ABSTRACT

Langmuir monolayers are a collection of surfactant molecules on the surface of a sub-phase that spread out to form a one molecule thick layer. The surfactant molecules composing the monolayer are amphiphilic compounds composed of a hydrophilic head group that is attracted to water and a hydrophobic tail group which is repelled by water, this combination of interactions gives rise to structural and dynamic physics including, but not limited to, tilting of the surfactant tail groups and buckling of the monolayer when it is placed under high surface pressure. Langmuir monolayers are fundamentally related to many biological systems and have applications in material science and engineering. In this thesis we investigate structural and dynamic properties of Langmuir monolayers through discontinuous molecular dynamics simulations in the NVE ensemble. We model surfactant molecules with a single-site head group connected to a 10-site, single-chain tail. Two solvent models are explored: a hard-surface continuum model and an explicit one-site model. The hard-surface model is used to study high-pressure tilting transitions of Langmuir monolayers and the explicit solvent model is used to investigate non-equilibrium collapse dynamics. First-order tilting transitions are observed with the hard-surface model, including transitions predicted from low temperature analysis but not yet seen in simulations. Evidence of a hexatic phase, where surfactant molecules are un-tilted but ordered on a hexagonal head-group lattice, is also observed. The explicit solvent model is rigorously tested and a liquid-gas coexistence curve is constructed. In the coexistence region, collapse phenomena are investigated for a model Langmuir monolayer. This is accomplished by
ABSTRACT

examining pressure isotherms of an equilibrated surfactant layer located at the liquid-gas interface. At high pressures, the initial stages of collapse are noted by the development of curvature at the surfactant/solvent interface. Collapse rates determined from surface tension profiles are comparable to other recent simulation studies. At higher pressures, and with large system sizes, there is a buckling instability in the monolayer followed by the formation of large folds. This behaviour is discussed in relation to several proposed mechanisms of collapse observed in experiment. Future simulations in the NIIT ensemble will allow a better understanding of the high-pressure behaviour of Langmuir monolayers both structurally and dynamically.
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CHAPTER 1
INTRODUCTION

1.1 Langmuir Monolayers and Surfactants

Langmuir monolayers are systems composed of surfactant molecules that are deposited at an air/water interface. Surfactants contain a head group, which is attracted to water (hydrophilic), and a tail group, which is repelled by water (hydrophobic). Stearic acid ($CH_3(CH_2)_{16}COOH$ or Octadecanoic acid) is an example of a surfactant molecule. These two above interactions cause the surfactants to spread out into a layer that is one surfactant thick with the heads on the surface of the water and the tails out of the water. This layer is called a Langmuir monolayer and is shown in Figure 1.1. Stearic acid is shown in Figure 1.2.

![Figure 1.1: A Langmuir monolayer: The red beads represent fatty acids or alcohols (head groups) and the tails represent a chain of hydrocarbon molecules (tail group).](image)

Surfactants have two main parts (see Figure 1.2). The head group contains hydrophilic compounds, for example, fatty acids, esters or alcohol groups that form hydrogen bonds with the water, giving rise to attractive forces between the head group and the water;
the head group determines the type of surfactant. The hydrocarbon chain or tail group is composed of a series of $CH_2$ groups terminated by a $CH_3$ group. The length of this chain determines the prefix of the compound (octadecanoic for example with 18 carbon atoms in series). The hydrocarbon groups are non-polar molecules and are therefore hydrophobic; however, due to van der Waal forces, tail molecules are attracted to one another.

1.2 Scientific Significance

Langmuir monolayers have many practical applications: material science, biology and engineering, to name a few. One of the interesting properties of surfactant molecules is the ability to reduce the surface tension of substances they are placed on, water being a prime example. For this reason, surfactants are ideal for everyday products such as detergents; the surfactants reduce the surface tension of the water and allow for increased

Figure 1.2: Stearic acid in full atomic form: Red atoms are oxygen, gray are carbon and blue are hydrogen. Lines and double lines represent single or double bonds respectively.
wetting action\textsuperscript{1}. The surfactants can trap foreign objects - oil, dirt and other non-polar objects - in the centre of structures called micelles; these are then carried away with rinsing. Surfactants can also be employed in removing oils from contaminated soils; the process is similar to detergents.

