hoover in 1985, and has become one of the most broadly used thermostatting techniques. Hoover expands on the Nosé thermostat and introduces an additional fictitious variable, \( \xi \), representing friction. The purpose of \( \xi \) is
to slow down or accelerate atoms to maintain the target system temperature. The modified Nosé-Hoover equations of motion are as follows,

\[ \ddot{r}_i = \frac{f_i}{m_i} - \xi \dot{r}_i, \quad \dot{\xi} = \frac{1}{Q} \left( \sum_{i=1}^{N} m_i \dot{r}_i^2 - \frac{1}{2} N_d g k_B T \right) \tag{3.33} \]

The friction coefficient \( \xi \) can be viewed as replacing the momentum term from the fictitious portion of the Nosé thermostat, \( \tilde{p} \). The velocity update of a atom closely resembles the classic Newtonian equations with an additional force (friction) that is directly proportional to the atom velocity. Moreover, \( \xi \) does not influence the system when the instantaneous kinetic energy of the system equals \( \frac{1}{2} N_d g k_B T \). This additionally helps counteract the high frequency temperature oscillations issues seen in the Nosé thermostat.

### 3.5.5 Langevin Thermostat

The Langevin thermostat [33] assumes that all atoms in the simulation are embedded in a fictional continuum of much smaller atoms. These smaller, fictitious atoms impart a damping force \( \gamma \) directly to the momenta, \( p_i \), of the larger, real atoms as they push the smaller atoms out of the way. For each time step \( dt \) the Langevin thermostat alters the equations of motion such that the momentum change becomes,

\[ dp_i = \left( \frac{\partial U(r)}{\partial r_i} - \gamma p_i + \delta p \right) dt \tag{3.34} \]

where, \( \gamma p_i \) represents the damped momenta for the atoms in the system, while \( \delta p \) is a Gaussian distributed random number with probability,

\[ p(\delta p) = \frac{1}{\sqrt{2\pi}\sigma} exp\left(\frac{-|\delta p|^2}{2\sigma^2}\right) \tag{3.35} \]

and standard deviation of \( \sigma^2 = 2\gamma m_i k_B T \). This standard deviation is derived through using a fluctuation-dissipation relationship. This randomly fluctuating force is representative of thermal kicks that the large atoms receive from the small, fictitious continuum atoms. The damping factor effectively stabilises the equations of motion. Together, the damping force and the randomly generated force combine to recover a full canonical ensemble for the simulation [22, 24].

In summary, there are many options for thermostatting an MD simulation. Gaussian velocity scaling is perhaps the most straightforward technique but does not capture a pure canonical ensemble and interrupts the natural progression of the dynamics. The Berendsen
thermostat does not permit energy fluctuations. Nosé-Hoover is one of the most widely applied thermostats but can encounter issues with high-frequency temperature fluctuations about the desired temperature. The Langevin thermostat disturbs the natural dynamics occurring in the simulation. Figure 20 provides a graphical comparison between the thermostating techniques for a system after a step change to a reference temperature.

3.6 Barostats

Often it is desirable to maintain a simulation system at a constant pressure. Thermodynamically, a system maintained at constant pressure inherently undergoes an exchange of volume between the system and its surroundings. This indicates that simulations done under constant pressure conditions experience volume fluctuations. The *Clausius virial theorem* is often used to compute the pressure of an $N$-atom system \[22, 24\],

$$ P = \frac{2}{3V} \left( K + \Xi \right) $$

(3.36)

with volume $V$, kinetic energy $K$, and the *inner virial* $\Xi$. The *virial* involves a summation on all pairwise interactions occurring in the system,

$$ \Xi = \frac{1}{2} \sum_{i<j} r_{ij} \cdot f(r_{ij}) $$

(3.37)
$f(r_{ij})$ is the force between atoms $i$ and $j$ at distance $r_{ij}$. Following the derivation of Eqn. (3.36) is discussed [24]. To begin, assume that the asymptotic average of the derivative of a bounded function equals 0. Noting that for any constant $k$ and function $r(t)$ bounded by $|r(t_2) - r(t_1)| < k$ for all $t_1$ and $t_2$, the average of the derivative of $r$ from $t_1 \to t_2$ is given as,

$$\langle \dot{r} \rangle = \left( \frac{1}{t_2 - t_1} \right) \int_{t_1}^{t_2} \frac{dr}{dt} dt = \frac{r(t_2) - r(t_1)}{t_2 - t_1}$$

(3.38)

Here, the numerator is directly bound ($|r(t_2) - r(t_1)| < k$) whereas the denominator is unbound and can be increased without limitations. We can conclude that as the time interval increases (i.e. $t_2 - t_1 \to \infty$) the average of $dr/dt$ goes to 0,

$$\left| \frac{r(t_2) - r(t_1)}{t_2 - t_1} \right| < \frac{k}{t_2 - t_1} \to 0$$

(3.39)

We are assuming both $dr/dt$ and $r$ are bounded functions of $t$, meaning that their product is also bound by $t$. The product rule yields,

$$\left\langle \frac{d(r \cdot \dot{r})}{dt} \right\rangle = \langle r \cdot \ddot{r} + |\dot{r}|^2 \rangle = \langle r \cdot \ddot{r} \rangle + \langle |\dot{r}|^2 \rangle = 0$$

(3.40)

The net force $f_{\text{net}}$ acting on a atom of mass $m$ and position $r$ equals $m\ddot{r}$. Furthermore $m|\dot{r}|^2$ represents twice the total kinetic energy of the atom. By multiplying $m$ through Eqn. (3.40), and considering a simulation system consisting of $N$ total atoms we obtain the following expression,

$$\left\langle \sum_{i=1}^{N} (r_i \cdot f_{\text{net},i}) \right\rangle + 2K = 0$$

(3.41)

The first term is the virial, which can be deconstructed into terms for both an inner ($\Xi$) and outer ($W$) virial. The outer virial $W$ is derived through assuming all $N$ atoms exert an outward pressure $P$ onto the walls of a box of volume $V$. Therefore, a differential area of the wall exerts an inward force of $PdA$ onto adjacent atoms (Fig. 21). The contribution of $dA$ to the outer portion of the virial can be calculated as,

$$\sum_{i=1}^{N} r_i \cdot f_{P,i} = r \cdot \sum_{i=1}^{N} f_{P,i} = -Pr \cdot ndA$$

(3.42)
Integrating this term over the entire volume, with an application of the divergence theorem (where, \( \text{div} r = \sum \frac{\partial r_i}{\partial x_i} = 3 \) for this case) we arrive at an expression for the outer virial \( W \),

\[
W = -P \int \frac{r \cdot ndA}{\partial V} = -P \int \frac{\text{div}rdV}{V} = -3PV
\]  

(3.43)

Through combining eqns. (3.41) and (3.43) the following expression is found,

\[
\Xi - 3PV + 2K = 0 \implies P = \frac{2}{3V} \left( K + \frac{1}{2} \sum_{i=1}^{N} r_i \cdot f_i \right)
\]  

(3.44)

There is one final transformation that is required to fully derive the expression for calculating pressure in the system (Eqn. 3.36). Recall that the inner virial \( \Xi \) involves a summation on all pairwise interactions occurring in the system, it is therefore more convenient to express in a form that is completely independent of the origin coordinates \( (r_i) \), and fully dependent on pairwise distances between atoms \( (r_{ij}) \). We can express \( f_i \) as a summation of all forces \( f_{ij} \) acting on atom \( i \) due to atom \( j \),

\[
\sum_i r_i \cdot f_i = \sum_i \sum_{j \neq i} r_i \cdot f_{ij}
\]

\[
= \frac{1}{2} \sum_i \sum_{j \neq i} r_i \cdot f_{ij} + r_j \cdot f_{ji}
\]

(3.45)
The second equality is made under the assumption that \(i\) and \(j\) are equivalent indices. With this, Newton’s third law dictates that \(f_{ij} = -f_{ji}\) yielding,

\[
\sum_{i} r_{i} \cdot f_{i} = \frac{1}{2} \sum_{i} \sum_{j \neq i} (r_{i} - r_{j}) \cdot f_{ij} \\
= \frac{1}{2} \sum_{i} \sum_{j \neq i} r_{ij} \cdot f_{ij} \\
= \sum_{i} \sum_{j > i} r_{ij} \cdot f_{ij} \quad (3.46)
\]

Substituting this into Eqn. (3.44) give the final formulation used for the calculation of pressure in a simulation system,

\[
P = \frac{2}{3 V} \left( K + \frac{1}{2} \sum_{i} \sum_{j > i} r_{ij} \cdot f_{ij} \right) \quad (3.47)
\]

It is important to note that, realistically, the pressure \(P\) is not a scalar value but rather takes the form of a second order tensor \(P_{ij}\). As an example, the pressure component \(P_{xy}\) represents the force applied in the \(y\)-direction acting on a surface area with a normal vector in the \(x\)-direction.

\[
P_{ij} = \begin{pmatrix}
P_{xx} & P_{xy} & P_{xz} \\
P_{yx} & P_{yy} & P_{yz} \\
P_{zx} & P_{zy} & P_{zz}
\end{pmatrix}
\]

for the case of hydrostatic pressure, where \(P_{xx} = P_{yy} = P_{zz}\), the pressure of the system can be expressed as a scalar value calculated from the trace of the pressure tensor,

\[
P = \text{Tr}(P_{ij})/3 \quad (3.48)
\]

Fundamentally, modulating the pressure in a molecular dynamics simulation is achieved through manipulating the inner virial \(\Xi\) through scaling the pairwise distances between atoms \((r_{ij})\). Pressure modulation can be achieved through a number of barostatting techniques. The following subsections will discuss the Berendsen, the Andersen, and the Parrinell-Rahman barostats.

### 3.6.1 The Berendsen Barostat

The Berendsen barostat [30] introduces a weak coupled external pressure bath to the system. Like the Berendsen temperature coupling discussed earlier, an extra parameter is included to the equations of motion that effects pressure change in the system. While
the Berendsen thermostat and barostat are closely related, and are even proposed in the same publication, it should be noted they are fully independent and can be used separately. Essentially, the system pressure is modulated towards the desired pressure by changing the size of the simulation cell during a simulation. The scaling factor applied in each dimension is given as,

$$
\mu = \left[1 - \frac{\beta \delta t}{\tau} (P_0 - P(t))\right]^{1/3}
$$

(3.49)

where $P_0$ is the desired pressure for the system, $\tau$ is the coupling time constant, and $\beta$ is the isothermal compressibility for the system, Commonly, taken as the isothermal compressibility of liquid water. The scaling factor $\mu$ is applied to all components of each atoms positions as well as to the simulation cell dimensions. Note, as $\beta$ appears in the scaling factor as a product with $\frac{\delta t}{\tau}$, that if the time step and the time coupling parameter are carefully selected (generally $\tau > 100\delta t$) we do not need to know the explicit isothermal compressibility for the system.

The strength of the coupling between the system and the external pressure bath is dictated through the user specified time coupling constant $\tau$. Much in the same fashion as the Berendsen thermostat, a larger value of $\tau$ indicates weaker coupling, while smaller values indicate stronger coupling. This is illustrated in Fig. 22.

### 3.6.2 Andersen Barostat

The Andersen barostatting technique [35] is an extended system method (like the Nosé-Hoover thermostat) that involves coupling the system to a fictional piston as a means of

Figure 22: The strength of the coupling between the system and the external pressure bath as it varies with the coupling time constant $\tau$ [30]
controlling the overall volume of the simulation cell. Andersen proposes mapping the real system coordinates \( r_i \) and velocities \( \dot{r}_i \) to scaled coordinates \( s_i \) and velocities \( \dot{s}_i \) in the box of volume \( V \),

\[
\begin{align*}
  r_i &= V^{1/3} s_i \\
  \dot{r}_i &= V^{1/3} \dot{s}_i
\end{align*}
\]  

(3.50)

Andersen provides the Lagrangian in terms of the scaled system, were a new variable \( Q \) is introduces. \( Q \) is interpreted as the volume \( V \),

\[
\mathcal{L} = \frac{1}{2} m_i Q^{2/3} \sum_{i=1}^{N} \dot{s}_i^2 - \sum_{i<j=1} U(Q^{1/3}s_{ij}) + \frac{1}{2} M \dot{Q}^2 - PQ
\]  

(3.51)

On investigation of the Lagrangian it is seen that the first two terms are merely the kinetic and potential energies of the real system in terms of the scaled system parameter \( s_{ij} \). The third and fourth terms represent the kinetic and potential energies associated with \( Q \) resulting from an external pressure \( P \) acting on the fictional piston.

With this the Lagrangian equations of motion of the scaled system become,

\[
\ddot{s}_i = \frac{f_i}{m_i V^{1/3}} - \frac{2}{3} \frac{\dot{s}_i \dot{V}}{V} \\
\ddot{V} = \frac{P(t) - P}{Q}
\]  

(3.52)

where the forces \( f_i \) and pressure at the current timestep \( P(t) \) are calculated using the real, unscaled system coordinates and momenta. The Hamiltonian of the system,

\[
\mathcal{H} = K + U + K_V + U_V
\]  

(3.53)

being equal to the enthalpy of the system \( H \) plus an additional term of \( 1/2k_B T \) associated with the volume fluctuations of the fictional piston. This means that the Andersen equations of motion will produce a system trajectory which samples the isobaric-isenthalpic (NPH) ensemble. Though also including a thermostatting technique the canonical (NPT) ensemble can by sampled.

The parameter \( Q \), representing the mass of the external piston, is the controlling parameter in the magnitude of pressure oscillations in the system (compare with the mass \( Q \) in the Nosé-Hoover thermostat). Where, as \( Q \to 0 \) the system will undergo high frequency oscillations in volume of the simulation box. With a large value of \( Q \) the system volume and pressure will slowly adjust, and \( Q \to \infty \) will restore normal dynamics in the system.

### 3.6.3 Parrinello-Rahman Barostat

The Parrinello-Rahman barostat [36–38] is fundamentally an extension on the Andersen barostat to allow the shape of the simulation box to change along with volume. This proves
to be useful for simulations of liquids, but less so in the study of solid mechanics. If the simulation cell is defined as having an arbitrary shape described by three vectors $a$, $b$, and $c$. Each vector can have different length and orientations. With this, the volume is given as,

$$V = \det H = a \cdot (b \times c)$$  \hspace{1cm} (3.54)$$

where $H = a, b, c$ is a $3 \times 3$ matrix. The atom positions $r_i$ can now be written in terms of $H$ and a column vector $s_i$ with components $\xi_i, \eta_i, \text{ and } \zeta_i$,

$$r_i = Hs_i = \xi_i a + \eta_i b + \zeta_i c$$  \hspace{1cm} (3.55)$$

with $0 \leq \xi_i, \eta_i, \zeta_i \leq 1$. note, compare this now with the form of the Andersen scaling given in Eqn. (3.50). The square of the distance between atoms $i$ and $j$ is given as,

$$r_{ij}^2 = s_{ij}^T H^T H s_{ij}$$  \hspace{1cm} (3.56)$$

The modified Lagrangian of the system can now be expressed as,

$$\mathcal{L} = \frac{1}{2} \sum m_i \dot{s}_i^T H^T H \dot{s}_i - \sum \sum U(r_{ij}) + \frac{1}{2} Q \text{Tr}(\dot{H}^T \dot{H}) - PV$$  \hspace{1cm} (3.57)$$

where $T$ denotes the transpose and $Q$ is again the mass of the fictitious cell. The Lagrangian equations of motion given by,

$$\ddot{s}_i = \frac{H^{-1} f_i}{m_i} - G^{-1} G \dot{s}_i \hspace{1cm} \ddot{H} = \frac{(P_{ij}(t) - P)V(H^{-1})^T}{Q}$$  \hspace{1cm} (3.58)$$

where $G = H^T H$ and the pressure tensor $P_{ij}(t)$ was used. This means that anisotropic pressures are permitted in the system and the cell changes shape accordingly.
4 Literature Review

This literature review will first establish a foundation of works completed regarding water absorption and water induced damage in epoxies and fibre reinforced polymer composites. Studies discussing the interface will then be considered in detail. Finally, molecular dynamics methods and their applications to epoxies, composites, and interfaces are reviewed.

4.1 Mechanisms of water Absorption in Polymeric Composites

It is widely accepted that fibre reinforced polymer (FRP) composite laminates absorb water when subjected to humid environments; this phenomenon has been well documented, most notably by Springer and Shen [39]. The polymer matrix compound constitutes the preferred water penetration path for water molecules, especially when the fibre reinforcements are impermeable. Glass fibres, for example, are impermeable while carbon fibres do absorb a certain amount of water, though a negligible amount in comparison to that of a polymer matrix. This introduces several issues related to the design of composite structures intended to operate in humid conditions, primarily relating to water diffusion into the composite and how water ultimately influences mechanical properties.

Overall, water transport in FRP composites can be complicated to fully define as it involves several mechanisms working in parallel. Hopfenberg and Frish [40] detailed several transport mechanisms of molecules moving through amorphous polymer structures. More specifically, Fig. 23 provides a summary of the primary water transport mechanisms in FRP composite systems. Individually, these mechanisms will be discussed in greater detail throughout the literature review section. Summarising, water may be,

(i) diffused into the polymer microstructure as either isolated molecules or as clusters
(ii) diffused into a swollen region of the polymer microstructure
(iii) absorbed directly into nanovoids (free-volume) within the polymer. Both pre-existing and newly formed voids caused by moisture ingress.
(iv) absorbed into micro-damage, both pre-existing and those caused by moisture ingress (e.g. fibre-matrix delamination, micro-cracks, etc...)
(v) absorbed into preferential locations in the microstructure (e.g. areas with reduced crosslink density, or areas with a greater number of active polar-interaction sites on the polymer chains)
4.1.1 Concentration Dependent Fickian Diffusion

Moisture transport in polymers is related to molecular sized nanovoids within the structure of the polymer matrix. Driven by concentration gradients, moisture diffuses directly into these free volume voids throughout the polymer microstructure. It has been reported that the material void diameter must be larger than 3 Å to facilitate diffusion of a water molecule [42, 43]. As diffusion progresses, the moisture concentration gradient decreases, slowing uptake; at equilibrium, the net gradient becomes zero, stopping the diffusion process.

Soles et al. employed a relatively new spectroscopic technique known as Positron Annihilation Lifetime Spectroscopy (PALS); PALS is capable of measuring both the size and number of nanovoids within the polymer [44, 45]. It was reported that the dependence of moisture diffusion on topology was greatest at low temperatures (5 °C) and that this dependence dissipates with increasing temperature. Additionally, it was stated that polarity was of primary importance to the diffusion process; wherein highly polar resins absorbed significantly more water than less polar resins. For this reason, their results indicated that nanovoid size holds no correlation with the kinetics of moisture transport, it was only when comparing resins of similar polarity that the topology was found to have a notable effect. It was proposed that nanovoid structure, the polarity, and molecular motions of the epoxy network combine to control moisture transport.

Musto et al. studied the interactions between absorbed water and a tetra-functional epoxy network using both mid- and near-infrared Fourier transform spectroscopy; their results
affirmed the existence of both free and bound water molecules within the polymer [46, 47]. A relatively low activation energy was required to facilitate individual water molecule diffusion through a polymer network, where no bonding interactions occur between the polymer and water molecules. In this case, the water molecules were free (non-bound) throughout and the molecular movement was not impeded and was completely driven by concentration gradients. They suggest that as the ageing process matures the water molecules begin to chemically bond to the polymer network, causing nanovoids to become blocked which decays the rate of moisture absorption into the system. Bonding interaction sites effectively bottlenecked water transport in that the rate of formation and breakage of internal hydrogen bonds dictated the rate at which water penetrated the epoxy network.

A study by Zhou et al. assessed the nature of absorbed water in epoxy resins, where Nuclear Magnetic Resonance (NMR) was conducted to determine the mobility of the absorbed water [48]. It was confirmed that water molecules bond with epoxy resins at specific hydrogen bonding sites throughout the structure. Two types of bonding types were reported, Type I and Type II, depending on differences in bond and activation energies, Figure 24. Type I bonding corresponded to a water molecule which formed a single hydrogen bond with the epoxy network. Type II bonding occurred as a result of a single water molecule forming multiple hydrogen bonds with the epoxy resin network. Type I bonds possessed lower activation energy and was easier to remove from the epoxy network. The activation energies for Type I and Type II bound water were found to be 9.5 and 15.1 kcal mol\(^{-1}\), respectively. They conclude that Type I bound water was the dominant form of absorbed water held within an epoxy network. It was stated that Type II bond formation depended heavily on exposure time and temperature, where higher temperature and longer exposure times tended to result in a greater number of Type II bonds being formed.

4.1.2 Non-Fickian Diffusion

Non-Fickian diffusion generally occurs when the stress relaxation of the polymer influences the moisture uptake behaviour. Such responses are conventionally divided into two groups; one known as Class II (Class I being Fickian diffusion) and the other being anomalous. Class II occurs when the relaxation rate, rather than the diffusion rate, controls the moisture uptake of the system. In Class II cases, the moisture uptake rate commonly increases linearly with time and occurs at temperature below glass transition temperatures of the material. Anomalous uptake occurs when moisture diffusion and stress relaxation have comparable rates[49, 50]. When discussing anomalous diffusion, a common moisture uptake profile is dual stage uptake [51–53], exhibiting an initial Fickian diffusion profile followed by a significant reduction in rate of moisture uptake, and finally reaching an equilibrium.
4.1.3 Solvent Crazing and Stress Cracking

Solvent crazing and stress cracking refer to water induced cracking and damage in polymeric composite structures. This occur as a direct result of Class II and anomalous moisture transport in glassy polymer structures below the glass transition of the material [40, 41]. Therefore, water induced damage, and the subsequent degradations, primarily occur upon departure from Fickian diffusion.

In composite materials, residual stresses are commonly introduced during the fabrication process. These residual stresses can be a consequence of mismatched expansion coefficients between fibre and matrix or purely interlaminar in nature. Micro-cracks commonly develop at concentrated areas of residual stress. Moisture penetrates these micro-cracks, leading to an increase in both size and severity of the crack, this is known as solvent crazing-stress cracking [41]. The cracked interface between fibre and matrix sees higher concentrations of moisture than the bulk. This occurs as a result of capillary action [54–56]. Consequently, this new damage only lead to further moisture absorption at the interface, eventually leading to interface debonding [57].

Figure 24: Possible types of bonding between absorbed water molecules and an epoxy network: (a) Type I: water molecules form only a single hydrogen bond with the epoxy structure, lower activation energy, (b) Type II: water molecules form more than one hydrogen bond with the epoxy, higher activation energy. [48]
4.2 Factors Affecting Moisture Absorption in Polymeric Composites

4.2.1 Polymer System

The nature of the polymer system is the primary factor controlling moisture transport in FRP composites. The free volume and the chain mobility of the polymer are the predominant characteristics that have a direct, and substantial effect on moisture diffusion. While, crosslink density, water content, degree of crystallinity, and reinforcement type influence moisture transport indirectly, and to a lesser extent [58]. Glassy polymers, such as epoxies, when compared to rubbery polymers are relatively hard and brittle with comparatively low chain segment mobility. Moreover, glassy polymers generally have higher densities, with lower total void space (free volume), leading to more complex diffusion behaviours. George and Thomas [58] provided discussions relating to $T_g$ and how it directly correlated to the free volume of the system. More specifically, they described that an increase in total free volume led to a decrease in the $T_g$, and that a lower $T_g$ (a higher chain segment mobility) led to greater diffusivity of water for the system.

The crosslink density of an epoxy resin system directly affects the $T_g$. Wherein, the higher the degree of crosslinks formed, the higher the $T_g$. This relationship is demonstrated in several studies [59, 60]. Therefore, an increase in system crosslink density leads directly leads to a decrease in diffusivity of water.

4.2.2 Temperature and Pressure

In general, increasing ambient temperature leads to significant increases in diffusivity of water, and slightly increases maximum solubility. Broutman and Gillat studied unidirectional graphite composite systems in water at 25 and 80 °C [61]. Their results showed an increase in both diffusivity and solubility limit at higher temperatures. They noted Fickian uptake behaviour for the samples aged at 25 °C, but interestingly non-Fickian behaviour was observed for the samples at 80 °C. Mijovic et al. showed that elevated temperature led to an increase in polymer chain relaxation, decreasing the system $T_g$ [62]. Continuing, they explained that this led to increased space between the polymer molecules themselves, enhancing moisture uptake.

Dewimille and Bunsell investigated the concept of accelerating the ageing effects of water on a unidirectional GFRP composite by immersing the composite in water at elevated temperatures [63]. Their results showed that as the water temperature increased, both the amount and rate of water uptake, as well as the magnitude of damage produced, greatly increased. They implied that other damage mechanisms were more than likely induced as a consequence of the high environmental temperature.
Tsotsis et al [64] reported on the accelerated ageing of polymeric composites at elevated pressure and temperature. Their results suggested that elevated ambient pressure can be used to significantly reduce overall screening times for materials that will operate in humid environments by increasing the system diffusivity. Pilli et al [65] studied the effects of partial vapour pressure on moisture diffusivity and solubility limit, their results suggested that increasing partial vapour pressure increases diffusivity and solubility limit of polymeric systems.

### 4.2.3 External Loading

Moisture absorption in polymeric fibre composite systems can be dependent on the applied stress. Neumann and Marom investigated the changes in rate of diffusion, solubility limit, and Fickian diffusion coefficient with applied stress levels and proposed a model to predict these changes [66, 67]. Their model was based on calculating stress dependent free volume changes in the polymer structure through laminate plate theory. Their model found good agreement with experimentally determined values for a CFRP composite with varying fibre contents, orientations, and stress levels. Their findings indicated that moisture absorption properties remain relatively unchanged when loaded in the fibre direction, $0^\circ$. In this situation, most of the loading was carried in the fibre, rather than the matrix, which led to negligible free volume changes. Conversely, substantial changes in moisture absorption properties were observed as the loading angle tends towards transverse fibre direction, $90^\circ$. In this case, the matrix material was carrying the most of the loading, which led to substantial free volume changes.

Yousseff et al. proposed a multi-scale model that accounted for internal stresses in the matrix [68]. They considered evolution of moisture diffusivity as a function of internal stress states (induced between composite plies as a consequence of moisture ingress). While not experimentally verified, they found reasonable agreement with reported values for similar material systems.

### 4.3 Environmental Effects on Properties of Epoxies

Epoxy resin systems are known to be exceptionally sensitive to environmental conditions. The effects of absorbed water in crosslinked epoxy resins has received a lot of attention [57, 69–81]. Commonly, studies have concluded that the presence of absorbed moisture directly leads to degradations of both thermal and mechanical properties of an epoxy system. For typical epoxy systems, the presence of absorbed moisture has been reported to lead to a decrease in static strength in the range of 10-20% [57, 73–75].
Zhou et al. investigated variations in glass transition temperature as a consequence of hygrothermal ageing for three epoxy systems (DGEBA/mPDA, TGDDM-DDS, and Fiberite 934) [72]. The epoxies were all immersed in distilled water at temperatures of 45 °C, 60 °C, 75 °C, and 90 °C until full saturation was achieved. Thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) were carried out to determine changes in $T_g$. They conclude that,

(i) $T_g$ changes were not solely dependent on the amount of water absorbed

(ii) magnitude of $T_g$ change heavily depended on the hygrothermal history

(iii) for a given epoxy system, higher values of $T_g$ were found for longer total immersion time and higher immersion temperatures

Individually, both Type I and Type II bound water influenced total variations in $T_g$, albeit in different ways. Type I bound water disrupted original Van der Waal forces and hydrogen bonds in place within the polymer chain, this resulted in increased chain mobility and therefore a reduction in $T_g$. Conversely, Type II bound water was postulated to increase the system $T_g$ as a consequence of the secondary crosslink bond formation (recall Fig. 24). Therefore, it was suggested that an epoxy system will experience a drop in $T_g$ as a result of the initial formation of Type I bonds, followed by a relative increase in system $T_g$ after long immersion times due to the slower development of Type II bonds.

Luo et al. investigated water mobility in epoxy materials and its influence on the rate of interfacial adhesion loss [81]. They showed that the presence of absorbed water reduced the glass transition temperature of polymeric materials. Additionally, their results showed that water molecules held in an epoxy system above its $T_g$ had much higher diffusivity than in a polymer in its glassy state, noting that the relative mobility of water absorbed by a polymer in its rubbery state was similar to that of pure water, which indicated that most of the water molecules were not bound to the polymer structure.

In a study conducted by Papanicolaou et al. the mechanical and viscoelastic behaviour of a DGEBA/DETA epoxy resin system was investigated as a function of absorbed water, immersion temperature, and immersion time [57]. Specifically, $T_g$, tan $\delta$, bending modulus, and strength were reported as functions of exposure time, and weight percent (wt.%) water for immersion temperatures of 60 and 80 °C. An increase in $T_g$ accompanied by a respective decrease in tan $\delta$ with immersion time were observed, these results aligned well with Zhou et al. [72]. Variations in storage modulus, $E'$, were negligible, while static mechanical properties of the epoxy were seen to decrease with immersion time and water content. Static strength decreased by nearly 10% for an immersion temperature of 60 °C compared to 20 °C, while a decrease of just over 20% was reported for 80 °C, this further confirmed that higher temperatures lead to further degradation in epoxy systems.
Moisture [73, 82, 83] and thermal [50, 73, 84, 85] induced swelling characteristics of crosslinked epoxy networks have seen experimental investigations. Xiao et al. showed that as water molecules were absorbed into the epoxy the microstructure tended to swell and expand in the direction of diffusion. Swelling inherently led to a more porous polymer network, this allowed for further water uptake, which led to further reductions in $T_g$. They concluded that swelling is generally reversible, though significant swelling can induce irreversible damage in the form of microcracking and crazing [73].

4.4 Environmental Effects on Properties of FRP Composites

Irreversible degradation of composite laminate occurs as a direct consequence of the absorption of the moisture by the epoxy matrix [81, 86–97]. Browning et al. [86] reported that moisture and temperature tend to have diminished effects on longitudinal (fibre dominated) properties. Bradley and Grant studied the effects of moisture absorption on the interfacial strength of seven different fibre reinforced polymer composite systems (five carbon fibre, two glass fibre) [87]. Their results showed a correlation between the decrease in interfacial shear strength and moisture absorption, along with a decrease in transverse tensile strength. These changes supported the hypothesis that moisture induced degradation occurred as a consequence of interfacial strength (adhesion) loss rather than a degradation of the material properties in the matrix itself. Similar findings were presented in other works [81, 88–90], where degradation was attributed to a combination of a loss in adhesion strength along the interface (due to matrix plasticization) and residual stresses introduced through swelling.

Ogi et al. reported on the effects hygrothermal conditions on damage development in quasi-isotropic CFRP composites [91]. Their results indicated that the presence of absorbed moisture increased the critical stresses for transverse cracking and delamination as a result of the water reducing cross-ply residual stresses. High temperature was shown to decrease the critical stresses.

4.4.1 Static Loading

The severity of degradation in composite laminates is generally worsened by sustained external loading conditions. Commonly, leading to a departure from Fickian uptake behaviour and increased diffusivity or water, and is accompanied by significant interfacial property degradation [61, 98–103]. Figure 25 provides experimental results for an epoxy-glass composite laminate ($[0]_2$ lay-up) that was aged over a range of temperatures as well as under sustained tensile loading conditions of $\sigma = 0.2\sigma_{UTS}$. The severity of degradation increased directly with surrounding environmental temperature.
Gillat and Broutman indicated that the external stress accelerated the degradation of the interface and matrix dominated properties of the composite [61]. Meanwhile, the flexural strength, which is a fibre dominated property, was not significantly affected. Buck et al. concluded that the combined effect of load, temperature, and moisture greatly reduced the ultimate tensile strength of composite materials, even for relatively short conditioning periods [98]. Additionally, it was shown that the severity of degradation was more pronounced at higher temperatures. They also reported a significant decrease in strain to failure for specimens which were loaded during conditioning.

Autran et al. investigated the influence of conditioning under both sustained flexural and sustained tensile loading on the mechanical properties of polyester composites [100]. Their findings indicated that for applied stresses less than 10% of the dry strength, the influence on ageing is negligible, but for larger stresses the property loss of the system becomes accelerated, and in many cases premature failure occurred.

Abdel-Magid et al. examined the properties of an GFRP composites under sustained loading and moisture conditioning, their results showed that the modulus, strength, and strain at failure of the composite are substantially affected [99]. Samples were conditioned both unstressed and stressed at \( \sigma = 0.2\sigma_{UTS} \) at room temperature, and at 65 °C, and were tested after conditioning times of 500, 1000, and 3000h. At shorter conditioning durations (500 h) at room temperature, slight increases in strength and slight decrease in modulus were seen; while for longer conditioning durations (3000 h) significant reductions in strength and
strain at failure were observed. Specimens that were conditioned under sustained loading exhibited higher modulus loss in all cases. Stoffels and Miller [101, 102] observed failure of unidirectional FRP composite samples which were both immersed and subjected to sustained tensile loading conditions. The samples failed unexpectedly while loaded only to 50% of their ultimate tensile strength.

4.5 The Interface

Commonly, a composite laminate fails at the fibre-matrix interface due to de-bonding of the matrix from the fibres: it follows that an understanding of all mechanisms occurring at the fibre matrix interface is critical. The important effect of the interface on the properties of glass FRP composites has led into efforts to understand, control, and even to modify the interfacial area. The direct examination of the fibre-matrix interface in fibre-reinforced polymer matrix composites is inherently complicated due to structures that range from the microscopic scale down to the molecular scale. The specific adhesion mechanisms and associated chemical interactions that occur at the fibre-matrix interface are not fully understood due to the difficulty in experimentally probing the structure without introducing experimental artefacts.

4.5.1 Fibre Sizing

Fibre sizing is used to improve the adhesion between the epoxy and fibre reinforcement material of a composite system. The sizing serves the primary function of establishing covalent bonds across the interface, which can drastically improve the properties of the composite [13, 104–106]. There are several techniques that have been used to investigate the effects of surface treatments on the interfacial properties of FRP composites, such as single-fibre fragmentation [105, 107, 108] and pull-out tests [108, 109].

Coupling agents have been shown to comprise 10-20% of sizing solutions, where the primary component is a film forming compound, representing up to 90% [12, 110–112]. For glass fibre, silanes are a common choice for a coupling agent as they contain silicon and organic function groups capable of bonding to both the glass fibre and to the epoxy matrix [110]. The film former is generally added to provide ease of handling and better overall processing characteristics. Common film forming compounds include; polyesters, polyalkenes, polyurethanes, and epoxies [12, 111, 112].

J.L. Thomason and L.J. Adzima undertook an extensive investigation on several commercially available epoxy-Compatible E-Glass fibre rovings [12, 111]. Extraction of sizing combined with burning of the fibres was conducted to obtain the amount of physisorbed, loosely
bound, and strongly bound sizing material. Extraction removed physisorbed organosilanes, while fibre burnoff entirely removed organic functional groups which left only the portion of the sizing chemically bound to the fibre surface via covalent Si-O bonding.

Their results indicated that the amount of sizing varied between manufactures between 0.2 to 1.0 wt.%. It was shown that approximately 80-90% of the sizing could be extracted in boiling acetone, and the remaining 10-20% was assumed to be strongly bound silane component. Their results found reasonable agreement with those later presented by Petersen et al. [112]. FTIR analysis suggested that the main components in the coating extract were epoxy resin and polyethylene oxide (PEO) in approximately a 70:30 mixing ratio. The interlaminar shear strength (ILSS) for the composite correlated to the amount of non-extractable (strongly bound) sizing on the fibre surface, see Fig. 26.

Iglesias et al. investigated the effects of various aminosilane glass surface treatments on the mechanical properties of epoxy based composite materials under both dry and wet conditions [113]. Three silane treatments were considered: γ-Aminopropyltriethoxysilane (AMPTES), γ-Aminopropyltrimethoxysilane (AMPDES), and γ-Aminopropylmethyldiethoxysilane (AMPMES). Their study correlated data taken from SEM fractographic analysis with mechanical data obtained from tensile testing. They concluded that,

(i) Crosslink density and interface rigidity increased with a high number of accessible functional silane groups

(ii) Interpenetrating network adhesion was the controlling adhesion mechanism, and
therefore controlled interface strength

(iii) Hygrothermal damage rate was dependent on the surface treatment, where the damage rate increased with the number of $\text{Si}_{\text{silane}}$-$\text{O}$-$\text{Si}_{\text{silane}}$ siloxane bonds.

### 4.5.2 Infrared Spectroscopy

Studies have made use of IR spectroscopy methods to better understand the interactions occurring at the interface [54–56, 114–116]. Arvanitopoulos et al. [114, 115] used FTIR mapping techniques to investigate the behaviour of fibre-matrix interfacial area in composites subjected to wet environments. They indicated that the interface experienced increased moisture uptake in comparison to the bulk material, and that silane treated fibres mitigated this effect. McKnight and Gillespie [55] studied the moisture absorption process in a polypropylene-silane interface using in-situ FTIR methods. Their results showed changes in spectra over the course of the diffusion experiments, they concluded that these changes were indicative of chemical reactions between the water and polymer system. Noobut and Koenig investigated the glass fibre-epoxy interface using FTIR microspectroscopy techniques [116]. Their results suggested that an interface treated with a silane coupling agent tended to take up less water than an unsized fibre.

Gonzalez-Benito used FTIR imaging to investigate the structural gradient at the interface formed with a silane coated glass fibres [54, 56]. Images for OH and H-N-H within the system were obtained. Their results indicated that there is a variation in the chemical structure of the matrix moving from the fibre to the bulk polymer. Additionally, they reported that the degree at which the resin is cured varied from the fibre interface region to the bulk matrix. Sharma et al. [117], through using FTIR imaging, focused on hygrothermal ageing and its effects on the glass-epoxy interface. Single fibre micro-composites were manufactured by embedding silane coated glass fibres in a bisphenol-A based epoxy system. Their results, much like Gonzalez-Benito [54], suggested a curing gradient moving from the fibre into the bulk polymer. After hygrothermally conditioning their FTIR results showed a distinct increase in absorbance peaks of OH stretching. They speculated that this may be due to moisture absorption into micro-voids formed during curing and differential expansion between matrix and fibre.

### 4.5.3 Fluorescence Spectroscopy

Olmos et al. presented a novel method to study the kinetic curing process of epoxy in glass fibre-epoxy interfaces using Fluorescence and Fourier Transform Infrared Spectroscopy [118, 119]. The effect of two glass fibre surface treatments were initially investigated: com-
commercial E-glass fibres surface coated with $\gamma$-Aminopropyltriethoxysilane (APTES) and $\gamma$-Aminopropyltrimethylethoxysilane (APDES). Their results showed no variation in the activation energy of the epoxy curing reaction, this indicated that there was no change in the curing mechanisms through the process. Fluorescence clearly indicated that the type of surface treatment used affected the curing process. They concluded that APDES had a much more open structure and is therefore it was easier for the epoxy to penetrate the coupling region, which increased the amine concentration. Summarising, the surface treatment used on the glass fibre seemed to alter mostly the rate at which the curing occurred, but the overall curing reaction did not change.

Olmos et al. followed up their previous work and investigated the effects of the glass fibre surface on the moisture absorption process [56]. Three silane treatments were considered: $\gamma$-Aminopropyltriethoxysilane (AMPTES), $\gamma$-Aminopropyltrimethylethoxysilane (AMPDES), and $\gamma$-Aminopropylmethyldiethoxysilane (AMPDES). Their findings indicated that the presence of sized glass fibres induced changes in the moisture absorption process, wherein the total moisture uptake decreased. Additionally, the fibre itself interacted with structure of the epoxy matrix, this interaction resulted in slower water uptake at the interface in comparison to the bulk matrix. These findings directly contradict what was presented by Arvanitopoulos and Kotsikos [114, 115, 120], where capillary action was said to increase the moisture uptake rate along the interface.

4.5.4 Raman Spectroscopy

While many of the previously discussed IR methods have distinguished interface areas, at the smallest their sampling spot sizes were 8 $\mu$m $\times$ 8 $\mu$m. More recently, Raman Spectroscopy has been used in micro-mechanical studies of composite interfaces, one of the major advantages that Raman Spectroscopy carries over other IR spectroscopy methods is that the sampling spot size can be much finer, approaching 1 $\mu$m in spot size and therefore more localised readings can be taken.

Chaudhuri et al. used Raman Spectroscopy to quantify the degree of chemical bonding across the interface in carbon-epoxy composites [121]. Cervenka et al. further employed Raman spectroscopy as a means of investigating hygrothermal ageing of epoxy composites [122]. Through normalising Raman strain profiles along the fibre length an interface fracture energy term is purposed. Kawagoe et al. employ both Raman and FTIR microspectroscopic investigations to monitor interfacial degradation processes of an aramid fibre-polyester composite exposed to water [123]. Their results showed isolated and clustered water exists at the interface, and that clustered water tended to remain in the system even after drying processes were carried out.
Zafar et al. investigated the long term effects of moisture on the carbon-epoxy interface [90]. DSC was used to analyse the moisture effects on the glass transition of the epoxy system being used, results showed a reduction in $T_g$. Raman Spectroscopy was used to investigate the effects at the interface, specifically the stress transfer at the interface as a function of exposure time. Their results indicated that water absorption drastically decreased mechanical and interfacial properties of the composite.

4.6 Molecular Dynamics

Despite the great number of experimental studies, there still exists a distinct gap in knowledge pertaining to the specific molecular interactions occurring between epoxy and water. Recent advancements in molecular level simulations, such as molecular dynamics simulations, have provided an alternative approach to investigating molecular level interactions in polymeric structures.

4.6.1 Epoxy Systems

Simulating polymeric systems, as compared to crystalline solids, inherently carries several challenges as polymers are random in orientation, and in the case of a crosslinked polymer network, randomly connect to one another. Accurately capturing the random nature of a crosslinked polymer structure within an MD simulation has historically proved to be tedious and computationally intensive process. More recently, fully modelled atomistic representations of crosslinked polymer networks have been proposed and validated [59, 124–128].

Yarovsky and Evans discussed a static crosslinking method, where MD is used in undertaking the crosslinking reaction and bond formation [124]. Xu et al. presented an iterative molecular dynamics/molecular minimization technique for crosslinking an epoxy network [125, 126]. Alternatively, Varshney et al. presented a dynamic crosslinking method that is found to be more efficient in building larger polymer networks [127]. Bandyopadhyay et al. explored the effects of crosslink density on various thermomechanical properties of an epoxy system [59]. Their results indicated that glass transition temperature and the elastic stiffness increased with increasing levels of crosslink density, and that the thermal expansion coefficient decreased with crosslink density. Shenogina et al. employed a dynamic deformation technique to predict the elastic properties of a DGEBA/DETDA epoxy system [128]. A novel algorithm is proposed to calculate the Poisson’s ratio for the system. When compared to traditional methods, this algorithm was found to significantly reduce statistical errors.

Traditionally, MD simulations have been carried out in purely organic environments, and therefore there have been few efforts made regarding the use of MD techniques in simulating
organic-inorganic interfaces. The interaction between dissimilar entities is formed through the definition of a force field. This concept is analogous to that of constitutive modelling used throughout Finite Element Modelling to form the basis of material behaviours. The corresponding parameters used in the mathematical formulations of the force field models for each different atom are experimentally obtained through Nuclear Magnetic Resonance (NMR) or quantum mechanics calculations. Some commonly used force fields are COMPASS [129], Amber [130, 131], DREIDING [132], CHARMM [25, 133], consistent force field (CFF91) [134–136], and consistent valence force field (CVFF) [137, 138]. Each of these force field models were optimised for simulating proteins and polymer systems.

Several studies have utilized Molecular Dynamics simulations to investigate the effects of moisture on cross-linked polymer systems [125, 139–143]. Wu and Xu investigated the influence of water on the structure and properties of cross-linked polymer systems; in particular, the density, diffusion coefficient of water, fractional free volume, and polymer chain mobility were investigated [125, 139]. Their simulation results indicated that the density of the polymer increases with the addition of water molecules, while the overall mobility of the network chains increases with higher water concentrations. Whereas, at lower water concentrations, inverse trends are clearly seen. Their analysis further indicates that these changes could be attributed to interactions between hydrogen bonding and the free volume of the polymer.