Langmuir monolayers are also very common in biological systems; they are an essential component of cell membranes. Cell membranes are made of two lipid\textsuperscript{2} monolayers placed tail to tail (bi-layer) that work together, along with many other cell membrane components, to transport proteins, nutrients, and fluids in and out of cells. Another biological system that monolayers play a key part in is the respiratory system. On the surface of the alveoli in the lungs is a layer of fluid with surfactants. These surfactants form a monolayer and reduce the surface tension allowing the alveoli to fill with air easier than if the surfactant was not present. Since this lung surfactant is one of the last crucial components formed during pregnancy, many pre-mature babies suffer from Respiratory Distress Syndrome (RDS) where there is insufficient surfactant lining the alveoli. RDS is currently combated with surfactant treatments to help the breathing process. The study of pure Langmuir monolayers on water gives insight into these more complex systems (cell membranes, bi-layers, and lung surfactants) while still being a relatively simple system to study.

1.3 Historical Background

Benjamin Franklin was one of the first scientists to study the effects of monolayers [22]. He investigated some interesting properties of oil when it was placed on water. The first of these properties was that the oil spread out to a large area. He also noticed that oil caused a damping effect in ripples and waves, due to the decreased friction between the air and water. Lord Rayleigh quantified the thickness of these oil slicks and determined

\begin{footnotesize}
\begin{itemize}
\item[\textsuperscript{1}] Wetting refers to the contact between a fluid and a surface
\item[\textsuperscript{2}] Lipid monolayers contain two tail-groups per surfactant molecule instead of one like stearic acid.
\end{itemize}
\end{footnotesize}
them to be on the order of nanometers. When the size of atoms was first proposed in the early 1900’s, scientists used what Lord Rayleigh found as evidence to support this theory, the size of molecules was found to be on the same order as the thickness of the oil slicks, as predicted by Rayleigh.

In the late 1800’s Agnus Pockels took surface pressure measurements (determined through surface tension measurements) of surfactants using a tin trough and a button [23]. These experiments determined, qualitatively, the surface pressure as a function of concentration (referred as a pressure-isotherm) of Langmuir monolayers on the surface of the water. Since these first measurements, many more pressure-isotherms have been experimentally found to much greater accuracy using devices called Langmuir troughs as shown in Figure 1.3. A Langmuir trough is used to change the concentration of surfactants on a surface and make measurements of the surface pressure.

Irving Langmuir was a scientist who extensively studied monolayers and surfactants. He first determined the molecular structure of monolayers and developed a way to transport them from the surface of water to a more stable, non-liquid substrate. He received a Nobel Prize for his work on monolayers in 1933.

![Figure 1.3: A schematic diagram of a Langmuir trough used to measure surface pressure.](image-url)
1.4 Pressure Isotherms and the Langmuir Monolayer Phase Diagram

When surfactants are deposited at an air/water interface, they will tend to spread out in order to increase the surface coverage (area) and decrease the pressure. A horizontal piston (see Figure 1.3) is used to increase or decrease the area of the monolayer, surface pressure measurements are made for different surfactant concentrations at constant temperature, this is called a pressure isotherm. A generic pressure isotherm is shown in Figure 1.4.