Xin and Han carried out MD simulations to study water diffusion coefficients in crosslinked DGEBA/MDA epoxy networks; their study accounted for the influence of temperature, water concentration, and cross-linked polymer conversion [140]. Epoxy networks consisting of 8 DGEBA molecules and 4 MDA molecules were generated and crosslinked to 50, 62.5, 75, and 87.5% crosslink density. Structures saturated to 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 wt.% water were considered. It was shown that diffusivity clearly increased with temperature and concentration, whereas the diffusivity decreases with an increase in polymer crosslink conversion.

Lin and Chen investigated the moisture diffusion characteristics in a DGEBA/DDA epoxy system [141]. Their experimental results indicated that the desorption from full saturation left a small residual water content, which could only be removed by heating the system to relatively high temperatures. MD simulations were used as a means of verifying the experimental work. Through investigating activations energies they report that water tends to exist in two distinct states within the polymer structure; Type I: easily removed at low exposure temperature (lower activation energy) and Type II: can nearly be removed at high temperature (much higher activation energy). This is in agreement with other studies, [72, 81].

Fan et al. [142] studied moisture diffusion in an epoxy-Cu interface, with implications
in electronic packaging. The COMPASS force field [129] was implemented in generating a DGEBA/MDA epoxy network within a $19.7 \times 19.7 \times 19.7 \text{ Å}^3$ simulation box. Simulations were carried out at 85°C. Their results indicated that diffusion is more prevalent along interfacial area when compared to the bulk epoxy.

Mijovic and Zhang conducted MD simulations of water in a DGEBA/DETA network, specifically they investigated different types of hydrogen bonding occurring with polar groups throughout the system [143]. The COMPASS force field was used in generating an epoxy network consisting of 25 DGEBA molecules and 10 DETA molecules. The epoxy network was saturated in steps of 0.5 wt.% ranging from 0-8 wt.%. After water is inserted, the system was allowed to relax and dynamically evolve for 100 ps. They identified three types of hydrogen bonds, where each involves hydrogen of the network hydroxyl group (HO) and one of three acceptors: oxygen of the network ether group, oxygen of the network hydroxyl group, or nitrogen of the network amine. Their results show the majority of water molecules were located near the polar groups of the polymer network.

### 4.6.2 Solubility of Water in Polymeric Systems

For a polymer structure, there is an equilibrium mass of moisture content at which point the system absorbs no further moisture from its surroundings, referred to as the solubility limit of the system. Limiting water uptake in polymers is the key to mitigating many of the damaging effects. MD simulation offers the tool to probe the underlying physics of water solubility in a polymer and hence limit its total water solubility. Most commonly, the solubility limit of water is experimentally determined by soaking the test sample and monitoring weight gain throughout the saturation process. This becomes a tedious process, especially given the large time frames typically needed to conduct these kinds of experiments. With ever increasing computational capabilities the applications for MD simulations in polymer science applications is apparent. Surprisingly, there have not been many studies undertaken to characterize the equilibrium moisture content for a crosslinked epoxy systems using molecular dynamics (MD) simulations.

Equilibrium is determined through investigations of the chemical potential of moisture held within the polymer and the chemical potential of surrounding water. Widom’s test particle insertion has been used in the determination of excess chemical potentials, but becomes problematic and inefficient in highly dense systems [144, 145]. An accelerated Widom particle insertion method has been developed to calculate excess chemical potential of water held within polymer structures [146–150]. Knopp et al. provide a combination thermodynamic integration and test particle insertion method for uses in estimating the excess chemical potential of solutes held in dense polymer systems [146, 147]. They introduce what they refer
to as *noble water*, in which the size (radius) and relative force field interactions are scaled as a means of optimising the particle insertion process and the difficulties that arise due to the dense surrounding microstructure. They calculated the chemical potential of a water model without charges and scaled down size, that is, noble water, by Widom's test particle method and then used thermodynamic coupling parameter integration of the coupling parameters to estimate the chemical potential of the full water model. Using their method, they are able to estimate the equilibrium moisture content of water held in an amorphous PA-6 polymer network.

Domotor et al. proposed a grid search algorithm that identified test particle insertion points that would yield negligible contributions to the excess chemical potential [148, 149]. Fundamentally, this method exploits the fact that there are only a few suitable insertion locations in each configuration. Therefore, they aimed to identify where these are approximately located as to reduce overall computational time. Their results are impressive, wherein they demonstrate the method can increase computational efficiency by as much as a factor of 100 for pure, liquid water.

Hostermann et al. expanded this algorithm for uses with PA-6 and diglycidyl ether bisphenol A (DGEBA)-isophorone diamine (IPD) [150]. Ten separate epoxy networks consisting of 23 DGEBA and 11 IPD molecules (containing 1501 total atoms) were generated at 300 K. Non-bonded interactions were modelled via a 9-6 potential for Van der Waals and Coulomb interactions. While a global non-bonded interaction cutoff of 12 Å was used for both. For the DGEBA/IPD system they tested two different force field implementations, GROMOS [151] and ENCAD [152]. They found the ENCAD force field generally provided more accurate results in predicting volume swelling and equilibrium water content.

The Gibbs ensemble provides another method of equilibrium absorption prediction. This method involves two separate simulation boxes, one containing the polymer with the absorbed solvent and the other the solvent only. De Pablo et al. combined the Gibbs ensemble method and a modified test particle grid search as a means of estimating alkane solubility in polymers. They were able to predict the sorption of pentane in polyethylene with reasonable accuracy [153]. While, Kenkare et al. investigated the solubility limit and swelling of a polymer by implementing a *hard sphere* solvent through using a combined MD and Monte Carlo (MC) simulation study [154].

### 4.6.3 Amorphous SiO$_2$

Fundamentally, the process for making an amorphous SiO$_2$ system follows a melt-quench procedure; where, initially the system is melted, then is systematically quenched to lower and lower temperatures until your desired temperature is reached. A modified Born-Mayer-
Huggins (BMH) potential has commonly been used to simulate oxide glass structures using MD techniques [155–163]. Woodcock et al. first presented MD calculation methods for obtaining the structure of amorphous silicate glasses. Their calculated radial distribution functions exhibited good agreement with existing x-ray diffraction data [155]. S.H. Garofalini [157] then expanded on these methods to simulate the surface, rather than bulk, structure of vitreous silica.

Garofalini’s MD procedures were as follows, initially, bulk amorphous SiO$_2$ containing 288 atoms was placed in a simulation box with periodic boundary conditions in all directions. The system was then melted and equilibrated to 9000 K under NPT conditions (constant Pressure and Temperature). Still using an NPT ensemble, the system was then allowed to quench at a constant rate to lower temperatures. Once the system reached 1500 K, the surface is created by removing the periodic boundary conditions in the thickness direction while maintaining periodicity in all others. This essentially simulated a thin surface extending semi-infinitely in the direct parallel to the surface. Additionally, the bottommost 100 atoms were immobilised, leaving on the remaining 188 atoms free for all further simulations. The surface system was then allowed to quench to 300 K and equilibrate. His simulation results indicated that oxygen, rather than silicon atoms dominated along the outer surface. Additionally, that both bridging and non-bridging oxygens were found along the surface.

Expanding on Garofalini’s previous work, Levine and Garofalini [158] used MD simulations to further investigate the surface of pure SiO$_2$ glasses. They produced several surfaces through varying starting configurations, system sizes, and quench procedures. Their results indicated that the O-Si-O bond angle distributions around Si within 2 Å of the surface varied significantly from the normal intratetrahedral bonds, which are commonly symmetric about 109.5° (Fig. 27). The difference was attributed to thermally excited non-bridging oxygens deforming adjacent tetrahedra, and causing a defect in the SiO$_2$ structure. Though not found in crystalline form, this type of SiO$_2$ tetrahedra defect was originally proposed as an intermediate step in diffusion and condensation processes by F. Liebau [164]. The geometry of the surface tetrahedra reported by Levine and Garofalini was similar to that proposed by Liebau.

Stillinger and Weber developed an efficient energy potential function to describe the solid and liquid forms of SiO$_2$ [165]. The Stillinger-Weber (SW) potential included contributions from both two- and three-body terms, and is designed to provide a means of studying the solid to liquid phase transformation as well the structure of the liquid. The SW potential has parameters that are empirically determined from liquid and crystalline experimental data, and has been successfully implemented in MD studies on the investigation of a-SiO$_2$ [159, 160, 166–168], silicon surfaces [169–171], epitaxial growth [172, 173], and microclusters [174, 175]. The SW three-body potential contribution was designed to provide a lower
binding energy when the angle formed with the central atom differs from the perfect tetrahedral bonding angle, this ensured that the minimum potential energy obtained was for the optimum configuration (i.e. tetrahedra).

Feuston and Garofalini employed a modified SW three-body potential in addition to the modified BMH two-body potential to simulate the structure of sodium trisilicate glass [159, 166]. Their results found that with the proposed three-body potential the structure of the simulated SiO$_2$ was in closer agreement to published experimental values. Delaye et al. [160] further verified the accuracy of the BMH and the three-body potentials for silicate glasses, where the amorphous structure for a series of 5-oxide glasses (SiO$_2$, B$_2$O$_3$, Na$_2$O, Al$_2$O$_3$, and ZrO$_2$) were developed. Their results demonstrated that these potentials are widely applicable to a range of silicate glasses.

### 4.6.4 The Interface

Clancy et al. investigated the interface between polymer-polymer interfaces using atomistic simulation methods [176]. Simulation procedures were presented for the generation of bulk and thin surface structures, and for the calculation of surface energy and work of adhesion. The following steps were applied to determine the work of adhesion of the interface: (i) bulk, amorphous cells were generated under periodic boundary conditions, (ii) thin surface structures were subsequently generated from the bulk cell, (iii) thin surfaces were brought together to form an interface, (iv) the two surfaces were pulled apart to separate the
interface and equilibrated, and \((v)\) the work of adhesion \(W_{12}\) at the interface was calculated,

\[
W_{12} = \frac{U_{\text{slab},1} + U_{\text{slab},2} - U_{12}}{2A}
\]  

(4.1)

where, \(U_{\text{slab},1}\) and \(U_{\text{slab},2}\) are the potential energies for the slab materials 1 and 2, \(U_{12}\) is the potential energy for the entire system, while \(A\) is the projected interfacial area.

Deng et al. investigated the interfaces between two common silane class coupling agents (AMPTES and SPTES) and a polycarbonate (PC) matrix material [177]. They stated that due to strong bonds between the glass fibre and silane coupling agents that a glass fibre composite interface will likely fail at either \((i)\) at the silane-matrix interface or \((ii)\) in the bulk silane. Therefore, they proposed that it was sufficient to model only the silane and matrix portion of the interface to study the mechanical properties. The work of adhesion for the PC-APTES and PC-SPTES systems was determined from the surface energies of PC, AMPTES, and SPTES by considering the difference in potential energies between bulk and thin surface surfaces. Gou et al. [178] explored the applications of MD simulations for the study on interfacial bonding of single-walled nanotube reinforced composites. They discussed methods for the calculation of the interfacial bonding energy between the nanotube and the epoxy resin.

Natarajan et al. [179] studied the interface between two polymeric hydrocarbons, polypropylene (PP) and poly(1,4-cis-butadiene) (PBD), using full atomistic simulation methods [179]. Both surfaces were constructed as films of 25-30 Å in thickness. The interface was formed by bringing the two films close together and running iterative MD simulations under two-dimensional periodicity conditions. They reported a final interface thickness of 10-15 Å. The interfacial tension between PP and PBD found reasonable agreement with experimentally determined values.

Holck et al. investigated the interface between a crosslinked epoxy network and silica [180]. Using similar methods to those presented by Clancy et al. [176] the interfacial work of adhesion for epoxy-silica was found to be in the range of 147 to 188 mJ/m². They additionally considered the behaviour of moisture at the interface. Specifically, they studied the relative mobility of water molecules at the interface by tracking particle trajectories in attempt to see if the water tends to move towards the bulk or towards the interface.

Buyukozturk et al. demonstrated that solutions gained through MD simulations can be expanded to provide insight into failure mechanisms of laminate systems subjected to prolonged moisture exposure [181]. A molecular simulation of a reinforced concrete elements which are strengthened by FRP composites was carried out, of interest to the study was the effects of prolonged moisture exposure on the FRP-concrete interface (an epoxy-silica bonding region). Though it is important to note that the epoxy model used neglected to
include a hardening agent, wherein only a one part epoxy polymer was used throughout the simulations. Buyukozturk et al. used a reduced form of the CVFF potential energy function [138, 182] as the basis for force field terms for the epoxy-silica interactions. The water potential energy function [183] was used in defining the flexibility of the water molecules.

Through using Steered Molecular Dynamics (SMD) [184] a pulling velocity was applied to the end carbon atom in the epoxy chain, while allowing all water and epoxy atoms to move freely otherwise; this pulling velocity effectively simulated shear tests at the interface. Tam and Lau [185] expanded on the work of Buyukozturk et al. and provided methods for quantifying adhesion at the SU-8/Silica interface through studying the surface energy. Tam and Lau investigated changes in surface energy under both dry and wet conditions. Their MD results indicated that the presence of moisture led to a 77.1% reduction in surface energy. They concluded that MD can give insight into the weakening of the bond strength between the epoxy and the silica substrate, the decrease was quantified by the decrease of the effective energy barrier.

4.6.5 MD and the Sized Fibre Composite Interface

Overall, the MD methods used in determining surface energies and work of adhesion at an interface are well understood. However, there are currently no studies on the applications of MD to examining adhesion at a fully sized interface in fibre reinforced polymer composites. Successful implementation of MD requires a well developed understanding of initial atomic structures and relative molecular arrangements. Specifics on fibre sizing are ambiguous, where the precise amount and exact composition at any given portion of the fibre is generally not known. Further, proprietary interests tend to obscure the composition and relative application of many commercial sizing formulations. MD studies that consider the sizing as part of the molecular description of the fibre-matrix interface have been lacking in the literature. This is primarily attributed to the relatively difficult barrier to entry and computational costs for successfully undertaking MD simulations paired with a minimal molecular-level understanding of fibre sizing systems.
5 MD Simulations of DGEBA/IPD

The LAMMPS (Large Scale Atomic/Molecular Massively Parallel Simulator) software package [186] was used for all molecular dynamics (MD) simulations described herein. The temperature is modulated through application of the Nosé-Hoover thermostat [32] while the pressure inside the simulation box is controlled through application of the weak coupling method of the Berendsen barostat [30]. The CHARMM force field was employed in defining the bond, angle, and dihedral parameters [25], see Appendix A. The potential energy contributions from bonded interactions are defined as follows,

\[ U = \sum_b K_b (b - b_0)^2 + \sum_{\theta} K_{\theta} (\theta - \theta_0)^2 + \sum_\phi K_{\phi} (1 + d \cos(n\phi)) \]  

where \( K_b, K_{\theta}, \text{ and } K_{\phi} \) are force (spring) constants, \( b_0, \theta_0, \text{ and } \phi \) are equilibrium bond length, bond angle, and dihedral angle, respectively; \( b \) and \( \theta \) are bond length and bond angle. The CHARMM force field provides the equilibrium and force constants for each given species in the simulation. It is noted that the potential energy of the system has significant contributions from non-bonded interactions. The Lennard-Jones potential and Coulombic pairwise interactions are calculated for all atoms \( i,j \).

\[ U_{LJ} = \sum_{ij \neq j} 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]

\[ U_{el} = \sum_{ij \neq j} \frac{C q_i q_j}{\epsilon_0 r_{ij}} \]

respectively, where, \( \epsilon_{ij} \) defines how strongly the atoms attract each other and \( \sigma_{ij} \) is the cut-off distance at which the intermolecular potential between atoms \( i \) and \( j \) is zero. \( C \) is an energy-conversion constant, \( q_i \) and \( q_j \) are the charges for atoms \( i \) and \( j \), \( \epsilon_0 \) is the permittivity of free space, and \( r_{ij} \) is the distance between the atoms. The CHARMM force field provides the parameters for each pair of atoms in the system.

5.1 Crosslinking the System

All simulations were carried out using copolymer systems consisting of diglycidyl ether bisphenol A (DGEBA) using isophorone diamine (IPD) as the curing agent. The molecular structures are presented in Fig. 28. A DGEBA/IPD epoxy network was selected as it is widely used throughout industry. The crosslinking procedure presented was based upon methods developed by Xu et al. [125].
Initially, molecular models of DGEBA and IPD were constructed within the Avogadro molecule editor [187, 188]. Reactive bonding sites were created by removing the active hydrogens at the end functional groups for each molecule (Fig. 29). Following the creation of reactive states for DGEBA and IPD, steepest decent energy minimization was performed using Avogadro to geometrically optimize the structure of each molecule. Partial charges were then assigned to each atom through application of the Q_{eq} method at 300 K [189].

256 reactive DGEBA molecules and 128 reactive IPD molecules (2:1 stoichiometric mixing ratio) were packed into a 60×60×60 Å³ simulation box using Packmol [190]. The packing strategy employed packs all molecules into specified space in such a way that the minimum distance between atoms of different molecules was greater than a fixed tolerance [191]. The tolerance was specified as 2 Å. The output from one instance of this molecular packing is given in Fig. 30.

The system was initially subjected to 10,000 steps of energy minimization to relax the simulation cell. The relaxed structure was dynamically crosslinked under a constant volume and temperature (canonical NVT) process at 300 K. The temperature of the system was modulated using the Nosé-Hoover thermostat [32]. The crosslinking algorithm was based on the root mean square (RMS) distance between reactive CH₂ groups of DGEBA and the
reactive N atoms of the IPD. A crosslink was formed when the RMS distance between a reactive CH$_2$ group and a reactive N atom was within a specified cutoff distance. If several reactive CH$_2$-N pairs are within the specified cutoff distance then the closest such partner becomes the sole bonding partner. Once a reactive site has formed a crosslink the site becomes non-reactive and was unable to undergo further crosslinking.

The crosslink density of the epoxy system was defined as the ratio of the total number of crosslink bonds that were formed to that of the theoretical maximum. For example, an epoxy network that forms 16 out of a possible 32 crosslink bonds is defined as having a 50% crosslink density. For many epoxy systems, it is difficult to achieve crosslink densities much higher than 93%. Each step of the crosslinking algorithm used is as follows:

1. User specified target system crosslink density.
2. The RMS cutoff distance increased by 0.1 Å.
3. Crosslink bonds are formed if within the current RMS cutoff.
4. 50 ps of NVT dynamics at 300 K to equilibrate the crosslinked system and release the strain imposed by the formation of crosslink bonds.
5. Steps 2-4 are repeated until target crosslink density has been reached.
5.2 Simulated System Properties

To validate the simulation model, system properties were derived using MD methods and then directly compared with experimentally determined values. Through following the procedures outlined previously, each structure was built from a different starting configuration of DGEBA and IPD molecules and was crosslinked to 91.5%. First, the density of the system were examined. Then, several elastic properties were derived. Finally, the glass transition temperature were considered. In total, ten separate DGEBA/IPD MD structures were investigated.

5.2.1 Density

In order to compute the final density, $\rho$, of the crosslinked system 800 ps of NPT dynamics at 300 K, 1 atm were carried out. This routine effectively shrinks the simulation box to its equilibrium density. To include a stopping criteria, every 20 ps a time-averaged value for $\rho$ was calculated over the previous 20 ps. Through comparing these time-averaged values from consecutive calculations the relative percent change in system density over the past 20 ps was estimated. The simulation finishes when this difference was less than 0.5% from the previous time-averaging, or at a hard time of 800 ps.

5.2.2 Elastic Properties

Elastic properties for the system were derived through first considering the stiffness matrix for the system. The stiffness matrix, $C_{ij}$ was calculated from the second derivative of potential energy ($U$) with respect to strain ($\epsilon$) \cite{125, 192},

$$C_{ij} = \frac{1}{V} \frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} = \frac{\partial \sigma_i}{\partial \epsilon_j} = \frac{\sigma(+) - \sigma(-)}{2 \epsilon_j}$$ \hspace{1cm} (5.3)

where, $\sigma_i$ is the stress component calculated by the first derivative of potential energy per unit volume with respect to strain. The individual stiffness terms can now be represented using three readily available quantities, stress under tension, $\sigma(+)$, stress under compression, $\sigma(-)$, and applied strain, $\epsilon_j$.

To calculate $C_{ij}$, small directional strains were applied to the simulation box. For each deformation applied to the system, (twelve in total, positive and negative of each the six principle directions), the system was equilibrated for 20 ps under NVT. The contributions to the system stiffness matrix were calculated as the average over a further 1 ps, Eqn. (5.3). The stiffness matrix, $C_{ij}$, for one of the ten considered DGEBA/IPD systems of 91.5%
crosslink density is given as follows,

\[
C_{ij} = \begin{pmatrix}
7.19 & 3.55 & 3.34 & 0.68 & -0.25 & -0.84 \\
3.53 & 7.55 & 3.62 & 0.51 & -0.09 & -0.96 \\
2.96 & 3.65 & 7.23 & 0.43 & -0.26 & -0.24 \\
0.56 & 0.50 & 0.39 & 1.98 & 0.13 & -0.11 \\
-0.13 & 0.01 & -0.29 & -0.21 & 1.80 & 0.16 \\
-0.03 & -0.16 & -0.24 & -0.28 & -0.04 & 1.82
\end{pmatrix} \text{ GPa}
\]

For an isotropic linearly elastic material, the non-diagonal components of \(C_{ij}\), which are not in the first quadrant, should be zero. It is seen that this is very nearly the case, with most terms being negligible in magnitude, especially in comparison to the diagonal components of the matrix. Additionally, \(C_{ij}\) is almost perfectly symmetrical about the diagonal components. Fundamentally, \(C_{ij}\) is of the correct form and can be used moving forward with calculations of mechanical properties. Lame constants (\(\lambda\) and \(\mu\)) are calculated from \(C_{ij}\) as follows,

\[
\lambda = \frac{1}{3}(C_{11} + C_{22} + C_{33}) - \frac{2}{3}(C_{44} + C_{55} + C_{66}) \\
\mu = \frac{1}{3}(C_{44} + C_{55} + C_{66})
\]

several mechanical properties are then directly derived from the two Lame constants,

\[
E = \mu \frac{3\lambda + 2\mu}{\lambda + \mu} \hspace{1cm} G = \mu \hspace{1cm} \nu = \frac{\lambda}{2(\lambda + \mu)} \hspace{1cm} K = \lambda + \frac{2}{3}\mu
\]

where \(E\), \(G\), \(\nu\), and \(K\) represent the elastic modulus, shear modulus, Poisson’s Ratio, and bulk modulus, respectively. Equation (5.5) was used in the calculation of all simulated system properties.

**5.2.3 Glass Transition Temperature**

To further validate the simulation, the glass transition temperature was calculated for each of the ten structures and compared with experimental results. Recall, the storage modulus, \(E'\), is a dynamic property of viscoelastic materials that represents the stored, elastic response of the system and \(E'\) decreases while passing through the glass transition temperature. It is not simple to directly simulate dynamic properties (\(E', E''\), and \(\tan(\delta)\)), therefore an alternative approach was used. Characteristically, the Elastic Modulus shows
a similar response to the storage modulus and will decrease while passing through the glass transition temperature. Therefore, to determine the glass transition temperature for the DGEBA/IPD system, the modulus of elasticity, $E$, was investigated as a function of system temperature over the range of 50 - 200 °C.

The system was first equilibrated to 50 °C, 1 atm under NPT. Once equilibration was reached the modulus of elasticity for the system was calculated (Eqn. 5.5). The system temperature was then increased by 5 °C, equilibrated, and the modulus again calculated. This process was iterated over the entire temperature range. Note, the NPT ensemble was used for all data collection as a means of allowing the volume of the system to fluctuate due to thermal expansions.

5.3 Experimental Validation

DGEBA/IPD samples were manufactured to provide validation for the proposed MD simulation model. DGEBA resin and IPD curing agent were provided by Sigma-Aldrich [193, 194], following the recommended manufacturing procedures, a mixing ratio of 2:1 DGEBA to IPD by volume was employed. This formulation was continuously mixed for five minutes, with careful attention taken to minimize the introduction of air bubbles into the system. The system cured for 24 hours at ambient room temperature.

The density of the manufactured DGEBA/IPD samples was measured in accordance with ASTM Standard D792-13 [195]. Over the ten considered epoxy samples an average experimental density of $1.131 \pm 0.055$ g cm$^{-3}$ was found. The simulated density for the system was taken as an average over ten structures, and was calculated as $1.128 \pm 0.062$ g cm$^{-3}$. The simulated system finds excellent agreement with experimental values, Fig. 31.

Figure 31: The experimental and simulated DGEBA/IPD system density. Error bars indicating standard deviation.
Table 3: Simulation and experimental results for the dry system.

<table>
<thead>
<tr>
<th>Property</th>
<th>Simulation</th>
<th>Experimental</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$ (GPa)</td>
<td>$4.92 \pm 0.09$</td>
<td>$4.34 \pm 0.14$</td>
<td>11.6</td>
</tr>
<tr>
<td>$K$ (GPa)</td>
<td>$4.84 \pm 0.16$</td>
<td>5.01 [70]</td>
<td>-3.5</td>
</tr>
<tr>
<td>$G$ (GPa)</td>
<td>$1.86 \pm 0.10$</td>
<td>1.75 [70]</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Tensile testing was done to experimentally determine tensile properties for a dry DGEBA/IPD epoxy system, and was done following the guidelines specified in ASTM D638 [196]. Eight dogbone samples were cut from the epoxy plate, in accordance with ASTM D638, and friction tabs were used to help mitigate gripping damage to the specimens. A constant crosshead speed of 2 mm/min was used and axial strain was recorded via video extensometer. The majority of samples exhibited a relatively linear response, resulting in an average elastic modulus of $4.34 \pm 0.14$ GPa. The tensile strength was found as $112.2 \pm 3.2$ MPa, while strain to failure was found to be $2.56 \pm 0.11\%$. Comparisons between simulated and experimental elastic properties for the dry epoxy system are provided in Table 3.

Overall, the simulated system slightly overestimated the stiffness of the structure, a similar trend has been reported in literature for simulated epoxy systems [125, 192, 197]. This may partially be due to the simulation not accounting for voids, defects, or imperfections in the structure. Furthermore, the simulated system structurally represents a highly crosslinked system, which may not align with what was experimentally tested at present.

Dynamic Mechanical Analysis (DMA) was performed using a TA DMA Q800 instrument. The testing was done in single cantilever bending mode at a loading frequency of 1 Hz, where a sampling rate of 2 seconds per point was used for all data collection. Each epoxy sample was first allowed to equilibrate to 50 °C and was then heated at a constant 5 °C/min to 200 °C. Altogether, ten DGEBA/IPD epoxy samples were investigated. Figure 32 provides the storage modulus and tan(δ) plotted against temperature for one of the DMA samples. An average $T_g$ onset of $108.21 \pm 1.02$ °C was found. Note, the $T_g$ was tabulated from the peak of the tan(δ) with an average value of $147.04 \pm 0.92$ °C.

The experimental DMA storage modulus vs. temperature results for one sample was compared with the simulated elastic modulus vs. temperature, Fig. 33(a). Figure 33(b) presents a comparison between the averaged simulated and experimental results for the system onset of glass transition temperature. Over the ten systems, an average simulated $T_g$ onset of $117.62 \pm 3.77$ °C was found, representing an 8% difference. The simulated system finds reasonable agreement with experimental values, but overall, tended to overestimate the glass transition temperature. Similar sources of error seem plausible, wherein the simulated system does not account of imperfections in the structure (which are unavoidable in practice).
Perhaps more significantly, in this case, is the highly crosslinked nature of the simulated structure. By definition, a higher crosslink density decreases the overall mobility of polymer (epoxy) chains throughout the system.

Figure 32: DMA results showing $E'$ (MPa) and tan(δ) vs. temperature.

Figure 33: (a) The experimental and simulation results for $T_g$ onset and (b) the average onset of $T_g$ onset for the experimental and simulated systems. Error bars indicate the standard deviation.
6 MD Simulations of DGEBA/IPD-Water Interactions

The interactions between epoxy systems and absorbed water molecules are discussed in this section. First, computational methods for determining the equilibrium moisture content for a crosslinked epoxy network are proposed. The effects of absorbed moisture on the thermomechanical properties of the system are then be considered.

6.1 Reduced Chemical Potential

Thermodynamically, the condition of chemical equilibrium between two phases, $I$ and $II$ for each species $i$ is given as,

$$\mu_{i,I} = \mu_{i,II}$$  \hspace{1cm} (6.1)

where $\mu$ is the chemical potential. Hostermann et al. [150] state that chemical equilibrium for species $i$ between the two states $I$ and $II$ is additionally satisfied as follows,

$$RT\ln\left(\frac{n_I}{n_{II}}\right) = \mu_{ex}^{II} - \mu_{ex}^{I}$$  \hspace{1cm} (6.2)

where $R$ is the universal gas constant, $T$ the temperature, and $n$ is the number density of the species in each state. While, $\mu_{ex}$ represents the excess chemical potential for each given state. A new term is proposed through rearranging Eqn. (6.2) such that the contributions from each state are isolated on each side of the equality. This term is referred to as the reduced chemical potential, $\tilde{\mu}$,

$$\tilde{\mu} = \mu_{ex} + RT\ln(n)$$  \hspace{1cm} (6.3)

Furthermore, if chemical equilibrium exists between states $I$ and $II$ for each species, then the following condition must also be satisfied,

$$\tilde{\mu}_I = \tilde{\mu}_{II}$$  \hspace{1cm} (6.4)

For the remaining work, the only species under consideration is water (i.e. $i = H_2O$). Considering the case of a polymer submerged in pure water, the solubility of the polymer is determined through examination of Eqn. (6.4) (where, pure water is state $I$, and absorbed water is state $II$). At saturation, the equality will be satisfied. If $\tilde{\mu}_I > \tilde{\mu}_{II}$, this indicates the system is not yet saturated, and the system will absorb further water. Conversely, if $\tilde{\mu}_I < \tilde{\mu}_{II}$, this indicates the polymer is oversaturated, and there is a driving force for water to desorb. This offers the means for assessing the solubility of water in a polymeric system.
6.2 Excess Chemical Potential

On the calculation of excess chemical potential, first consider the chemical potential $\mu$ of water present within a polymer [198],

$$\mu = \left. \frac{\partial A}{\partial N} \right|_{N_p,V,T}$$ (6.5)

where $A$ is the Helmholtz free energy of the system, $V$ the volume, $T$ the temperature, and $N$ and $N_p$ are the number of water and polymer molecules respectively. For an ideal gas, the Helmholtz energy is readily evaluated, as such only the excess portion of the chemical potential need be considered,

$$\mu^{ex} = \mu - \mu^{ideal} = \left. \frac{\partial A^{ex}}{\partial N} \right|_{N_p,V,T}$$ (6.6)

Widom’s test particle insertion [144, 145] can be used in the determination of excess chemical potentials. The excess chemical potential of water in a temporarily frozen $N$-molecule system is determined through observing changes in potential energy of a system with $N$ number of water molecules, due to the insertion of an additional test particle at randomly selected positions. Widom’s formulation for excess chemical potential is as follows,

$$\mu^{ex} = -k_B T \ln \left< \frac{-\Delta U_{pot}^{(N+1;N)}}{k_B T} \right>_{N}$$ (6.7)

where $k_B$ in the Boltzmann constant, $T$ the temperature, and $\Delta U_{pot}^{(N+1;N)}$ is the change of system potential energy due to test particle insertion. The $\langle ... \rangle_N$ represents the ensemble average over the original system. However, the application of Widom’s method is problematic in systems with either relatively large solute molecules, strong long-range interactions between solute and solvent species, or high density systems such as polymers. In the above instances, the insertion of a test particle results in large values of $\Delta U$, leading to a negligible contribution to $\mu^{ex}$ due to the exponential form of Eqn. (6.7).

Alternatively, thermodynamic integration methods can be used in the calculation of excess chemical potential [199–201]. A function is defined combining two states of interest as a function of a coupling parameter $\lambda$, where $0 \leq \lambda \leq 1$ and the two states of interest occur at $\lambda = 0$ and $\lambda = 1$. If one of the states (typically $\lambda = 0$) describes a situation with no solute,
the excess chemical potential is then given as follows,

\[
\mu^{ex} = \frac{\Delta A^{ex}}{N} = \frac{1}{N} \int_0^1 \left( \frac{\partial U_{pot}(\lambda)}{\partial \lambda} \right) d\lambda
\]  

(6.8)

where, \( N \) is the number of solute molecules, and \( U_{pot}(\lambda) \) is the potential energy of the system as a function of \( \lambda \). For MD, the interaction force field terms are activated as \( \lambda \) increases, which directly yields changes in potential energy of the system. Limitations of thermodynamic integration method arise as singularities in the derivative of the potential energy occur while approaching the ideal gas state (\( \lambda = 0 \)), since non-bonded interactions are fully deactivated.

Knopp et al. [146, 147] describe methods for determining excess chemical potential of small molecules held within a dense microstructure; their novel methods combine thermodynamic integration methods with Widom’s test particle insertion method. Individually, the Widom insertion method and thermodynamic integration are impractical for this purpose due to limitations imposed by the dense polymer structure. In approaching these issues Knopp et al. introduced an intermediate phase of water in between the real water and water as an ideal gas. This is referred to as noble water. The purpose of this intermediate state is to make the noble water molecules small enough that the Widom insertion method can be used in the calculation of the excess chemical potential. The excess chemical potential for water held within the polymer structure can be expressed by combining eqns. (6.7) and (6.8) to give,

\[
\mu^{ex}_{H_2O} = \frac{\Delta A^{ex}}{N_{H_2O}} + \mu^{ex}_{WI}
\]  

(6.9)

where the first term is obtained by thermodynamic integration while \( \mu^{ex}_{WI} \) is found though Widom test particle insertion of the newly introduced noble water molecule.

The noble water model is defined as follows. At \( \lambda = 1 \), a real water model is used, with full interactions and atom size. At \( \lambda = 0 \), a noble water model has no Coulombic interactions, Lennard-Jones interactions of the hydrogen atoms are switched off, and the oxygen atoms in all water molecules are scaled to 80% of their original Lennard-Jones size. This scaling value was chosen based on efficiency optimization of the Widom insertion process. A mathematical breakdown of how the noble water model is implemented is given in Table 4, where the subscript \( \text{org} \) denotes the original, unaltered parameter as defined by the CHARMM force field.

The step-by-step procedures used in determining the excess chemical potential:

1. For each \( \lambda \), the system is equilibrated and the potential energy is obtained.

2. Through evaluation of the integral from \( \lambda = 0 \) to 1 the difference in Helmholtz free
Table 4: Lennard-Jones and Coulombic parameter dependence on the $\lambda$

<table>
<thead>
<tr>
<th>Atom</th>
<th>$q_i$</th>
<th>$r_i$</th>
<th>$\epsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>$2\lambda q_{org}$</td>
<td>$(0.8+0.2\lambda)r_{org}$</td>
<td>$\epsilon_{org}$</td>
</tr>
<tr>
<td>H</td>
<td>$\lambda q_{org}$</td>
<td>$r_{org}$</td>
<td>$\lambda^2 \epsilon_{org}$</td>
</tr>
</tbody>
</table>

energy is calculated (Eqn. 6.8).

3. Widom test particle insertion of a noble water molecule ($\lambda = 0$) to obtain the remaining portion of the excess chemical potential (Eqn. 6.7); and

4. The excess chemical potential is determined from Eqn. (6.9).

### 6.2.1 Pure Water System

Initially, the case of a pure water system was considered for validation of the selected computational method since the excess chemical potential of pure water is known ($\mu_{ex} = -23.8$ kJ mol$^{-1}$ [202]). 50 total MD configurations of a 500 molecule pure water system are investigated, what follows are the simulation procedures for a single configuration. The Nosé-Hoover thermostat [32] is used for controlling the temperature of the system, while the Berendsen barostat [30] is used for any required pressure modulations.

The 500 water molecules were packed into $22\times22\times22$ Å$^3$ simulation box using Packmol. The packing tolerance was specified as 2 Å. The TIP3P water model [203] was employed in defining interaction parameters ($q_{org}$, $r_{org}$, and $\epsilon_{org}$) as well as bonding, and angle coefficients for all water molecules within the system.

A constant pressure and temperature (NPT ensemble) MD process was carried out at 1 atm and 300 K for 50 ps to optimize the system density, resulting in a final system density of 0.997 g cm$^{-3}$. A constant volume and temperature (NVT ensemble) process was then carried out at 300 K for 100 ps. This allowed the molecules to move freely within the simulation box to reach a fully optimized molecular arrangement. The system interaction parameters were then redefined as a function of the coupling parameter ($\lambda$) as described previously (Table 4).

To numerically determine the excess chemical potential of the system, it is first necessary to sample the potential energy of the system at various values of $\lambda$, calculate the derivates of potential energy, and then integrate over $\lambda$. Nine equidistant values for $\lambda$ between 1 and 0 were considered as integration points (i.e. $\lambda = 1.0, 0.905, 0.805,...,0.105,0.0$). Additionally, for each $\lambda$, further values are gathered at $\lambda \pm \Delta \lambda$, where $\Delta \lambda = 0.005$. This allows for a
Table 5: Averaged value of $\frac{1}{N} \frac{\partial U_{\text{pot}}(\lambda)}{\partial \lambda}$ at varying simulation time for pure water

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>50ps</th>
<th>200ps</th>
<th>500ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.619</td>
<td>0.626</td>
<td>0.627</td>
</tr>
<tr>
<td>0.105</td>
<td>0.406</td>
<td>0.411</td>
<td>0.411</td>
</tr>
<tr>
<td>0.205</td>
<td>-1.919</td>
<td>-1.941</td>
<td>-1.942</td>
</tr>
<tr>
<td>0.305</td>
<td>-8.062</td>
<td>-8.151</td>
<td>-8.155</td>
</tr>
<tr>
<td>0.405</td>
<td>-11.93</td>
<td>-12.06</td>
<td>-12.07</td>
</tr>
<tr>
<td>0.505</td>
<td>-16.37</td>
<td>-16.55</td>
<td>-16.57</td>
</tr>
<tr>
<td>0.605</td>
<td>-22.69</td>
<td>-22.94</td>
<td>-22.96</td>
</tr>
<tr>
<td>0.705</td>
<td>-31.31</td>
<td>-31.66</td>
<td>-31.68</td>
</tr>
<tr>
<td>0.805</td>
<td>-41.80</td>
<td>-42.26</td>
<td>-42.29</td>
</tr>
<tr>
<td>0.905</td>
<td>-52.13</td>
<td>-52.70</td>
<td>-52.73</td>
</tr>
<tr>
<td>1.000</td>
<td>-68.52</td>
<td>-69.27</td>
<td>-69.32</td>
</tr>
</tbody>
</table>

$\frac{1}{N} \int_0^1 \left( \frac{\partial U_{\text{pot}}(\lambda)}{\partial \lambda} \right) d\lambda = -21.82 \text{, -22.06 and -22.08 kJ mol}^{-1}$ after simulation times of 50, 200 and 500 ps, respectively.

After all values of $\lambda$ have been processed through thermodynamic integration, a test particle insertion of a noble water molecule is needed to calculate the final contribution to the excess chemical potential. To do this, the simulation box was divided into a uniformly spaced three-dimensional grid pattern ($25 \times 25 \times 25$), where each grid point serves as the insertion coordinates for the test particle. The noble water molecule is placed at each point in the insertion grid for each of the 100 sampled MD configurations, each of which are sampled at 1 ps intervals from 500-600 ps during the simulation. Therefore, for each of the 100 MD configurations there are 15,625 insertions that contribute a single data point.
Figure 34: The excess chemical potential of noble water calculated through Widom’s test particle insertion for 100 separate MD configurations (500-600ps). The solid line representing the moving average up to the current MD frame.

towards the calculation of $\mu_{WI}^{ex}$ using Eqn. (6.7). The resulting value of $\mu_{WI}^{ex}$ is taken as an average of all 100 configurations. Figure 34 illustrates the progress of these calculations, where each data point indicates a single application of Eqn. (6.7) to a given MD frame over the 15,625 insertion points. The excess chemical potential of the noble water is found to be $\mu_{WI}^{ex} = -1.66$ kJ mol$^{-1}$ with a standard deviation of 0.062 kJ mol$^{-1}$.

The excess chemical potential of this configuration of the pure water system can now be fully obtained through Eqn. (6.9), wherein the excess potential found through thermodynamic integration (-22.08 kJ mol$^{-1}$) is added to the value found through Widom’s insertions method (-1.66 kJ mol$^{-1}$), giving a total excess chemical potential of -23.74 kJ mol$^{-1}$.

The excess chemical potential for the pure water system is taken as an average of all 50 sampled MD configurations, see Fig. 35. The excess chemical potential is found to have an average value of -23.79 kJ mol$^{-1}$ with a standard deviation of 0.05 kJ mol$^{-1}$. This aligns exceptionally well with the experimentally determined value of -23.8 kJ mol$^{-1}$ [202]. Additionally, this value shows reasonable agreement with other values found through employing different simulation techniques ($\mu_{WI}^{ex} = -23.4$ to -24.3 kJ mol$^{-1}$)[204–206]. The methods discussed have been successfully implemented in determination of the excess chemical potential of pure water, and therefore the next step is now to expand to the determination of the solubility of the DGEBA/IPD structure.
6.3 Solubility Determination of DGEBA/IPD System

At full saturation, the reduced chemical potential of absorbed water molecules held within a polymer structure will be equal to that of pure water, thereby satisfying Eqn. (6.4). For pure water, the reduced chemical potential is calculated as $\tilde{\mu}_I = 140.06 \text{ kJ mol}^{-1}$; where $\mu^{ex}_I = -23.79 \text{ kJ mol}^{-1}$, and $n_I = 500/volume$ of simulation cell. For each level of moisture investigated (i.e. 1%, 2%, 3% etc...) the excess chemical potential is taken as an average of ten separate DGEBA/IPD structures, each with 91.5% crosslink density. For each structure considered, three randomly generated water molecule positions are investigated. In total, 30 values for excess chemical potential are taken for each moisture content.

Firstly, water molecules were introduced into the crosslinked DGEBA/IPD structure at various saturation levels. The structure will then be equilibrated, and the excess chemical potential of the water molecules were calculated using the previously described approach. To determine the solubility of water in the crosslinked DGEBA/IPD system, $\Delta \mu^{ex}$ for a range of different water contents were determined using Eqn. (6.2). Thus, it was possible to determine at which water content the crosslinked DGEBA/IPD is fully saturated to determine the maximum solubility.

What follows are the procedures and specific outputs used in the excess chemical potential determination for a DGEBA/IPD system saturated to a moisture content of 1 wt.%. The number of water molecules to be inserted was based on the molecular mass of the water and epoxy. It was determined that 60 water molecules were required to obtain a moisture content of 1 wt.% in the system.
Table 6: Time-averaged value of $\frac{1}{N} \frac{\partial U_{pot}(\lambda)}{\partial \lambda}$ at varying MD simulation time for a single system saturated to 1 wt.% water

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>50ps</th>
<th>200ps</th>
<th>500ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>-0.624</td>
<td>-0.063</td>
<td>-0.063</td>
</tr>
<tr>
<td>0.105</td>
<td>-0.040</td>
<td>-0.041</td>
<td>-0.041</td>
</tr>
<tr>
<td>0.205</td>
<td>-0.193</td>
<td>-0.195</td>
<td>-0.196</td>
</tr>
<tr>
<td>0.305</td>
<td>-0.813</td>
<td>-0.819</td>
<td>-0.821</td>
</tr>
<tr>
<td>0.405</td>
<td>-1.203</td>
<td>-1.213</td>
<td>-1.215</td>
</tr>
<tr>
<td>0.505</td>
<td>-1.651</td>
<td>-1.665</td>
<td>-1.667</td>
</tr>
<tr>
<td>0.605</td>
<td>-2.287</td>
<td>-2.307</td>
<td>-2.311</td>
</tr>
<tr>
<td>0.705</td>
<td>-3.158</td>
<td>-3.184</td>
<td>-3.189</td>
</tr>
<tr>
<td>0.805</td>
<td>-4.216</td>
<td>-4.251</td>
<td>-4.258</td>
</tr>
<tr>
<td>0.905</td>
<td>-5.257</td>
<td>-5.301</td>
<td>-5.310</td>
</tr>
<tr>
<td>1.000</td>
<td>-6.911</td>
<td>-6.968</td>
<td>-6.980</td>
</tr>
</tbody>
</table>

$\frac{1}{N} \int_0^1 \left( \frac{\partial U_{pot}(\lambda)}{\partial \lambda} \right) d\lambda = -19.57, -19.72, -19.75$ kJ mol$^{-1}$

The 60 water molecules were then inserted at randomly assigned positions throughout the simulation box. 10,000 steps of energy minimization were performed, along with 200 ps of NVT dynamics, to equilibrate the saturated DGEBA/IPD structure. The $\lambda$-modified force field parameters were then implemented in the simulation. NVT dynamics were run at a temperature of 300 K for each value of $\lambda$. Every 20,000 time steps a time-averaged value was calculated over the previous 20,000 steps for each energy term ($U_{lj}(\lambda)$, $U_{el}(\lambda)$, and $U_{ns}$). Individually, the potential energy terms are much smaller than that of the pure water system, because there are only 60 molecules in the system (whereas the pure water simulation had 500 water molecules). The same trends are seen in that the Lennard-Jones and Coulombic energy terms are activated to full-scale interactions, while the bonded (non-scaled) energy terms remain comparatively stable.