![Figure 1.4: This shows a generic pressure isotherm for Langmuir monolayers. Figure taken from Ref. [17].](image)

In Figure 1.4, changes in the slope of the curve correspond to different equilibrium phases. The plateau regions represent coexisting phases. In addition to standard gas, liquid, and solid phases, there is also a so-called liquid-condensed region whereby the surfactants adopt a uniform tilted structure. This tilting is due to the relatively long-ranged attractive interaction between tail segments. Surfactants adopt this uniform tilted structure in order to minimize the system free energy. Depending on the temperature and pressure, surfactants will tilt in one of two basic directions; nearest neighbour (NN)
or next-nearest neighbour (NNN) direction as depicted in Figure 1.5. There is a six-fold degeneracy in the tilting direction of the tail groups for both NN and NNN tilting. At sufficiently high pressures, the most optimal tilting structure for surfactant molecules is the untilted phase because the density is too high for tilting to be energetically favourable.

Figure 1.5: NN (left) and NNN (right) tilting of tail groups in surfactant molecules. The line represents the collection of surfactant tail group molecules, the line points in the tilt direction. Each bead is a head group.

By combining the results of isotherms obtained at different temperatures, one can construct a phase diagram of temperature versus area per molecule. The phase diagram for Langmuir monolayers is quite complicated, as can be seen in Figure 1.6. Several experimental techniques are used in combination with Langmuir troughs to obtain the information needed to construct a phase diagram, including Brewster-angle microscopy, X-ray scattering, and polarized fluorescence microscopy. These techniques study the structure, order and phase transitions of Langmuir monolayers. Further information on these techniques can be found in [4], [5], and [27].
Figure 1.6: A generic phase diagram for a Langmuir monolayer. Colours represent different tilting phases. Other properties of Langmuir monolayers not described here distinguish between phases with common tilt.

1.5 Collapse of a Monolayer

At pressures lower than or equal to the equilibrium spreading pressure, $\Pi_{sp}$, the monolayer is stable. Over a wide range of pressures greater than $\Pi_{sp}$, the monolayer is in equilibrium with the 3D bulk phase [30]. At high pressures, the isotherm may go through a maximum, $\Pi_c$. At these high pressures, the monolayer may undergo transitions to reduce the surface energy. These transitions are referred to as collapse transitions and there are several different proposed mechanisms for collapse [29] further described in Section 1.6. The particular type of collapse depends on the conditions and properties of the monolayer. The onset of collapse may be noted by the development of curvature to increase the surface area per molecule and thereby decrease the surface energy [20]. It has been experimentally shown in previous work, [21], that the collapse pressure, $\Pi_c$ for stearic acid at room temperature is located at 22 Å²/molecule, as seen in Figure 1.7.
Figure 1.7: Experimental pressure isotherm of stearic acid. Collapse occurs around 22 Å²/molecule [21], data taken at room temperature.

Collapse in monolayers is an important physical phenomenon to study, as it leads to a better understanding of why and how collapse occurs in biologically relevant systems. Schief et al. [26] investigate the phenomenon of collapse for lung surfactants. As air is exhaled from the lungs, the surfactants on the alveoli experience large surface pressures due to the decrease in the surface area of the alveoli. In-vitro compression of calf lung surfactant extract shows collapse in lab experiments at surface pressures much less than those present in the lungs upon exhalation. The surfactants collapse at this lower pressure in such a way to create 3D structures that can reverse back upon inhalation.

1.6 Recent Studies

There are still many unresolved issues regarding the phase diagram for Langmuir monolayers. The location and order of certain phase boundaries are subject to debate as well as how these change due to properties such as head group composition and size, length of tail group, and pH of the water. Areas of the phase diagram dealing with collapse are
no exception to this statement, because of this, interest in collapse studies of Langmuir monolayers has recently increased.

Ybert et al. [29] demonstrate experimentally three mechanisms for the collapse of a monolayer: slow collapse, giant folds and multiple folds. They observed that the method of collapse depends on pressure and compression rates ((a) slow collapse at low pressures, (b) giant folds at low compression rates and high pressures and (c) multiple folds at high compression rates and high pressures). Some 3D structures they find include penetration into the sub-phase and giant folds which are depicted in Figure 1.8.