As previously, the term $\frac{1}{N} \frac{\partial U_{pot}(\lambda)}{\partial \lambda}$ is numerically determined for each given value of $\lambda$, Table 6 provides these outputs after total simulation times of 50, 200 and 500 ps for one of the sampled polymer configurations. The integral over the potential energy derivative, representing the Helmholtz free energy difference of the system, is obtained by the trapezoidal integration method, the results of which are given as the final row of Table 6. The integral is observed to converge with increasing MD simulation time, taking values of -19.57, -19.72 and -19.75 kJ mol$^{-1}$ after simulation times of 50, 200 and 500 ps, respectively.

Widom’s particle insertion of a noble water ($\lambda = 0$) molecule was then performed and 100 MD frame collections yielded the final average value of $\mu_{WI}^{ex} = +1.53$ kJ mol$^{-1}$. By adding this to the thermodynamic integration contribution (-19.75 kJ mol$^{-1}$) the final value for the
Figure 36: Each plot represents the distribution of 30 excess chemical potentials calculated for 1, 2, and 3 wt.% water in epoxy systems. The box plots illustrate ± one standard deviation about the mean.

excess chemical potential of the water held within the system at a 1 wt.% moisture content was found to be $\mu^{ex} = -18.22 \text{ kJ mol}^{-1}$.

The excess chemical potential for the 1% moisture content is taken as an average of 30 sampled MD configurations (ten DGEBA/IPD structures, each with three randomly generated water molecule positions). The excess chemical potential is found to have an average value of -18.24 kJ mol$^{-1}$ with a standard deviation of 0.12 kJ mol$^{-1}$. Figure 36 shows the excess chemical potential distributions calculated for 1, 2, and 3 wt.%.

The determination of chemical potential equilibrium, through the evaluation of Eqn. (6.4) is the final step in determining the maximum solubility of water in the system. The reduced chemical potential for pure water is calculated as $\tilde{\mu}_{\text{pure}} = 140.06 \text{ kJ mol}^{-1}$, while for 1 wt.% moisture content it is calculated as $\tilde{\mu}_{\text{absorbed}} = 134.28 \text{ kJ mol}^{-1}$. Therefore, $\tilde{\mu}_{\text{pure}} > \tilde{\mu}_{\text{absorbed}}$ indicating that the DGEBA/IPD structure is not yet saturated. Additional iterations were required at higher moisture contents to obtain the maximum solubility. The calculated excess chemical potentials for each moisture content are given in Fig. 37. The DGEBA/IPD structure is found to reach full saturation in the range of 3.50-3.75 wt.%.
Figure 37: The reduced chemical potential, $\tilde{\mu}$, plotted against weight content of water at 300 K, 1 atm. Each point represents the average of 30 values. The error bars represent standard deviation. The horizontal, dashed line is the constant value $\tilde{\mu}_{\text{pure}}$, with ± one standard deviation. Full saturation of the DGEBA/IPD system occurs at the intersection.
6.4 Simulated System Properties

Simulated properties for the saturated system were calculated (§5.2) and compared with experimental values. Each simulated property was taken as an average of ten separate DGEBA/IPD structures, each with 91.5% crosslink density; each structure was saturated to 3.6 wt.% water using three randomly generated sets of water molecule positions. 3.6 wt.% water was selected, as this falls directly within the simulated solubility range for DGEBA/IPD of 3.5-3.75 wt.%, Fig. 37. In total, 30 values for each property were taken (ten DGEBA/IPD structures, three sets of water molecule positions).

6.5 Experimental Validation

Half of the samples manufactured previously (§5.3) were placed in distilled water at room temperature and weight gains were tracked until full saturation was achieved. Figure 38 presents the water uptake data for all considered epoxy samples, with an average maximum water content of 2.66 ± 0.03 wt.%, representing a difference of just over 26% when compared to the simulated saturation range of 3.5-3.75 wt.%. All samples exhibited Fickian uptake behaviours, with initially linear uptake portion before diffusion slows and the solubility limit is reached.

Further, published experimental values for maximum moisture content for DGEBA/IPD systems are reported in the range of 1.5-2.6 wt.% [207–209]. Marie et al. [207] report an equilibrium content of 2.3 wt.% for a DGEBA/IPD network at 300 K, 1 atm, though they do not provide the crosslink density for the system. Berruet et al. [208] provide a value of 2.6 wt.% for DGEBA/IPD at 300 K, 1 atm, the crosslink density is again not provided.
Table 7: Experimental tensile properties of dry and saturated DGEBA/IPD.

<table>
<thead>
<tr>
<th></th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Strain to failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>4.34 ± 0.14</td>
<td>112.2 ± 3.2</td>
<td>2.56 ± 0.11</td>
</tr>
<tr>
<td>Saturated</td>
<td>3.74 ± 0.08</td>
<td>87.32 ± 4.1</td>
<td>2.31 ± 0.17</td>
</tr>
</tbody>
</table>

Finally, Morel et al. [209] report 1.5 wt.% at 293K, 1 atm, with no specifics provided for crosslink density.

For all simulations, the crosslink density used was 91.5%, and while this value was chosen to be reasonably attainable, the experimental values may not align at the same crosslink density. Furthermore, crosslink density directly influences the resulting equilibrium moisture content, where higher crosslink densities leave fewer available polar bonding sites, hindering moisture solubility [45, 139, 207]. Incorporating polar bonding would introduce another layer of complexities into the simulation, and was outside the scope of this study.

The methods presented in this work rely on differentiating very small energy differences, where small variations can carry large impacts, this could cause more uncertainty in the simulated solubility limit. Though, conscious efforts have been made to minimise these kinds of errors, with the rigorous time-averaging techniques used. Further work is needed to gain a complete understanding of the specific interactions between epoxy and water.

### 6.5.1 Density and Elastic Properties

The simulated density for the saturated system was taken as an average over the thirty total configurations (§5.2.1), and was calculated as 1.121 ± 0.041 g cm$^{-3}$, representing a decrease of only 1.24% when compared to the dry DGEBA/IPD system. Experimentally (§5.3.1), the saturated density was found as $\rho = 1.114 ± 0.077$ g cm$^{-3}$, representing a decrease of 0.88% when compared to the simulated dry DGEBA/IPD system, Fig. 39(a).

Ten tensile testing coupons were tested, following ASTM D638 [196]. Friction tabs were used to mitigate gripping damage to the specimens. A constant crosshead speed of 2 mm/min was used and axial strain was recorded via video extensometer. Table 7 summarises the tensile testing data for the dry and saturated DGEBA/IPD samples. The average elastic modulus of the saturated samples decreased by 13.8%, tensile strength showed a 22.1% decrease, while strain to failure decreased by 9.4%, aligning well with other studies on the effects of water on the mechanical properties of epoxy systems [57, 74]. Overall, the saturated samples exhibited noticeable reductions in tensile strength and modulus, with a less significant decrease in strain to failure.
Comparative results of elastic modulus for the saturated experimental and simulated systems are given in Fig. 39(b). For the simulated system, $E$ was found as $4.11 \pm 0.10$ GPa, a decrease of 16.5% when compared to the dry simulated system. Overall, the simulated system captures the relative loss of elastic modulus due to the presence of absorbed water well. Though, much like the dry system, the simulation slightly overestimated the stiffness of the structure. This may partially be due to the simulation not accounting for voids, defects, or imperfections in the structure. Also, the simulated system structurally represents a highly crosslinked system, which may not align with what was experimentally tested at present. Furthermore, the simulation does not account for polar bonding of water molecules to the epoxy structure, this would likely further reduce the overall stiffness of the system.

Figure 39: Results for dry and saturated DGEBA/IPD: (a) density and (b) elastic modulus. Error bars indicating the standard deviation.

6.5.2 Glass Transition Temperature

Dynamic Mechanical Analysis (DMA) was performed on the saturated DGEBA/IPD samples using a TA DMA Q800 instrument. The testing was done in single cantilever bending mode at a loading frequency of 1 Hz, a sampling rate of 2 seconds per point was used for all data collection. Each sample was first allowed to equilibrate to 50 °C and was then heated at a constant 5 °C/min to 200 °C, Fig. 40. Altogether, ten fully saturated DGEBA/IPD epoxy samples were investigated. Table 8 summarises the data.

The average glass transition temperature for the saturated system was found as 128.62 ± 1.28 °C, a decrease of 12.5% when compared to the dry system. This result finds agreement with several other studies on the effects of absorbed water on the glass transition temperature.
Table 8: Glass transition properties of dry and saturated DGEBA/IPD.

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$T_{g \text{ onset}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>147.04 ± 0.92</td>
<td>108.21 ± 1.02</td>
</tr>
<tr>
<td>Saturated</td>
<td>128.62 ± 1.28</td>
<td>91.54 ± 1.12</td>
</tr>
</tbody>
</table>

Figure 40: Storage Modulus and tan(δ) against temperature for one dry and one fully saturated DGEBA/IPD sample.

of epoxy systems, where it is commonly cited that $T_g$ will decrease between 10-20°C/wt.% water [57, 72, 74, 75].

$T_g$ was not directly simulated, but rather the onset of $T_g$ was investigated. The average simulated $T_{g \text{ onset}}$ for the saturated system was found as 96.48 ± 3.2 °C, a decrease of 17.9% when compared to the dry system. Further, this is only 5.4% higher than the average experimental $T_{g \text{ onset}}$. Figure 41 presents comparative results on $T_{g \text{ onset}}$ for the saturated experimental and simulated systems.

Much like the elastic modulus, the simulation tends to overestimate $T_g$ for the DGEBA/IPD system. Similar sources of error seem plausible, wherein the simulated system does not account of imperfections in the structure. The highly crosslinked nature of the simulated structure artificially increases the overall stiffness and decreases chain mobility, increasing the glass transition temperature. Perhaps more significant would be the lack of accounting for polar bonding of water to the epoxy structure. Absorbed water is known to increase the chain mobility and plasticise epoxy systems, primarily as a result of water binding to polar sites throughout the polymer backbone [57, 72, 74, 75].
7 MD Simulations of Interface Adhesion

7.1 Molecular Modelling of the Slab Composite

The following chapter provides the specific procedures used in the creation of a single glass fibre slab composite interface. Details on molecular modelling of the bulk amorphous glass fibre structure are presented, where specifics of the two and three-body potentials are outlined. Simulation procedures are then provided for developing an accurate structure for an amorphous glass fibre surface. The fibre sizing system will then be considered and applied to the fibre surface. Finally, the epoxy system and the role it plays in the structure of the interface are reviewed.

The interface simulation cell was built in a stepwise fashion. First, the amorphous glass fibre structure was generated. The sizing was then applied to the glass fibre, and finally the epoxy system was introduced to the simulation. The process was carried out this way to better simulate experimental processing conditions, where the fibre is sized prior to being used for a composite layup. The result of this simulation process yields a representative glass fibre slab composite interface cell with two distinct material interfaces (i.e. fibre-sizing and sizing-epoxy).

The LAMMPS package [186] was used for all MD simulations. The Nosé-Hoover thermostat [32] and Berendsen barostat [30] were employed. Unless otherwise specified, all simulations were carried out at a pressure of 1 atm and temperature of 300 K, with full periodicity. A cutoff distance of 10 Å was used to calculate contributions per atoms to the potential energy and net forces. The procedure for making composites described next was

Figure 41: (a) Simulated elastic modulus vs. temperature for the dry and system saturated to 3.6 wt.% water and (b) \( T_g \) onset for the saturated experimental and simulated systems. Error bars indicating standard deviation.
replicated ten times to generate ten thermodynamically equivalent slab composite systems.

### 7.1.1 Glass Fibre

A modified Born-Mayer-Huggins (BMH) two-body potential [156–158, 161] was used to describe all pairwise interactions of atoms in the SiO₂ glass structure,

\[
\phi_2(r_{ij}) = A_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) + \frac{q_i q_j}{r_{ij}} \exp \left( \frac{r_{ij}}{\beta_{ij}} \right)
\]

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( q_i \) and \( q_j \) are the charges for atoms \( i \) and \( j \), and \( A_{ij} \) is a coefficient on short range repulsive terms. Table 9 provides these parameters for each pair of atoms in the system.

The Stillinger-Weber (SW) three-body potential constitutes all three atom interactions [165]. Functionally, this potential raises the system energy when the angle between covalently bonded atoms deviate from a preferred, equilibrium angle. The SW three-body potential is defined as follows,

\[
\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \left[ \cos \theta_{ijk} - \cos \theta_{ijk}^0 \right]^2 e^{\frac{\gamma_{ij}}{r_{ij} - r_{ij}^0}} e^{\frac{\gamma_{ik}}{r_{ik} - r_{ik}^0}}
\]

where \( \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) \) calculates the three body contribution to the energy potential for the three atoms \( i, j, \) and \( k \), with \( i \) as the central atom and \( j \) and \( k \) its two covalently bonded neighbours. \( \theta_{ijk} \) is the angle subtended by \( r_{ij} \) and \( r_{ik} \) with a vertex at \( i \), and \( \theta_{ijk}^0 \) is the equilibrium angle. \( \lambda_{ijk}, \gamma_{ij}, \gamma_{ik}, \) and \( r_{ij}^0 \) are constants. Table 10 provides these parameters for the system. The total potential energy for the system was calculated through combining the two and three-body contributions,

\[
U = \sum_{ij} \phi_2(r_{ij}) + \sum_{ijk} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})
\]

A melt-quench procedure was used to simulate the bulk amorphous SiO₂ (a-SiO₂) glass.
Table 10: Parameters in the three-body contribution to the energy potential

<table>
<thead>
<tr>
<th></th>
<th>Si-O-Si</th>
<th>O-Si-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ (kcal mol$^{-1}$)</td>
<td>2734.10</td>
<td>43.17</td>
</tr>
<tr>
<td>$\theta^0$ (deg)</td>
<td>160.50</td>
<td>109.50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Si-O</th>
<th>O-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (Å)</td>
<td>2.8</td>
<td>—</td>
</tr>
<tr>
<td>$r^0$ (Å)</td>
<td>Si-O</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>O-Si</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Fibre surfaces were then created from each 2880 atom bulk a-SiO$_2$ structure by immobilising the bottom 720 atoms in the simulation cell and removing the periodic boundary conditions in the $z$-direction. Together, this simulates the top 2160 atoms of the simulation
Figure 43: The RDF for the generated a-SiO$_2$ structure (solid) vs. experimentally determined values [210] (dashed)

cell being in direct contact with vacuum conditions while the bottommost atoms are fixed, indicating bulk material. To allow the surface to relax, 50 ps of NVT dynamics were run at 300 K. Altogether, ten separate a-SiO$_2$ surface structures were generated, each simulated from an independently generated bulk, a-SiO$_2$ structure.

Figure 44 provides the Si-O-Si bond angle distributions for (a) bulk and (b) within 1 Å from surface. Investigations on Fig. 44 show that the Si-O-Si bond angles within bulk SiO$_2$ are well grouped about the equilibrium angle value provided through the force field for the system. When the SiO$_2$ surface was formed, Fig. 44 shows an emergence of lower angle Si-O-Si bonds, predominately near 110°. Similar shifts in Si-O-Si bond angles when forming SiO$_2$ surfaces have been seen previously [158].

This shift can be attributed to strained siloxane bonds forming along the surface structure. The number of strained siloxane bonds along the surface can be determined by taking the area under the 110° peak and dividing by the area under the entire surface curve (Fig. 44(b)) and multiplying this by number of contributing oxygen atoms [157]. Over the ten simulated SiO$_2$ surface structures, an average value of 1.61 strained siloxane bonds per 100 Å$^2$ was calculated. This finds reasonable agreement with values reported in literature; where Altug et al. [211] reported a value of 1.4 per 100 Å$^2$, and Garofalini [157] indicated a value of 1.54 per 100 Å$^2$.

7.1.2 Fibre Sizing

Specifics on fibre sizing are ambiguous, where the precise amount and exact composition at any given portion of the fibre is generally not known. The amount of sizing applied to
7 MD SIMULATIONS OF INTERFACE ADHESION

Figure 44: The Si-O-Si bond angle distribution for bulk (solid-red) and atoms within 1Å from surface (dashed-blue).

a glass fibre surface is generally reported as a wt.% and can vary between 0.2 to 1.0 wt.%. Of this 0.2 to 1.0 wt.%, it has been shown that approximately 10 - 20% is assumed to be strongly bounded silane coupling agent component, while the remaining 80 - 90% constitute film forming agents and other additives that ease handling and manufacturing procedures, but do not significantly contribute to overall interface strength [12, 111]. For the purposes of this work only the strongly bound silane coupling agent portion of the sizing was modelled.

The silane coupling agent γ-Aminopropyltriethoxysilane (AMPTES) was selected as sizing for the system, see Fig. 45. A molecular model of AMPTES was constructed within the Avogadro molecule editor [187, 188]. Steepest decent energy minimization was then performed using Avogadro to geometrically optimize the molecular structure. Partial charges were then assigned to each atom through application of the Qeq method [189]. The CHARMM force field was employed in defining the bond, angle, and dihedral parameters [25].

Figure 45: The molecular structure of the silane coupling agent γ-Aminopropyltriethoxysilane (AMPTES)

The total unit mass for a complete fibre diameter was calculated to determine the number
of AMPTES molecules to include, where it was assumed that 0.2 wt.% represents the total mass of silane coupling agent on the fibre (20% of the assumed 1.0 wt.% sizing applied). Assuming a fibre diameter of 10 \( \mu \text{m} \), a total of 146 AMPTES molecules equates to 0.2 wt.% silane sizing on the simulated fibre surface. Using Packmol [190], 146 AMTPES molecules were placed adjacent to the fibre surface: the rotation and orientation of each molecule was constrained such that the functional silane group was perpendicular to the a-SiO\(_2\) surface. The packing tolerance was specified as 2 Å. The bottommost 720 atoms of the SiO\(_2\) were immobilised and the periodic boundary removed in the \( z \)-direction. The system was equilibrated with 50 ps of NVT, Fig 46.

### 7.1.3 Epoxy

The procedures for generating and crosslinking the bulk DGEBA/IPD epoxy system were identical to those discussed previously in Chapter 5. The \( x \) and \( y \) dimensions for the simulation cell were fixed and known from the a-SiO\(_2\) surface cell generated previously. In the present case, the simulation cell must be suitably thick in the \( z \)-direction as to provide the most accurate possible representation for bulk (non-interface) epoxy.

256 reactive DGEBA and 128 reactive IPD molecules were packed above the existing sized glass fibre cell to a thickness of 100 Å. The packing tolerance was specified as 2 Å. A cell thickness of 100 Å ensured the far field epoxy molecules remain unaffected by local interface interactions. At this point, the complete simulation cell dimensions (glass fibre, sizing, and epoxy) were 44.78 Å \( \times \) 45.05 Å \( \times \) 132.71 Å. Initially, the system was subjected to 50 ps of NVT. As with the previous simulations, the same 720 bottommost SiO\(_2\) atoms were immobilised. The relaxed epoxy structure was then dynamically crosslinked under NVT.
The DGEBA/IPD system was successfully crosslinked to 91.5%. All epoxy molecules within 15 Å of the top epoxy surface and the bottommost 720 atoms of the SiO₂ atoms were immobilised. This effectively simulated a semi-infinite composite slab interface where there exists bulk a-SiO₂ at one end of the cell and a bulk crosslinked DGEBA/IPD epoxy network at the other, Fig. 47. The full slab interface was further equilibrated under an NVT ensemble. After every 10 ps, a time-averaged potential energy value over the previous 10 ps was calculated. The system was considered equilibrated when the difference in system potential energy was less than 0.5% from the previous time-averaging, or after 200 ps of total simulation time.

Figure 47: MD visualisation of the complete slab composite interface structure with approximate dimensions.
7.1.4 Summary

1. Generation of glass fibre structure
   (a) 2880 atom $\alpha$-quartz $\text{SiO}_2$ structure used as the starting configuration
   (b) 20 ps of NVT dynamics at 5000 K to equilibrate the glass melt.
   (c) Quenched under NPT conditions at a constant rate over 200 ps to 300 K.
   (d) Further equilibration under NVT for 50 ps.
   (e) The bottommost 720 atoms were then immobilised and the periodic boundary removed in the $z$-direction.
   (f) 50 ps of NVT dynamics at 300 K.

2. Sizing the fibre
   (a) Assuming a fibre diameter of 10µm, a total of 146 AMPTES molecules equated to 0.2 wt.% sizing on the simulated fibre surface.
   (b) 146 AMTPES molecules are placed adjacent to the fibre surface, where the rotation and orientation of each AMPTES atom was restrained such that the functional silane group was aligned perpendicular to the fibre surface.
   (c) The bottommost 720 $\text{SiO}_2$ atoms were immobilised and the periodic boundary conditions removed in the $z$-direction.
   (d) 50 ps of NVT dynamics at 300 K.

3. Epoxy
   (a) 256 reactive DGEBA molecules and 128 reactive IPD molecules were packed above the existing sized glass fibre simulation cell.
   (b) 50 ps of NVT at 300 K (720 bottommost $\text{SiO}_2$ atoms immobilised.)
   (c) The DGEBA/IPD system was dynamically crosslinked to 91.5%

4. The interface
   (a) All epoxy molecules within 15 Å of the top surface were immobilised
   (b) The full interface structure was equilibrated for 200 ps under NVT conditions at 300 K.

7.2 Composite Manufacture

Unidirectional [0]_4 glass fibre [Saertex U14EU920] samples were manufactured using Vacuum Assisted Resin Transfer Moulding (VARTM) method. The VARTM process involves
pulling a vacuum across the work piece to assist the infusion of the resin into the fabric system. Most commonly, there is a rigid mould to provide part geometry on one side, with a thin flexible membrane, with outer atmospheric pressure compressing the fibers tightly against the mould, on the other. VARTM is a cost effective method in the production of high quality composite material parts, and consequently the process is common across industry. The epoxy DGEBA/IPD [Sigma-Aldrich] was allowed to cure for 24 hours at room temperature, and was post cured for 2 hours at 160 °C.

ImageJ was used to perform microstructure analysis on the composite to asses the fibre volume fraction $V_f$ of the resulting composite. For each plate manufactured, three microstructure samples were mounted, polished, and examined underneath a microscope. The fibre volume fraction was recorded through taking several representative images from each mounted sample, then converting these to a binary mask and taking a ratio between the binary portions of the image, Fig. 48. The average fibre volume fraction was found to be $56.3 \pm 2.5\%$.

All GFRP composite samples were submersed in distilled water which was held at ambient room temperature until full saturation was achieved. A consistent methodology of measuring the weight gain of the samples throughout the saturation process was established. Initially, the dry weights of all the samples were recorded and the samples were then placed in the water. In order to take weight gain measurements, the samples were removed from the water and were then dabbed dry using a paper towel, being careful to not leave any residual contaminants that may skew the resulting weight gain measurements. The samples were then allowed to dry for an hour to allow the majority of the surface moisture to evaporate off; the purpose of this drying period was to minimize weight gains from sources not related to diffusion. The samples were then individually weighed on a scale, with accuracy to $\pm 0.1$ mg. Finally, the samples were placed back into the water bath to continue the process. This
process was rigorously followed for each weight gain measurement throughout the entire saturation process. The average experimental solubility limit for the unidirectional [0]_{4} samples was found as $1.15 \pm 0.02$ wt.%, Fig. 49. All samples exhibited Fickian uptake behaviours, with initially linear uptake portion before diffusion slows and the solubility limit is reached.

### 7.3 Saturating the Interface

#### 7.3.1 Grand Canonical Monte Carlo Exchanges

Determining when the slab composite interface is saturated with water is complicated by the inhomogeneous nature of the system. In our previous work a hybrid particle insertion/thermodynamic integration method was used to determine the solubility limit of water in bulk DGEBA/IPD [212]. In this case the relative location of the absorbed water was of utmost importance, meaning that a different method was needed for placing water molecules at preferential locations.

In order to address this issue, Grand Canonical Monte Carlo (GCMC) exchanges of noble water molecules were performed. The noble molecules have Coulombic interactions deactivated, Lennard-Jones interactions of the hydrogen atoms switched off, and the oxygen atoms are scaled to 80% of their original size. This scaling leads to a much higher success rate of particle exchanges, greatly decreasing computational time. After saturation, all noble water molecules were scaled back to full TIP3P [203] water interactions.

Fundamentally, GCMC performs exchanges of atoms with a fictitious reservoir at a specified temperature $T$ and chemical potential $\mu$. For each exchange made, particle coordinates and relative orientation were randomly generated, the total potential energy for the system
was calculated. The relative orientation of the atom at the given coordinate was changed until either (i) the Metropolis Criterion [213, 214] was satisfied or (ii) the maximum number of orientation changes was reached. If the Metropolis Criterion was satisfied, the insertion was successful, the atom was permanently added to the system, and another insertion at a new, randomly generated coordinate was attempted. If the maximum number of orientation changes was reached without satisfying the Metropolis Criterion, then no molecule was added to the system and another insertion at a new, randomly generated coordinate was attempted.

In the context of determining the saturation, the interface reaches saturation when no further insertions are possible. To undertake GCMC exchanges it was inherently necessary to designate both the temperature and chemical potential for the fictitious reservoir. Therefore, the chemical potential for a reservoir of noble water atoms was calculated. Recall, the definition of chemical potential [149, 150],

\[ \mu = \mu_{\text{ex}} + \mu_{\text{id,trans}} + \mu_{\text{id,rot}} \] (7.4)

where \( \mu_{\text{ex}} \) is the excess chemical potential (Chapter 6 discusses the theory and methodology used in calculating the excess chemical potential). While, \( \mu_{\text{id,trans}} \) and \( \mu_{\text{id,rot}} \) are the translational and rotational portions of the ideal chemical potential, respectively. The translational portion of the ideal chemical potential is defined as follows,

\[ \mu_{\text{id,trans}} = RT \ln(n\Lambda_T^3) \] (7.5)

where \( R \) is the universal gas constant, \( T \) is the temperature, \( n \) is the number density, and \( \Lambda_T \) is the thermal de Broglie wavelength,

\[ \Lambda_T = \frac{h}{\sqrt{2\pi mk_BT}} \] (7.6)

where \( h \) is the Planck constant, \( m \) the mass of the atom, and \( k_B \) the Boltzmann constant. The rotational portion of the ideal chemical potential is as follows,

\[ \mu_{\text{id,rot}} = -RT \ln(q_{\text{rot}}) \] (7.7)

where,

\[ q_{\text{rot}} = \frac{(2k_BT)^{3/2}(\pi I_1 I_2 I_3)^{1/2}}{2h^3} \] (7.8)

is the classical rotational partition function. Here, \( I_1, I_2, \) and \( I_3 \) are principal moments of inertia.
To undertake GCMC exchanges, it was necessary to designate the temperature and chemical potential for the exchange reservoir. Therefore, the chemical potential for noble water was calculated [149, 150], where 30 configurations of a 500 molecule noble water system were considered. Widom’s particle insertion method [144] was used to find the excess chemical potential $\mu_{ex}$ of pure noble water (process as described previously in §6.2.1, but using noble water in place of pure, real water). The translational and rotational portions of the ideal chemical potential were then calculated using eqns. (7.5) and (7.7).

Altogether, using Eqn. (7.4), an average chemical potential of -14.86 kJ mol$^{-1}$ was found for noble water at 300 K and 1 atm, Fig. 50. GCMC exchanges were then undertaken in the epoxy and sizing. All noble water molecules were scaled back to the full TIP3P water model using ten equidistant scaling steps, where each step was equilibrated for 20 ps of NPT.

A brief, itemised summary of the processes used in saturating each of the ten interfaces considered is given as follows,

1. GCMC insertions of noble water atoms at 300 K and $\mu$ = -14.86 kJ mol$^{-1}$
   (a) Randomly selected insertion position throughout sizing and epoxy.
   (b) Metropolis Criterion used to determine if attempt was successful.
   (c) A maximum of 10,000 unsuccessful atom exchange per insertion attempt.
   (d) GCMC process cutoff after 1,000 unsuccessful insertion attempts.

2. Iterative resizing of noble water atoms back to full scale.
   (a) Ten equidistant scaling steps.
Figure 51: The water weight content calculated using a moving 5 Å window, where each point represents the average (over the ten simulated slab composites) wt.% water for the previous 5 Å. The shaded regions represent the average wt.% water in the epoxy (yellow) and the sizing (blue).

(b) After each step, 20 ps of NVT dynamics at 300 K.

### 7.3.2 Saturation

Using the GCMC insertion process, an average of 244 water molecules were successfully inserted into each slab composite, corresponding to 2.07 wt.% water. The water weight content was calculated from the top surface of the epoxy using a moving 5 Å window for the ten simulated composite slab structures, Fig. 51. The average average water contents was taken as the solubility limit. The epoxy shows a solubility limit of $3.35 \pm 0.23$ wt.%, aligning with a simulated solubility limit for bulk DGEBA/IPD in the range of 3.50 - 3.75 wt.% water found in our previous work (§6.2 and [212]). The sizing shows a distinct increase in solubility limit with an average of $5.35 \pm 0.33$ wt.%. This suggests that there are more preferential locations for absorbed water molecules closer to the fibre surface, in agreement with experimental studies [56, 120]. This could be attributed to the comparatively less dense sizing. Fibre volume fraction ($V_f$) was not taken into account when generating the simulated slab composite interface system, as a result, the simulated solubility limit cannot be immediately compared to experimental values. To provide a comparable simulated value for the solubility limit, the modelled interface geometry needs to be extrapolated to an
Figure 52: Extrapolation process used in moving from simulated interface to full composite cross-section.

The definition of $V_f$, $V_f = \frac{A_f}{A_e + A_s + A_f}$ (7.9)

where $A_f$, $A_e$, and $A_s$ represent the cross sectional area of the fibre, epoxy, and sizing. $A_f$ is found with a given $V_f$ and a total cross sectional area. By assuming a fibre diameter $d$, the total circumferential length for $n$-fibres can be found ($n$ being the number of fibres of diameter $d$ required to satisfy the given $A_f$). This total circumferential length $\times$ the thickness of the sizing layer gives the cross-sectional area of the sizing, $A_s$, and $A_e$ was then found, Eqn. (7.9). The solubility limit $M_c$ (wt.% water) for a equivalent full composite was calculated,

$$M_c = \frac{\rho_e V_e M_e + \rho_s V_s M_s + \rho_f V_f M_f}{\rho_e V_e + \rho_s V_s + \rho_f V_f}$$ (7.10)

where the subscripts $e$, $s$, and $f$ represent the epoxy, sizing, and fibre, and $V$ is the volume, $\rho$ the saturated density, and $M$ is the solubility limit in wt.% water. $M_e$ was taken as 3.35 wt.% and $M_s$ as 5.35 wt.% (Fig. 51) and, glass fibre was assumed impermeable, giving $M_f = 0$. The experimental volume fraction of fibres $V_f = 56\%$, an average fibre diameter of 10 $\mu$m, and a 10 Å thick sizing layer (Fig. 47) were used. Equation (7.10) gives the solubility limit for the full composite $M_c = 0.99$ wt.% The average experimental solubility limit for the unidirectional $[0]_4$ samples was found as 1.15 ± 0.02 wt.%, indicating the simulated system underestimated by 13.7%.
The simulated interface system used a fixed sizing thickness of 10 Å, while in reality this thickness will be far greater. An estimate for the sizing thickness can be made through iterative applications of Eqn. (7.10) until \( M_c \) equals the experimentally determined value of 1.15 wt.% water. Using this method, an estimated sizing thickness of 147.3 nm was found. This was within the range of silane sizing thickness reported, 1 nm - 1 \( \mu \)m [215, 216].

7.4 Adhesion at the Interface

7.4.1 Surface Energy

The surface energy \( \gamma \) is a material property that quantifies the amount of energy required to form a new surface. The surface energy was calculated as follows [176, 177],

\[
\gamma = \frac{U_{slab} - U_{bulk}}{2A}
\]  

where, \( U_{slab} \) and \( U_{bulk} \) are the potential energies for the slab and bulk material, while \( A \) is the projected surface between the surfaces.

The bulk structures for the a-SiO\(_2\), AMPTES sizing, and DGEBA/IPD epoxy were extracted from the slab composite interface (Fig. 47). Slab structures were created by extending the size of the periodic simulation box of the bulk material in the ±z-directions by 50 Å and padding with vacuum. This was done to prevent periodic interactions between the top and bottom surfaces; therefore, the resulting cell becomes representative of a semi-infinite, slab surface. Next, the slab surfaces were subjected to 100 ps of NVT, and the trajectory was saved every 0.5 ps over the final 20 ps. The trajectory with the lowest total potential energy was further minimised in order to create the final slab surface. Surface energy for each constituent was then calculated, Eqn. (7.11).

To better understand the effects of absorbed water on the a-SiO\(_2\) surface structure, the RDF for a-SiO\(_2\) extracted from the slab composite system was investigated as a function of depth for dry and fully saturated conditions, Fig. 53. The RDF was taken for 2 Å thick slabs moving from the free surface to the representative bulk material and is taken as an average of 1 ps of simulation. Moving from the bulk towards the surface, the RDF in both cases show unique characteristics not seen in the bulk, becoming especially pronounced at the 2 Å closest to the surface.

For the structure extracted from the dry system, Fig. 53(a), the Si-O peak is seen to decrease in height while increasing in width, in agreement with literature and has been shown to be due to straining of Si-O bonds at the surface [157]. The O-O peak becomes more pronounced while the Si-Si peak diminishes. Overall, the RDF for a-SiO\(_2\) structure extracted from the slab composite seems to be a reasonable representation of an a-SiO\(_2\)
Figure 53: The RDF as a function of depth for SiO$_2$ extracted from the (a) dry and (b) saturated slab composite. The top curve (0 Å) represents the surface, while the bottom (10 Å) represents the bulk.

Surface [157, 158]. For the a-SiO$_2$ extracted from the saturated structure, Fig. 53(b), the interactions with the absorbed water near the surface cause structural differences to arise. When compared to the dry structure, the Si-O became wider, while the O-O peak is not as pronounced. Characteristically, this aligns with other studies on the effects of water on the a-SiO$_2$ surface [217, 218]. With the present force field, the extracted a-SiO$_2$ surface structures seem to be structurally reasonable for both dry and saturated conditions.

Figure 54 provides a summary of each calculated surface energy value, while Table 11 provides the contributions to each potential energy term. For each, it was seen that non-bonded energy terms are generally larger than other internal, bonded interactions, and therefore carries a more significant contribution to the free surface energy in the system, consistent with other studies [176, 179].
Figure 54: Simulated surface energies for the dry system, represented as smoothed distributions over ten separately generated structures for each.

Table 11: The contributions to surface energy for SiO$_2$, sizing, and epoxy under dry conditions. The total potential represents the sum of all non-bonded (repulsive and dispersive Lennard-Jones and electrostatic terms) and bonded interactions (bond stretching, bond angle bending, and torsional terms).

<table>
<thead>
<tr>
<th></th>
<th>$U_{\text{bulk}}$ (kcal mol$^{-1}$)</th>
<th>$U_{\text{slab}}$ (kcal mol$^{-1}$)</th>
<th>$\gamma$ (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SiO$_2$</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Potential</td>
<td>211932.2</td>
<td>212397.4</td>
<td>59.79</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>121755.1</td>
<td>122035.6</td>
<td>36.06</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>28928.8</td>
<td>28876.1</td>
<td>-6.77</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>61248.4</td>
<td>61485.7</td>
<td>30.49</td>
</tr>
<tr>
<td>Torsion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sizing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Potential</td>
<td>37755.5</td>
<td>37897.7</td>
<td>18.28</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>13101.2</td>
<td>13207.8</td>
<td>13.71</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>6909.3</td>
<td>6875.5</td>
<td>-4.34</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>8457.2</td>
<td>8439.0</td>
<td>-2.35</td>
</tr>
<tr>
<td>Torsion</td>
<td>9287.9</td>
<td>9375.4</td>
<td>11.26</td>
</tr>
<tr>
<td><strong>Epoxy</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Potential</td>
<td>305792.4</td>
<td>306134.6</td>
<td>39.07</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>100636.3</td>
<td>100884.9</td>
<td>28.38</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>69200.8</td>
<td>69109.3</td>
<td>-10.45</td>
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<tr>
<td>Bond angle bending</td>
<td>75805.9</td>
<td>75756.1</td>
<td>-5.69</td>
</tr>
<tr>
<td>Torsion</td>
<td>60149.4</td>
<td>60384.3</td>
<td>26.83</td>
</tr>
</tbody>
</table>
Table 12: Surface energies (mJ m$^{-2}$) for dry and saturated conditions.

<table>
<thead>
<tr>
<th></th>
<th>Dry</th>
<th>Saturated</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>$59.79 \pm 3.01$</td>
<td>$55.11 \pm 5.81$</td>
<td>-6%</td>
</tr>
<tr>
<td>DGEBA/IPD</td>
<td>$39.07 \pm 2.24$</td>
<td>$28.28 \pm 4.08$</td>
<td>-28%</td>
</tr>
<tr>
<td>AMPTES</td>
<td>$18.28 \pm 1.83$</td>
<td>$14.81 \pm 3.74$</td>
<td>-20%</td>
</tr>
</tbody>
</table>

Figure 55: The surface energy, $\gamma$, for SiO$_2$, DGEBA/IPD epoxy, and AMPTES sizing under dry and saturated conditions. The error bars indicate standard deviation over the ten slab composites.

Table 12 and Fig. 55 provide summaries and comparisons of the calculated surface energies for dry and saturated conditions. Results show that SiO$_2$ exhibits the largest average surface energy, while the AMPTES sizing showed the lowest. The DGEBA/IPD epoxy experienced the greatest decrease due to the presence of absorbed water. Conversely, SiO$_2$ was least impacted. While there are no experimental values for a-SiO$_2$ in vacuum, the surface energy of bulk a-SiO$_2$ at 350 K in vacuum has been reported as 100 mJ m$^{-2}$ [219]. The discrepancy between this and the value of $59.79 \pm 3.01$ mJ m$^{-2}$ simulated presently may be related to differences in force field parameters. The simulated surface energy for AMPTES finds excellent agreement with a value of 18.08 mJ m$^{-2}$ previously simulated at 300K, 1 atm [177].

7.4.2 Work of Adhesion

The strength of fibre composites is directly derived from adhesion at the interface and its ability to transfer stress from the matrix to the reinforcement. Work of adhesion provides a means of quantifying the strength of a material interface. Therefore, through examining the work of adhesion for the composite interface, and observing changes under both dry and
saturated conditions, conclusions on moisture degradation can be reached. Fundamentally, the work of adhesion, $W_{12}$, is the amount of work required to separate two adjacent phases 1 and 2,

$$W_{12} = \frac{U_{\text{slab},1} + U_{\text{slab},2} - U_{12}}{2A} \quad (7.12)$$

where, $U_{\text{slab},1}$ and $U_{\text{slab},2}$ are the potential energies for slab materials 1 and 2, $U_{12}$ is the potential energy for the entire, combined system.

The work of adhesion was calculated for (i) fibre-sizing and (ii) sizing-epoxy interfaces, Fig. 56. The SiO$_2$-epoxy (unsized) interface was used as a point of comparison. Imagine separating the system at the interface between SiO$_2$-sizing, leaving two distinct structures (1) SiO$_2$ and (2) sizing-epoxy (sizing which is still bound to the epoxy). This means that, for each case, $U_{12}$ was the total potential energy of the entire interface simulation cell, and should remain constant throughout. While $U_{\text{slab},1}$ and $U_{\text{slab},2}$ are the potential energy of each separated constituent represented as a slab surface structure.

The potential energy for the slab composite $U_{12}$ was considered as a time-averaged value over 20 ps of simulation. The two instances of interface separation were then considered, each requiring the creation of two slab surfaces. Therefore, four slabs were created: SiO$_2$, sizing-epoxy, epoxy, and SiO$_2$-sizing. The slabs were created (as for surface energy) and potential energy determined. Work of adhesion was then calculated, Eqn. (7.12). A brief, itemised list of the simulation procedures used in the calculation of the work of adhesion,
7 MD SIMULATIONS OF INTERFACE ADHESION

Figure 57: Simulated work of adhesion for the dry system, represented as smoothed distributions over ten slab composite structures.

1. $U_{12}$ is taken as time average over 20 ps of NVT at 300 K (Fig. 47).
2. Structures are extracted for (i) SiO$_2$, (ii) sizing-epoxy, (iii) epoxy, and (iv) SiO$_2$-sizing. This represented each possible case of interface separation.
3. Slab surfaces are created for each by padding the simulation box with 50 Å of vacuum in the ±z directions.
4. 100 ps of NVT for each slab surface. For each, the lowest energy system trajectory over the final 20 ps is further minimised and used for potential energy collection.