Figure 1.8: Ries mechanism of collapse in Langmuir monolayers: Curvature develops in the monolayer and grows into a giant fold, this fold 'falls' back to form a tri-layer [29].

Since the advent of computers, molecular dynamics (MD) and Monte Carlo (MC) simulations have increasingly become popular methods for studying Langmuir monolayer systems not only because it eliminates problems that arise in experiment but also because the investigator has complete control over the system parameters. A typical MD simulation involves numerically solving Newton’s equations of motion using Lennard-Jones like pair-potentials between molecules. MC simulations randomly change configurations of a system relying, in the simplest case, on the change in the energy to determine whether to reject the new configuration or accept it. Both techniques have advantages and disadvan-
tages; one notable one being that MC simulations do not provide dynamical information about a system whereas a MD simulation does. The limitation of MD is that it can be computationally expensive to integrate the equations of motion for small time steps, when the system size is large and when the potentials are complicated. Discontinuous molecular dynamics (DMD) studies, where discontinuous potentials are used instead of continuous potentials, have not been used to study Langmuir monolayer systems to date. DMD, like MD, provides the user with a dynamic view of the system, but unlike MD, DMD does not have to calculate forces between all particles every time step. The discontinuous nature of the potentials gives rise to impulsive forces and constant velocities for the particles between collisions. The effect of eliminating all of the force calculations and particle updates that are present in an MD simulation, is that a DMD simulation can be performed in less time, especially when time saving techniques are incorporated. More details on this modelling technique are given in Chapters 2 and 3.

Recent computational studies of Langmuir monolayers and Langmuir monolayer-like systems have investigated collapse properties. Fenwick et al. [14] studied the collapse of a simple one-particle layer on the surface of solvent using MD simulations. Another MD simulation study by Nielsen et al., [20], investigated high-pressure collapse transitions where the surface relieves the excess surface energy via surfactant molecules expelled through a 'bridge' formed by the head-groups. One key result from Nielsen et al. that is pertinent to this study is the surface tension versus time plot for a collapsing monolayer, this is shown in Figure 1.9. The surface tension of a water/surfactant system and the surface pressure are related through Equation 1.1

\[ \Pi_s = \gamma_w - \gamma_{w,s}, \]  

(1.1)
where $\Pi_s$ is the surface pressure, $\gamma_w$ is the surface tension of water at an air/water interface and $\gamma_{w,s}$ is the surface tension at a water/surfactant interface.

![Figure 1.9](image_url)

**Figure 1.9:** Surface tension of a water/surfactant system versus time for a collapsing monolayer. The system started in an unstable configuration and collapsed to a stable system through the expulsion of surfactant molecules into the air. Figure adapted from Ref. [20].

### 1.7 Computational Model

When performing theoretical studies on Langmuir monolayers, models must be carefully chosen in order to capture the relevant physics responsible for the properties observed in experiments. Several choices exist with varying levels of complexity. It has been shown that basic physical attributes of Langmuir monolayers such as tilt order and tilt transitions (See Section 1.4) can be achieved with very simple models, such as the Coarse-Grain Rigid (CGR) model [22]. Tilting has also been demonstrated in simple one-dimensional situations [15]. In order to describe features such as backbone ordering, more realistic models with greater detail are required. A number of common models are depicted in Figure 1.10. All-atom and united-atom models are the most realistic, but in order to explore many aspects of Langmuir monolayers and to model a significant number of surfactants, this study utilizes the coarse-grain (CG) method, with the head group
represented by a single molecule and each hydrocarbon group on the tail represented by a single molecule. Each solvent molecule represents a single water molecule, this does not allow hydrogen bonding to be fully modelled since the hydrogen atoms are not present, two DMD all-atom models are discussed in Chapter 6 along with advantages and disadvantages.

![Surfactant structure approximations](image)

Figure 1.10: Various surfactant structure approximations: AA is All Atom, UA is United Atom, CG is Coarse-Grain and CGR is Coarse-Grain Rigid. Red particles are head groups, blue are tail molecules, and the letters denote the atomic element.