To illustrate the significant impact that fibre sizing systems have on the overall performance of glass fibre composites, an interface with no fibre sizing was also simulated using the same procedures as above. This yields a system with one effective interface directly between SiO$_2$ and epoxy. Figure 57 provides a summary of the data, while Table 13 provides the detailed time-averaged values for the interfacial and slab surface energies, and the work of adhesion $W_{12}$. Figure 57 provides a summary of the data for the dry system, while Table 13 provides the detailed time-averaged values for the interfacial and slab surface energies, and the work of adhesion $W_{12}$. On investigations it is seen that non-bonded interactions are the dominant contribution to the overall adhesion in the system. Torsional terms in the sizing and epoxy also are seen to make substantial contributions.
Table 13: The potential energy contributions to the average work of adhesion for each dry interface, taken as an average over ten separately generated structures. An unsized fibre system was also considered. Note, The total potential represents the sum of all non-bonded (repulsive and dispersive Lennard-jones and electrostatic terms for AMPTES and epoxy) and all bonded interactions (bond stretching, bond angle bending, and torsional terms)

<table>
<thead>
<tr>
<th>SiO$_2$-sizing</th>
<th>$U_{slab,1}$ (kcal mol$^{-1}$)</th>
<th>$U_{slab,2}$ (kcal mol$^{-1}$)</th>
<th>$U_{12}$ (kcal mol$^{-1}$)</th>
<th>$W_{12}$ (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Potential</td>
<td>212397.4</td>
<td>346134.0</td>
<td>555480.1</td>
<td>392.21</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>122022.3</td>
<td>120108.5</td>
<td>239785.7</td>
<td>310.44</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>28992.2</td>
<td>63342.5</td>
<td>92551.7</td>
<td>-27.89</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>61382.8</td>
<td>77534.0</td>
<td>139036.7</td>
<td>-15.40</td>
</tr>
<tr>
<td>Torsion</td>
<td>-</td>
<td>85149.0</td>
<td>84106.0</td>
<td>134.06</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sizing-epoxy</th>
<th>$U_{slab,1}$ (kcal mol$^{-1}$)</th>
<th>$U_{slab,2}$ (kcal mol$^{-1}$)</th>
<th>$U_{12}$ (kcal mol$^{-1}$)</th>
<th>$W_{12}$ (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Potential</td>
<td>251308.8</td>
<td>306143.6</td>
<td>555480.1</td>
<td>252.35</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>140414.7</td>
<td>100748.9</td>
<td>239785.7</td>
<td>177.11</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>23310.7</td>
<td>69278.3</td>
<td>92551.7</td>
<td>4.78</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>62943.0</td>
<td>75890.8</td>
<td>139036.7</td>
<td>-26.08</td>
</tr>
<tr>
<td>Torsion</td>
<td>24640.4</td>
<td>60216.7</td>
<td>84106.0</td>
<td>96.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SiO$_2$-epoxy</th>
<th>$U_{slab,1}$ (kcal mol$^{-1}$)</th>
<th>$U_{slab,2}$ (kcal mol$^{-1}$)</th>
<th>$U_{12}$ (kcal mol$^{-1}$)</th>
<th>$W_{12}$ (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Potential</td>
<td>212397.4</td>
<td>306143.6</td>
<td>516914.9</td>
<td>207.85</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>122022.3</td>
<td>100748.9</td>
<td>221751.7</td>
<td>131.05</td>
</tr>
<tr>
<td>Bond stretching</td>
<td>28992.2</td>
<td>69278.3</td>
<td>98131.1</td>
<td>17.92</td>
</tr>
<tr>
<td>Bond angle bending</td>
<td>61382.8</td>
<td>75890.8</td>
<td>137228.9</td>
<td>5.75</td>
</tr>
<tr>
<td>Torsion</td>
<td>-</td>
<td>60216.7</td>
<td>59803.3</td>
<td>53.13</td>
</tr>
</tbody>
</table>

The work of adhesion at each interface was then considered for both dry and saturated conditions, Table 14 and Fig. 58. For the dry system, the SiO$_2$-sizing interface was found to have the largest work of adhesion, while sizing-epoxy was much lower, indicating that sizing-epoxy in the critical interface for failure. The SiO$_2$-epoxy (unsized) interface shows significantly lower adhesion when compared to the sized system and was calculated as 207.85 mJ m$^{-2}$, in agreement with contact angle measurements, which have shown a range of $W_{12} = 178 - 291$ mJ m$^{-2}$ for SiO$_2$-epoxy interfaces [220]. Furthermore, the simulated value lies just above a range of 147 - 188 mJ m$^{-2}$ suggested for a simulated SiO$_2$-epoxy interface [180]. For saturated conditions, the relative adhesion difference between SiO$_2$-sizing and sizing-epoxy is greatly diminished, however, the sizing-epoxy interface was again found to be the critical system interface.
Table 14: Work of adhesion (mJ m$^{-2}$) for dry and saturated conditions for (a) SiO$_2$-sizing, (b) sizing-epoxy, and (c) SiO$_2$-epoxy (unsized)

<table>
<thead>
<tr>
<th></th>
<th>Dry</th>
<th>Saturated</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>392.21 ± 14.23</td>
<td>267.88 ± 21.33</td>
<td>-32%</td>
</tr>
<tr>
<td>(b)</td>
<td>252.35 ± 11.30</td>
<td>191.01 ± 26.07</td>
<td>-24%</td>
</tr>
<tr>
<td>(c)</td>
<td>207.85 ± 13.07</td>
<td>148.61 ± 22.19</td>
<td>-29%</td>
</tr>
</tbody>
</table>

Figure 58: The work of adhesion, $W_{12}$, for (a) SiO$_2$-sizing, (b) sizing-epoxy, and (c) SiO$_2$-epoxy (unsized) interfaces under dry and saturated conditions. The error bars indicate standard deviation over the ten slab composites.

It is important to note that, in reality, the sizing forms an interpenetrating polymer network with the epoxy [113]. These rather complex network interactions make it difficult predicting where in the interface failure will occur. The simulated slab composite had an idealised geometry, from which failure in both dry and saturated systems is predicted to occur at the sizing-epoxy interface.

Trajectories were saved throughout the GCMC saturation process at 0.5, 1.0, and 1.5 wt.% water, allowing $W_{12}$ for each interface as a function of equivalent composite water content to be calculated, Fig. 59. The steeper slope of the SiO$_2$-sizing interface indicates a higher sensitivity to water content compared to sizing-epoxy. If these trends were to continue, at some $M_c > 0.99$ wt.%, SiO$_2$-sizing could become the controlling, critical interface. This could be achieved at $T > 300$ K and/or $P > 1$ atm [64].

The work of adhesion for each interface in the slab composite was further investigated through breaking down the individual contributions at varying water contents, Table 15 and Fig. 60. It is clear that non-bonded (Van der Waals and Coulombic) and torsional terms make the largest contribution to adhesion. This result aligns with other studies on
Figure 59: The work of adhesion for each interface with increasing wt.% water in the equivalent full composite. Errors bars indicate standard deviation about the ten interface structures.

Table 15: Average contributions to the simulated interface work of adhesion (mJ m$^{-2}$) for dry and saturated conditions.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$ - sizing</th>
<th>sizing-epoxy</th>
<th>SiO$_2$ - epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Sat</td>
<td>Change</td>
</tr>
<tr>
<td>Non-bonded</td>
<td>303.48</td>
<td>213.20</td>
<td>-30%</td>
</tr>
<tr>
<td>Torsion</td>
<td>131.05</td>
<td>107.08</td>
<td>-18%</td>
</tr>
<tr>
<td>Stretching</td>
<td>-27.26</td>
<td>-33.27</td>
<td>-22%</td>
</tr>
<tr>
<td>Bending</td>
<td>-15.05</td>
<td>-19.13</td>
<td>-27%</td>
</tr>
<tr>
<td>Total</td>
<td>392.21</td>
<td>267.88</td>
<td>-32%</td>
</tr>
</tbody>
</table>

adhesion at polymer-polymer [176], SiO$_2$-epoxy [180], and polymer-silane [177] interfaces. In addition to making the largest overall contribution to adhesion, non-bonded terms exhibit the greatest sensitivity to the presence of absorbed water and dominate the loss of adhesive strength. Theoretically, adhesion loss could be significantly minimised through altering the sizing or epoxy systems in a way such that the non-bonded and torsional contributions are retained with increasing composite water content.

In addition to making the largest overall contribution to adhesion, non-bonded terms exhibit the greatest sensitivity to the presence of absorbed water. This indicates that non-bonded (and to a lesser degree torsional) contributions to the system potential are the primary contributors to adhesion loss at the interface. Theoretically, adhesion loss could be significantly minimised through altering the fibre sizing or epoxy systems in a way such that the non-bonded and torsional terms are retained with increasing water content.
Figure 60: Contributions to the work of adhesion for (a) SiO$_2$-sizing, (b) sizing-epoxy, and (c) SiO$_2$-epoxy (unsized). The error bars indicate standard deviation over the ten slab composite interface structures.
7.5 Tensile Testing

Tensile testing was conducted in accordance with ASTM D3039 [221], 20 individual tensile testing coupons were cut from the unidirectional composite plates to dimensions of 15 mm × 200 mm. Half of the samples were placed in distilled water at room temperature and weight gains were tracked until full saturation was achieved. Friction tabs were used during tensile testing to help mitigate gripping damage to the specimens. A constant crosshead speed of 1 mm/min was used and axial strain was recorded via video extensometer. When calculating the elastic modulus, the slope of the stress-strain curves between $\epsilon_1 = .001$ and $\epsilon_2 = .003$ (as per ASTM D3039).

Figure 61 provides the tensile stress-strain curves for the considered dry and saturated samples. Table 16 summarises the tensile testing data. For the dry samples, the average elastic modulus ($E$), tensile strength ($UTS$), and strain to failure ($\epsilon_f$) compared well with values of $E = 34.4$ GPa, $UTS = 763$ MPa, and $\epsilon_f = 2.61\%$ suggested for a $[0]_4$ composite with $V_f = 52\%$ using the same glass fibre [Saertex U14EU920] and epoxy system [222]. The average elastic modulus of the saturated samples decreased by 14%, tensile strength showed a 19% decrease, while strain to failure decreased by 11%, aligning well with other studies on the effects of water on the mechanical properties of glass fibre composites [87, 88]. Overall, the saturated samples exhibited noticeable reductions in Tensile Strength and Modulus, with
Figure 62: Predicted tensile strength with increasing composite water content.

...a less pronounced decrease in strain to failure.

The presence of absorbed water in the epoxy matrix is expected to plasticise the network, lowering the modulus and reducing its overall strength (recall §6.4, Table 7). These decreases in modulus and strength would directly lead to overall degradations in the composite system. From a strictly micromechanics (rule of mixtures) formulation, the matrix degradations alone would not account for all degradations in the composite.

Residual stresses are commonly introduced into a composite laminate during the fabrication process. These residual stresses can arise as a consequence of mismatched expansion coefficients between fibre and matrix, or purely interlaminar in nature. Micro-cracks commonly develop at concentrated areas of residual stress. When the system is subjected to long term moisture exposure, the water penetrates microcracks, leading to a further increase in both size and severity of the crack. This new damage only leads to further moisture absorption and eventually leads to interface failure. It is this cycle of residual stress, microcracking, and water absorption that more likely tends to control the overall performance of a composite system that is subjected to long term water exposure.

A linear relationship between work of adhesion and tensile strength for silica particle reinforced composites has been found [223, 224]. Under this assumption, predictions for tensile strength at varying composite water contents were made, Fig. 62. These lower water contents would correspond to full saturation for systems exposed to less humid environments or lower temperature or pressure.

It is not trivial to directly, quantitatively, compare experimental strength to the simulated work of adhesion. Importantly, the strength of fibre composites are directly derived from adhesion at the interface between the fibre and the matrix. A loss of strength in the system is
therefore a direct result of adhesion loss at the interface. While not perfectly reproduced with experimental tensile testing, the simulated interface adhesion finds general agreement in that a clear adhesion loss is seen with the presence of absorbed moisture. This behaviour, while expected, fundamentally represents the primary reason we are interested in understanding, controlling, and modifying the interfacial area.

7.6 SEM Fractographic Analysis

Fracture surfaces were examined with a JEOL JSM IT-300 variable pressure scanning electron microscope (SEM) equipped with an Oxford Aztec SDD energy dispersive spectrometer (EDS). SEM specimens were sputter-coated with carbon and imaged at an accelerating voltage of 5 kV.

Figure 63 shows representative images of the failure region for the dry and saturated samples, while Appendix C provides EDS spectra. The thickness of the sizing is sub-micron in scale and is not distinguishable from the more prominent fibre surface and bulk epoxy; therefore, it is difficult to say with certainty if the sizing remains on the surface of the fibre in either case. The dry samples showed substantially more epoxy remaining on the fibre surface, while the saturated samples showed a cleaner fibre surface. This suggests more cohesive failures in the matrix for the dry samples, while the relatively clean fibre surface of the saturated samples indicate adhesive failures at the interface. More frequent cohesive epoxy failures for dry samples indicated adhesive failures at the SiO$_2$-sizing or sizing-epoxy interface occurred more readily for saturated samples. Overall, the SEM results align with the MD predictions, wherein the adhesion at each interface was greatly decreased in
saturated conditions. This decrease in adhesion strength makes it seemingly more likely that adhesive interface failure will occur rather than cohesive failures in the bulk epoxy.
8 Conclusions

Overall, the work presented in this thesis demonstrated the viability of Molecular Dynamics Simulations as a tool for investigating the fibre composite interface. Novel contributions were made for; (i) determining the solubility limit of water in a crosslinked epoxy system, (ii) generating slab composite interfaces, (iii) determining the solubility limit of water at composite interfaces, and (iv) quantifying interfacial adhesion in a slab composite for both dry and saturated systems.

8.1 Summary of Results

Molecular Dynamics simulations were successfully employed for uses in investigating the interface in glass fibre reinforced polymer composites. First, specific procedures were developed, and validated for uses in modelling crosslinked DGEBA/IPD epoxy systems. A system containing 256 DGEBA and 128 IPD molecules was dynamically crosslinked successfully to 91.5%. The density, elastic modulus, and onset of glass transition temperature were calculated and compared to experimental values. An average simulated density was found as $1.128 \pm 0.062 \text{ g cm}^{-3}$, compared to an experimental density of $1.131 \pm 0.055 \text{ g cm}^{-3}$. The elastic modulus for the simulated system had an average value of $4.92 \pm 0.064 \text{ GPa}$. In comparison, an experimental value of $4.34 \pm 0.09 \text{ GPa}$ was determined. The onset of the system glass transition temperature was considered as a final validation. The simulation results indicated an average $T_{g \text{ onset}}$ of $116.62 \pm 1.77 \text{ °C}$, while experimentally DMA results showed a value of $108.21 \pm 1.02 \text{ °C}$.

Overall, the simulated system slightly overestimated the stiffness and glass transition temperature of the dry structure. This may partially be due to the simulation not accounting for voids, defects, or imperfections in the structure. Furthermore, the simulated system structurally represents a highly crosslinked system, which may not align with what was experimentally tested at present.

MD methods were then expanded to investigate interactions occurring between epoxy and absorbed water, wherein novel computational methods are developed for determining the solubility limit of absorbed water in a crosslinked polymer network. A new term was proposed, the reduced chemical potential $\tilde{\mu}$. At equilibrium the reduced chemical potential for I - pure water and II - absorbed water will be equal. If $\tilde{\mu}_I > \tilde{\mu}_{II}$, this indicates the system is not yet saturated, conversely, if $\tilde{\mu}_I < \tilde{\mu}_{II}$, this indicates the polymer is oversaturated. This offered the means for assessing the solubility of water in a polymeric system. DGEBA/IPD was found to have a moisture solubility of 3.50-3.75 wt.% when immersed in water at 300 K. Experimentally, an average maximum water content was found as $2.66 \pm 0.03 \text{ wt}.$%.
The average simulated elastic modulus for DGEBA/IPD saturated to 3.6 wt.% water was found as \(4.11 \pm 0.01\) GPa, a decrease of 16.5% from the dry system. Comparatively, tensile testing was undertaken and an experimental value of \(3.74 \pm 0.08\) GPa was found, a decrease of 13.8%. The onset of the glass transition temperature indicated a significant decrease of 17.9% with an average value of 96.48 °C, while experimentally DMA results showed a decrease of 15.4% to a value of 91.54 °C. In summary, simulation results for the saturated epoxy system compared relatively well with experimental results. The simulation overestimated the maximum water content, and also tends to slightly overestimated the relative loss of system properties due to the presence of absorbed moisture.

Much like the dry system, the simulation slightly overestimated the stiffness and glass transition temperature of the structure and similar sources of error seem plausible. The simulated system does not account of imperfections in the structure. The highly crosslinked nature of the simulated structure artificially increases the overall stiffness and decreases chain mobility, increasing the glass transition temperature. Perhaps more significant would be the lack of accounting for polar bonding of water to the epoxy structure. Absorbed water is known to increase the chain mobility and plasticise epoxy systems, primarily as a result of water binding to polar sites throughout the polymer backbone.

Finally, ten thermodynamically equivalent slab composite interface structures containing glass fibre, sizing, and epoxy were generated. Novel simulation procedures for saturating the heterogeneous system based on Grand Canonical Monte Carlo (GCMC) exchanges of noble water molecules were developed. The average solubility limit of 2.07 wt.% water was found corresponding to 0.99 wt.% water in the equivalent full composite. This compared favourably with the experimentally determined 1.15 \(\pm 0.02\) wt.% water.

Results for both dry and saturated conditions indicated sizing-epoxy as the critical interface for failure. However, the work of adhesion for SiO\(_2\)-sizing is more sensitive to absorbed water. Non-bonded and torsional contributions to the system potential dominated the interface adhesion. In addition to making the largest overall contribution to adhesion, non-bonded terms exhibit the greatest sensitivity to the presence of absorbed water and dominate the loss of adhesive strength. Theoretically, adhesion loss could be significantly minimised through altering the sizing or epoxy systems in a way such that the non-bonded and torsional contributions are retained with increasing composite water content.

SEM analysis further confirmed simulation outputs. After failure, the saturated samples displayed much cleaner fibre surfaces, with far less visibly adhered epoxy. This suggested more cohesive failures in the matrix for the dry samples, while the relatively clean fibre surface of the saturated samples indicate adhesive failures at the interface. More frequent cohesive epoxy failures for dry samples indicated adhesive failures at the SiO\(_2\)-sizing or sizing-epoxy interface occurred more readily for saturated samples. Overall, the SEM results align
with the MD predictions, wherein the adhesion at each interface was greatly decreased in saturated conditions. This decrease in adhesion strength makes it seemingly more likely that adhesive interface failure will occur rather than cohesive failures in the bulk epoxy.

8.2 Concluding Remarks and Future Work

In the present work, only a specific, idealised slab composite interface system was considered. The sizing system was carefully controlled; where, (i) only the silane coupling agent portion of the sizing was considered and (ii) the alignment, molecule rotation, and relative positions were constrained. While, in reality, sizing inherently forms an interpenetrating network with the epoxy system; fundamentally, this is not captured in the present work. Considering the formation of these interpenetrating networks, it seems reasonable to assume that the sizing would become less dense directly at the fibre surface. This lower density would directly lead to more available free space for absorbed water to occupy, which would cause drastic changes to overall interface adhesion. Expanding the simulations to better represent the nature of fibre sizing to form interpenetrating network with epoxies would give a better overall representation of the interface.

Bonding of water molecules to polar sites on the fibre surface, sizing, and epoxy were not considered in the present work. As a result, the conclusions found in this thesis do not account for the effects of polar bonding on the overall adhesion of the system. Incorporating polar bonding would introduce new layers of complexities to the simulation and would provide further understanding of the specific effects of absorbed water on interfacial adhesion.

Furthermore, expanding to include other epoxy (composition and crosslink density) and fibre sizing systems (composition and wt.% applied) would be greatly beneficial. The present work only considered a DGEBA/IPD epoxy system at 91.5% crosslink density, and AMPTES fibre sizing applied at 1 wt.% on the fibre surface. While this represents a common industrial epoxy and fibre sizing system, there are several other options that could be considered, helping further validate the simulations. Perhaps most important would be investigations on varying the crosslink density of the epoxy and wt.% sizing applied to the system, this could provide interesting insight into the overall behaviour of the system. Ultimately, this could lead into industrial applications in tailoring the design of epoxies and sizing formulations to mitigate the negative effects of absorbed water on composite performance.

In conclusion, the applications of Molecular Dynamics as a tool for better understanding adhesion at the fibre composite interface shows promise. With further development, the methods presented in this work may find direct, industrial applications in the overall design of fibre sizing, epoxy, and composite systems.
A Force Field Parameters

A.1 CHARMM

#### CHARMM FF Parameters for DGEBA-IPD and H2O ####

pair_style lj/cut/opt {cut}
bond_style harmonic
angle_style harmonic
dihedral_style charmm
pair_modify mix geometric tail yes
special_bonds lj/coul 0 1 1 extra 2

| pair_coeff | 1 1 | 0.066 3.000 | # C |
| pair_coeff | 2 2 | 0.030 2.020 | # H |
| pair_coeff | 3 3 | 0.170 3.050 | # N |
| pair_coeff | 4 4 | 0.170 3.070 | # OX |
| pair_coeff | 5 5 | 0.155 3.1507 | # O - H2O |
| pair_coeff | 6 6 | 0.046 0.4000 | # H1 - H2O |
| bond_coeff | 1 | 268.7158 1.526 | # C-C |
| bond_coeff | 2 | 340.6175 1.090 | # C-H |
| bond_coeff | 3 | 377.5752 1.460 | # C-N |
| bond_coeff | 4 | 273.2000 1.425 | # C-OX |
| bond_coeff | 5 | 377.5752 1.460 | # H-N |
| bond_coeff | 6 | 322.7158 1.526 | # H-OX |
| bond_coeff | 7 | 450.000 0.9572 | # H1-O - H2O |
| angle_coeff | 1 | 40.60 109.50 | # C-C-C |
| angle_coeff | 2 | 35.40 109.50 | # C-C-H |
| angle_coeff | 3 | 50.00 109.50 | # C-C-N |
| angle_coeff | 4 | 70.00 109.50 | # C-C-OX |
| angle_coeff | 5 | 50.00 109.50 | # C-N-C |
| angle_coeff | 6 | 51.50 109.50 | # C-N-H |
| angle_coeff | 7 | 60.00 109.50 | # C-OX-C |
| angle_coeff | 8 | 58.50 106.00 | # C-OX-H |
| angle_coeff | 9 | 35.50 109.50 | # H-C-H |
| angle_coeff | 10 | 51.50 109.50 | # H-C-N |
| angle_coeff | 11 | 57.00 109.50 | # H-C-OX |
| angle_coeff | 12 | 33.00 125.00 | # H-N-H |
| angle_coeff | 13 | 55.00 104.52 | # H1-O-H1 - H2O |
| dihedral_coeff | 1 | 6.400 2 180 0 | # C-C-C-C |
| dihedral_coeff | 2 | 3.900 2 180 0 | # C-C-C-H |
| dihedral_coeff | 3 | 5.000 2 180 0 | # C-C-C-N |
| dihedral_coeff | 4 | 0.800 2 180 0 | # C-C-C-OX |
| dihedral_coeff | 5 | 0.500 2 180 0 | # C-C-N-C |
| dihedral_coeff | 6 | 0.400 2 180 0 | # C-C-N-H |
A FORCE FIELD PARAMETERS

dihedral_coeff 7 3.100 2 180 0  # C-C-OX-C
dihedral_coeff 8 2.700 2 180 0  # C-C-OX-H
dihedral_coeff 9 1.000 2 180 0  # H-C-C-H
dihedral_coeff 10 1.000 2 180 0  # H-C-C-N
dihedral_coeff 11 8.000 2 180 0  # H-C-C-OX
dihedral_coeff 12 8.500 2 180 0  # H-C-N-C
dihedral_coeff 13 0.100 2 180 0  # H-C-N-H
dihedral_coeff 14 0.000 2 180 0  # H-C-OX-C
dihedral_coeff 15 3.450 2 180 0  # H-C-OX-H
dihedral_coeff 16 1.000 2 180 0  # N-C-C-OX
dihedral_coeff 17 0.000 2 180 0  # N-C-N-C
dihedral_coeff 18 0.300 2 180 0  # OX-C-C-OX