### 1.8 Objectives

In this thesis, Langmuir monolayers are studied using the coarse-grain model with an explicit solvent through DMD simulations. The focus of the thesis is to study the non-equilibrium properties of collapse of a Langmuir monolayer. However, tilt ordering transitions are also investigated using a continuum-like model for the solvent sub-phase. The non-equilibrium dynamics of collapse are investigated through surface tension profiles in an effort to elucidate the specific mechanisms and intermediate pathways leading to collapse.

The organizational structure of this thesis is as follows: Chapter 2 introduces the model being used in this study. Chapter 3 describes the DMD method used in the study,
including details of the main algorithm, efficiency techniques, initial conditions and simulation details. Included in the simulation details are recipes for the measurement, in the DMD context, of important quantities such as surface tension, pressure, and temperature. Chapter 4 presents the results of the continuum sub-phase model including simple investigations of the tilt ordering and tilt transitions of Langmuir monolayers. Chapter 5 presents the results of the explicit solvent model simulations. The solvent is first rigorously tested to ensure water-like behaviour in the temperature region under consideration, and then the solvent is combined with the surfactants to perform collapse studies. These studies are carried out using surface pressure measurements and visual structural analysis. Conclusions and future directions are discussed in Chapter 6.
A number of possible models can be used to study Langmuir monolayers. Section 1.7 introduced four possibilities and alluded to the benefits and disadvantages of each. The coarse-grained flexible model of surfactant and solvent molecules is used in this study; it treats water molecules as a single group, surfactant head molecules as a single group and each surfactant hydrocarbon tail unit as a single group. This is shown in Figure 2.1. In this figure, dotted particles are solvent, striped particles are tail group molecules, and the solid particle is the head group.

The coarse-grained flexible model is used in this study over the other choices for several reasons. An all-atom model is too complicated for the study of a 'macroscopic' property such as collapse. Many surfactant molecules are needed as well as many solvent particles, and including all atoms would make simulation sizes large and simulation times long. The united atom model, while closer to the model of choice, stills involves a more detailed description of the head group in the surfactant molecule. Simpler models, like the coarse-grained rigid model are too simple for modelling collapse and are difficult to model using a dynamic method like DMD because the rigid component of the tail complicates the formalism. A coarse-grained flexible model can be made to act very similar to a rigid-like model, this techniques is used in this work and is explain in the section to follow.

This chapter will introduce the two main models used in this study; they differ through how the solvent is represented. The first model implicitly models the solvent and restricts
2.1 The Surfactant Model

The equilibrium configuration of a system of molecules is strongly influenced by the temperature and on the various pair potentials between the different molecules. All physical processes depend heavily on these two elements. In simulations of Langmuir monolayers, the temperature is easily controllable, although the pair potentials must be chosen carefully to achieve the proper physical behaviour in the system.
In the surfactant molecule there are six possible interactions. These are presented in Table 2.1. The different potential types in relation to these interactions are described below.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential Type</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intramolecular</strong></td>
<td></td>
</tr>
<tr>
<td>Head-Tail (adjacent)</td>
<td>Bond</td>
</tr>
<tr>
<td>Tail-Tail (adjacent)</td>
<td>Bond</td>
</tr>
<tr>
<td>Tail-Tail (non-adjacent)</td>
<td>Hard-core</td>
</tr>
<tr>
<td><strong>Intermolecular</strong></td>
<td></td>
</tr>
<tr>
<td>Head-Head</td>
<td>Hard-core</td>
</tr>
<tr>
<td>Head-Tail</td>
<td>Hard-core</td>
</tr>
<tr>
<td>Tail-Tail</td>
<td>Double well</td>
</tr>
</tbody>
</table>

Table 2.1: A complete list of surfactant pair potentials, both intramolecular and intermolecular, is included in this table.