#########################################
#### CHARMM FF Parameters for AMPTES ####
#### Note: Ca = Carbon in AMPTES ####
#### Na = Nitrogen in AMPTES ####
#### etc... ####
#########################################

pair_style lj/cut/coul/cut ${cut}
bond_style harmonic
angle_style harmonic
dihedral_style charmm
pair_modify mix geometric tail yes
special_bonds lj/coul 0 1 1 extra 2

pair_coeff 1 1 0.066 3.500  # Ca
pair_coeff 2 2 0.030 2.420  # Ha
pair_coeff 3 3 0.170 3.250  # Na
pair_coeff 4 4 0.170 3.070  # Oa
pair_coeff 5 5 0.300 3.500  # Sia
pair_coeff 6 6 0.150 4.295  # aO
pair_coeff 7 7 0.300 3.500  # aSi
pair_coeff 8 8 0.300 3.500  # aSi
pair_coeff 9 9 0.170 3.070  # Oa

bond_coeff 1  377.5752 1.460  # Ca-Na
bond_coeff 2  268.7158 1.526  # Ca-Ca
bond_coeff 3  200.350 1.6097  # Oa-Sia
bond_coeff 4  400.5752 1.460  # Ca-Sia
bond_coeff 5  340.6175 1.090  # Ca-Ha
bond_coeff 6  414.350 1.6097  # Oa-Sia
bond_coeff 7  392.800 1.6097  # aO-aSi
bond_coeff 8  392.800 1.6097  # Sia-aO

125
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<td>2</td>
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<td>1.000</td>
<td>2</td>
<td>180</td>
<td>0</td>
<td>Ha-Ca-Ca-Ha</td>
</tr>
<tr>
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<td>5.000</td>
<td>2</td>
<td>180</td>
<td>0</td>
<td>Ca-Ca-Ca-Na</td>
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<td>0.400</td>
<td>2</td>
<td>180</td>
<td>0</td>
<td>aSi-aO-aSi-aO</td>
</tr>
<tr>
<td>9</td>
<td>1.000</td>
<td>2</td>
<td>180</td>
<td>0</td>
<td>Ha-Ca-Ca-Na</td>
</tr>
</tbody>
</table>
B LAMMPS Input Scripts

B.1 Packmol Input for DGEBA/IPD

tolerance 2.0
output output.pdb
filetype pdb
seed 487523
structure DGEBA.pdb
  number 256
  inside cube 0. 0. 0. 58
end structure
structure IPD.pdb
  number 128
  inside cube 0. 0. 0. 58
end structure

B.2 Dynamic Crosslinking

###### VARIABLE DEFINITIONS ######

variable num equal 1
variable cut equal 8.0
variable coff equal 0.921875
variable dcut equal 1.07

###### INITIALIZE DATA ######

units real
boundary p p p
atom_style full

read_data ../1_Setup/${num}.data
include ../FF/charmm.new

thermo 500
timestep 0.1
min_modify dmax .25
velocity all create 303.0 53244 dist gaussian mom no rot no
group active type 2 5

###### NVT DYNAMICS ######
neighbor 1.0 nsq
neigh_modify every 10 check yes
fix 1 all nvt temp 303.0 303.0 100.0
run 100000
reset_timestep 0

write_data ../1_Setup/${num}-nvt.data

##### DYNAMIC CROSSLINKING #####

variable cross1 equal 0

thermo 50
label loop
variable a loop 100
variable rmin equal 7*${a}/100
fix 3 active bond/create 50 2 5 ${rmin} 5 iparam 1 1 jparam 1 4
variable cross equal (${cross1}+f_3[1]/128)
thermo_style custom step v_rmin f_3[1] v_cross temp density
run 50
if "${cross} >= ${coff}" then "jump in.crosslink${num} break"
variable cross1 equal ${cross}
print "Crosslink = ${cross1}"
unfix 3
next a
jump in.crosslink${num} loop
label break
print "Crosslink = ${cross1}"
reset_timestep 0
unfix 2

minimize 0 0 40000 40000
write_data xlink_data/${num}.data.${cross1}crosslink

##### DENSITY OPTIMIZATION #####

fix 4 all npt temp 303.0 303.0 100.0 iso 1.0 1.0 1000
thermo 250
timestep 0.1

label denloop
variable b loop 2000
variable den equal density
thermo_style custom step temp pe v_den
run 10000
if " ${den}>= ${dcut}" then "jump in.crosslink${num} denbreak"
next b
jump in.crosslink${num} denloop
label denbreak
print "Final Density = ${den}"

minimize 0 0 40000 40000
write_data xlink_data/${num}.data.${cross1}crosslink_${den}

B.3 Calculation of Elastic Properties

variable num equal 2
variable run equal 1
variable cut equal 5
variable up equal 0.005
variable den equal density
variable per equal 2

# real units, elastic constants in GPa
units real
atom_style full
variable cfac equal 1.01325e-4
variable cunits string GPa

# Define minimization parameters
variable etol equal 0.0
variable ftol equal 0.0
variable maxiter equal 40000
variable maxeval equal 40000
variable dmax equal 1.0e-2

read_data ../WATER/wet_data/${num}_${run}.data.${per}%
include potential.mod

# Compute initial state
minimize ${etol} ${ftol} ${maxiter} ${maxeval}

variable tmp equal pxx
variable pxx0 equal ${tmp}
variable tmp equal pyy
variable pyy0 equal ${tmp}
variable tmp equal pzz
variable pzz0 equal ${tmp}
variable tmp equal pyz
variable pyz0 equal ${tmp}
variable tmp equal pxz
variable pxz0 equal ${tmp}
variable tmp equal pxy
variable pxy0 equal ${tmp}

variable tmp equal lx
variable lx0 equal ${tmp}
variable tmp equal ly
variable ly0 equal ${tmp}
variable tmp equal lz
variable lz0 equal ${tmp}

# These formulas define the derivatives w.r.t. strain components
# Constants use $, variables use v_
variable d1 equal -(v_pxx1-${pxx0})/(v_delta/v_len0)*${cfac}
variable d2 equal -(v_pyy1-${pyy0})/(v_delta/v_len0)*${cfac}
variable d3 equal -(v_pzz1-${pzz0})/(v_delta/v_len0)*${cfac}
variable d4 equal -(v_pyz1-${pyz0})/(v_delta/v_len0)*${cfac}
variable d5 equal -(v_pxz1-${pxz0})/(v_delta/v_len0)*${cfac}
variable d6 equal -(v_pxy1-${pxy0})/(v_delta/v_len0)*${cfac}

# Write restart
#unfix 3
write_restart restart.equil

###### Small displacements in the 6 principle directions
###### See displace.mod following this section ...
# uxx Perturbation
variable dir equal 1
include displace.mod

# uyy Perturbation
variable dir equal 2
include displace.mod

# uzz Perturbation
variable dir equal 3
include displace.mod

# uyz Perturbation
variable dir equal 4
include displace.mod
# uxz Perturbation
variable dir equal 5
include displace.mod

# uxy Perturbation
variable dir equal 6
include displace.mod

#### Output final values for the Stiffness matrix Cij
variable C11all equal \( {C_{11}} \)
variable C22all equal \( {C_{22}} \)
variable C33all equal \( {C_{33}} \)

variable C12all equal 0.5*(\( {C_{12}} + {C_{21}} \))
variable C13all equal 0.5*(\( {C_{13}} + {C_{31}} \))
variable C23all equal 0.5*(\( {C_{23}} + {C_{32}} \))

variable C44all equal \( {C_{44}} \)
variable C55all equal \( {C_{55}} \)
variable C66all equal \( {C_{66}} \)

variable C14all equal 0.5*(\( {C_{14}} + {C_{41}} \))
variable C15all equal 0.5*(\( {C_{15}} + {C_{51}} \))
variable C16all equal 0.5*(\( {C_{16}} + {C_{61}} \))

variable C24all equal 0.5*(\( {C_{24}} + {C_{42}} \))
variable C25all equal 0.5*(\( {C_{25}} + {C_{52}} \))
variable C26all equal 0.5*(\( {C_{26}} + {C_{62}} \))

variable C34all equal 0.5*(\( {C_{34}} + {C_{43}} \))
variable C35all equal 0.5*(\( {C_{35}} + {C_{53}} \))
variable C36all equal 0.5*(\( {C_{36}} + {C_{63}} \))

variable C45all equal 0.5*(\( {C_{45}} + {C_{54}} \))
variable C46all equal 0.5*(\( {C_{46}} + {C_{64}} \))
variable C56all equal 0.5*(\( {C_{56}} + {C_{65}} \))

#### Calculation of Lame Constants lambda and upsilon
variable lam equal 1/3*(\( {C_{11}} + {C_{22}} + {C_{33}} \)) - 2/3*(\( {C_{44}} + {C_{55}} + {C_{66}} \))
variable up equal 1/3*(\( {C_{44}}+{C_{55}}+{C_{66}} \))

#### Calculation of Elastic constants from Lame constants
variable E equal \( \frac{up \times (3 \times lam + 2 \times up)}{(lam + up)} \)
variable K equal \( \frac{lam + 2/3 \times up}{lam + up} \)
variable poi equal ${lam}/(2*(${lam}+${up}))

print "Elastic Modulus E = ${E} \text{ } \text{cunits}\"
print "Shear Modulus G = ${up} \text{ } \text{cunits}\"
print "Bulk Modulus K = ${K} \text{ } \text{cunits}\"
print "Poissons Ratio v = ${poi}\"

#### displace.mod referenced in the input script
#### used in calculating elastic constants
#### This applies the small + and - displacements
#### and calculates the changes to the pressure tensor

if "${dir} == 1" then &
 "variable len0 equal ${lx0}"
if "${dir} == 2" then &
 "variable len0 equal ${ly0}"
if "${dir} == 3" then &
 "variable len0 equal ${lz0}"
if "${dir} == 4" then &
 "variable len0 equal ${lz0}"
if "${dir} == 5" then &
 "variable len0 equal ${lz0}"
if "${dir} == 6" then &
 "variable len0 equal ${ly0}"

# Reset box and simulation parameters
clear
read_restart restart.equil
include potential.mod

# Negative deformation

variable delta equal -${up}*${len0}
if "${dir} == 1" then &
 "change_box all x delta 0 ${delta} remap units box"
if "${dir} == 2" then &
 "change_box all y delta 0 ${delta} remap units box"
if "${dir} == 3" then &
 "change_box all z delta 0 ${delta} remap units box"
if "${dir} == 4" then &
 "change_box all yz delta ${delta} remap units box"
if "${dir} == 5" then &
 "change_box all xz delta ${delta} remap units box"
if "${dir} == 6" then &
 "change_box all xy delta ${delta} remap units box"
# Relax atoms positions
minimize ${etol} ${ftol} ${maxiter} ${maxeval}

# Obtain new stress tensor

variable tmp equal pxx
variable pxx1 equal ${tmp}
variable tmp equal pyy
variable pyy1 equal ${tmp}
variable tmp equal pzz
variable pzz1 equal ${tmp}
variable tmp equal pxy
variable pxy1 equal ${tmp}
variable tmp equal pxz
variable pxz1 equal ${tmp}
variable tmp equal pyz
variable pyz1 equal ${tmp}

# Compute elastic constant from pressure tensor

variable C1neg equal ${d1}
variable C2neg equal ${d2}
variable C3neg equal ${d3}
variable C4neg equal ${d4}
variable C5neg equal ${d5}
variable C6neg equal ${d6}

# Reset box and simulation parameters

clear
read_restart restart.equil
include potential.mod

# Positive deformation
variable delta equal ${up}*${len0}
if "${dir} == 1" then &
  "change_box all x delta 0 ${delta} remap units box"
if "${dir} == 2" then &
  "change_box all y delta 0 ${delta} remap units box"
if "${dir} == 3" then &
  "change_box all z delta 0 ${delta} remap units box"
if "${dir} == 4" then &
  "change_box all yz delta ${delta} remap units box"
if "${dir} == 5" then &
  "change_box all xz delta ${delta} remap units box"
if "${dir} == 6" then &
   "change_box all xy delta ${delta} remap units box"

# Relax atoms positions
minimize ${etol} ${ftol} ${maxiter} ${maxeval}

# Obtain new stress tensor
variable tmp equal pe
variable e1 equal ${tmp}
variable tmp equal press
variable p1 equal ${tmp}
variable tmp equal pxx
variable pxx1 equal ${tmp}
variable tmp equal pyy
variable pyy1 equal ${tmp}
variable tmp equal pzz
variable pzz1 equal ${tmp}
variable tmp equal pxy
variable pxy1 equal ${tmp}
variable tmp equal pxz
variable pxz1 equal ${tmp}
variable tmp equal pyz
variable pyz1 equal ${tmp}

# Compute elastic constant from pressure tensor
variable C1pos equal ${d1}
variable C2pos equal ${d2}
variable C3pos equal ${d3}
variable C4pos equal ${d4}
variable C5pos equal ${d5}
variable C6pos equal ${d6}

# Combine positive and negative
variable C1${dir} equal 0.5*(${C1neg}+${C1pos})
variable C2${dir} equal 0.5*(${C2neg}+${C2pos})
variable C3${dir} equal 0.5*(${C3neg}+${C3pos})
variable C4${dir} equal 0.5*(${C4neg}+${C4pos})
variable C5${dir} equal 0.5*(${C5neg}+${C5pos})
variable C6${dir} equal 0.5*(${C6neg}+${C6pos})

# Delete dir to make sure it is not reused
variable dir delete
B.4 Reduced Chemical Potential

variable num equal 2
variable run equal 1
variable cut equal 8.0
variable simsize equal 256
variable percent equal .02
variable per equal ${percent}*100

units real
atom_style full
boundary p p p
read_data wet_data/${num}_${run}.data.${per}%
include charmm1.new

neighbor 1.0 bin
eigh_modify once no every 1 check yes
thermo 500
timestep 0.025

group H type 8
group O type 7
group OH type 7 8

write_restart restart_${num}_${run}.data

label loop
variable L index -0.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0
next L
print "Lambda = ${L}"
jump in.loop loop

label loop
# ff params f(lambda)
variable ro equal (0.8+0.2*${L})*3.1507
variable eh equal 0.0460*(${L}^2)
variable qo equal -0.834*${L}
variable qh equal 0.417*${L}

include charmm2.new

# units = kcal/mol
# pair = lj + el
compute Ulj2 OH pe/atom pair
compute Ulj1 OH reduce sum c_Ulj2
compute Unb2 OH pe/atom bond angle dihedral
compute Unb1 OH reduce sum c_Unb2

thermo_style custom step pe c_Ulj1 c_Unb1
run 0

# units = kj/mol
variable Ulj equal (c_Ulj1*4.1868)
variable Unb equal (c_Unb1*4.1868)
variable ui equal ${Ulj}

thermo_style custom step temp v_Ulj v_Unb
fix 2 all nvt temp 300.0 300.0 2.5
fix 3 all ave/time 2 20000 200000 v_Ulj v_Unb file data/${L}.${num}_${run}.data

label pote
variable a loop 100
run 200000
variable diff equal abs(($ui-f_3[1])/ui)
print "diff = ${diff}"
if "${diff}<=0.005" then "jump SELF break"
variable ljo1 equal f_3[1]
variable ljo equal ${ljo1}
print "Ulj = ${ljo1}"
next a
jump SELF pote

label break

clear
read_restart restart_${num}_${run}.data

neighbor 0.3 bin
neigh_modify once no every 1 check yes
thermo 500
timestep 0.05

jump in.lambda${num} loop

#### PARTICLE INSERTION ####

variable num equal 2
variable run equal 1
variable cut equal 8.0
variable simsize equal 256
variable percent equal .02
variable per equal ${percent}*100
units real
atom_style full
boundary p p p
read_data wet_data/$(num)$(run).data.$(per)
include charmm1.new.wi

group OH type 7 8

# units = kcal/mol
# pair = lj + el
compute Ulj2 OH1 pe/atom pair
compute Ulj1 OH1 reduce sum c_Ulj2
compute Unb2 OH1 pe/atom bond angle dihedral
compute Unb1 OH1 reduce sum c_Unb2

thermo_style custom step pe c_Ulj1 c_Unb1
fix 4 all nvt temp 303.0 303.0 100.0
run 0

# units = kj/mol
variable Ulj equal (c_Ulj1*4.1868)
variable Unb equal (c_Unb1*4.1868)

label iloop
molecule WI H2O.txt
create_atoms 1 random 1 NULL mol WI

thermo_style custom step temp v_Ulj v_Unb
thermo_modify norm no
fix 5 all ave/time 2 10000 100000 pe v_Ulj v_Unb file data/$(num)$(run).wi.data
run 100000
unfix 4
unfix 5
next a
next b
read_restart restart.data
jump in.lambda iloop
B.5  SiO$_2$ Melt-Quench Procedure

```
units  real
atom_style  full

read_data  data/bulk.data
include  Si.pot

thermo  500
timestep  1.0
velocity  all create 8000 27344 dist gaussian

fix  1 all nvt 8000.0 8000.0 33.333 48279
run  1000000
unfix  1

write_data  data/melt.data nocoeff
compute  1 all rdf 1000 1 1 1 2 2 2
compute  2 all pe
fix  2 all nvt 8000.0 300.0 33.333 48279
fix  3 all ave/time 25000 1 500000 c_1 file rdf/bulk.rdf mode vector
fix  4 all ave/time 50000 1 500000 c_2 file rdf/bulk.pe
run  5000000
unfix  2
unfix  3
unfix  4

write_data  data/bulk.data nocoeff
clear
include  in.surface
```

B.6  SiO$_2$ Surface Creation

```
variable  del equal 0.5
variable  buffer equal 50

boundary  p p p
units  real
atom_style  full

read_data  data/bulk.data
include  Si.pot
variable  zo equal zhi
thermo  500
```
timestep 1.0
neigh_modify every 1 delay 2 check yes page 100000

#############################
#### Loop defined to pad the ####
#### box with 50A of vacuum ####
#############################

label loop
cchange_box all z delta 0 ${del} units box

fix 1 top nve
fix 2 top langevin 300.0 300.0 33.333 48279
run 10000
unfix 1
unfix 2

variable zh equal zhi
if "${zh}>=zo+${buffer}" then "jump SELF out" else "jump SELF loop"
label out
write_data data/buffer.data

reset_timestep 0
velocity bottom set 0 0 0
velocity top create 300.0 27344 dist gaussian
compute 1 all rdf 1000 1 1 1 2 2 2
compute 2 all pe
compute 3 top angle/local theta
dump 1 top local 500000 angle.dump index c_3

fix 1 bottom setforce 0 0 0
fix 2 top nvt 300.0 300.0 33.333 48279
fix 3 top ave/time 50000 1 1000000 c_1 file rdf/surface.rdf mode vector
fix 4 top ave/time 50000 1 250000 c_2 file rdf/surface.pe
run 4000000

write_data data/surface.data nocoeff
quit
B.7 Surface Energy

variable del equal 0.5
variable type equal Silica

units real
boundary p p p
atom_style full

include int.pot
read_data data/Bulk_${type}.data

velocity all create 300 41344 dist gaussian
thermo 500
timestep 0.5
neigh_modify every 1 delay 2 check yes page 100000

#### Compute Full Bulk PE ####
compute pe calc pe/atom
compute 1 calc reduce sum c_pe
fix 1 all nvt 300.0 300.0 33.333 48279
fix 2 all ave/time 10000 1 20000 c_1 file ../Bulk_${type}.pe
run 1000000
unfix 1
unfix 2

#################################
#### Loop defined to pad the ####
#### box with 50Å of vacuum ####
#################################

label loop
change_box all z delta -${del} ${del} units box

fix 1 top nve
fix 2 top langevin 300.0 300.0 33.333 48279
run 100000
unfix 1
unfix 2

variable zh equal zhi
if "${zh}>=zo+50" then "jump SELF out" else "jump SELF loop"

label out
write_data data/film_${type}.data
reset_timestep 0

*************************************************************

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#### Compute Thin Film PE ####
fix 1 all nvt 300.0 300.0 33.333 48279
fix 2 all ave/time 100000 1 200000 c_1 file ../Film_${type}.pe
run 1000000
quit

#### Compute Full Interface PE ####
compute pe calc pe/atom
compute 1 calc reduce sum c_pe
fix 1 all nvt 300.0 300.0 33.333 48279

#### Time averaged values for PE ####
fix 2 all ave/time 200000 1 200000 c_1 file ../interface.pe
run 200000
unfix 1
unfix 2

---

**B.8 Work of Adhesion**

variable del equal 0.5
units real
boundary p p p
atom_style full

include int.pot
read_data data/int.data

velocity all create 300 41344 dist gaussian
thermo 500
timestep 0.5
neigh_modify every 1 delay 2 check yes page 100000

### Surface Energy Script is then used ###
### using combined structures (i.e. SiO2-sizing) ###
### in place of individual (i.e. SiO2) ###

---

---
B.9  GCMC Atom Exchange

variable  num equal 1
variable  cut equal 10.0
variable  L equal 0.0

units real
atom_style full
boundary p p p
read_data ../Interface/data/${num}.data

#### NOTE Potential for water is scaled as f(L)
include potential.txt
molecule H2O H2O.txt

velocity all create 300.0 4928459 rot yes dist gaussian
neighbor 1.0 bin
compute_modify thermo_temp dynamic yes
neigh_modify once no every 1 check yes
thermo 500
timestep 1

#### GCMC exchange at 300 K, NOTE -14.86 kj/mol = -3.55 kcal/mol
fix 1 water gcmc 1 10000 1000 0 345543 300.0 -3.55 0.1 mol H2O maxangle 180 full_energy
run 1000000
write_data ../Interface/wet_data/${num}_NOBLE.data

clear

#######################################
#### Rescale Noble ---> Full Water ####
#######################################
read_data ../Interface/wet_data/${num}_NOBLE.data

variable L index 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
label loop
next L
include potential.txt

fix 2 all nvt temp 300.0 300.0 0.5
run 2000000
if "${L}==1.0" then "jump SELF break" else "jump SELF loop"

label break
write_data ../Interface/wet_data/${num}_FULL.data
quit
C  EDS Spectra
References


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