2.1.1 Hard-core Potentials in the Surfactant Model

The hard-core pair potential in Table 2.1 is shown in Figure 2.2. This potential is used to model purely repulsive interactions between two molecules that occur due to (a), electrostatic interactions and (b), the Pauli Exclusion Principle. \( \sigma_{ij} \) in this figure is the arithmetic mean of the diameters of each of the two particles, Equation 2.1. In reduced units (Section 3.2.1) the tail particle’s diameter \( (\sigma_t) \) is taken to be equal to one \( \sigma^* \). For this study, the head particle’s diameter \( (\sigma_h) \) is \( 1.1\sigma_t \). This is taken to be larger than the tail’s diameter because the head group is physically larger. The ratio of the head’s diameter to the tail’s is an important quantity and changes many properties of the monolayer, for example tilting and surface pressure [22].

\[
\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}
\]  

(2.1)
CHAPTER 2: SURFACTANT AND SOLVENT MODELS

2.1.2 Covalent Bond Potentials in the Surfactant Model

Also in Table 2.1 are two potentials that are referred to as bond potentials. These potentials are used to model bonds between atoms or, in a coarse-grained model, surfactant groups. Any two particles experiencing this potential will always be within a certain distance of one another, typically $\pm 10\%$ of the bond length ($\sigma_{ij,l}$). $\sigma_{ij,l}$ is taken to be $75\%$ of the non-adjacent diameter, $\sigma_{ij}$, this is because covalent bonds typically bring the
atoms involved closer together. This potential is shown in Figure 2.3, and the numeric values are shown in Table 2.2.

\[
U_{\text{Bond}}(r) = \begin{cases} 
\infty & r \leq \sigma_{ij,t^-} \\
0 & \sigma_{ij,t^-} < r < \sigma_{ij,t^+} \\
\infty & r \geq \sigma_{ij,t^+}
\end{cases}
\]

Figure 2.3: Intramolecular bond interaction potential: This interaction potential models bond forces between adjacent particles within a molecule. \( \sigma_{ij,t^-} \) is the closest separation distance of the particles where as \( \sigma_{ij,t^+} \) is the farthest separation distance of the two particles. These values are \(-10\%\) and \(+10\%\) of the bond length, \( \sigma_{ij,t} \), respectively. \( ij \) is used here for the general case. If this potential is for adjacent tail-tail particles \( tt \) is used, and if this is for adjacent head-tail particles \( ht \) is used. Numeric values for these potentials are given in Table 2.2.

<table>
<thead>
<tr>
<th>Bond Parameters</th>
<th>Head-Tail Value</th>
<th>Tail-Tail Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Wall</td>
<td>0.704( \sigma_{tt} )</td>
<td>0.67( \sigma_{tt} )</td>
</tr>
<tr>
<td>Average Separation</td>
<td>0.787( \sigma_{tt} )</td>
<td>0.75( \sigma_{tt} )</td>
</tr>
<tr>
<td>Outer Wall</td>
<td>0.872( \sigma_{tt} )</td>
<td>0.83( \sigma_{tt} )</td>
</tr>
</tbody>
</table>

Table 2.2: Head-Tail and Tail-Tail bonded interaction parameters. Distances are given as centre-to-centre separation with \( \sigma_{tt} \) equal to the diameter of the tail particles.

2.1.3 The Double Well Potential in the Surfactant Model

For the surfactant molecule, the last interaction potential describes the intermolecular tail group - tail group interaction. Non-polar molecules like the hydrocarbon groups\(^1\) interact with each other by collectively inducing dipoles in the surrounding molecules. This results

\(^1\) The last group in the tail, which contains three hydrogen atoms, is slightly polar.
in a long-range attraction between the tail groups. This is modelled in molecular dynamic simulations with a Lennard-Jones-like (LJ) potential. This potential contains a short-ranged repulsive interaction ($\propto 1/r^{12}$) and a long-ranged attractive interaction ($\propto -1/r^6$). In DMD, an appropriate double well potential can be used to achieve these effects\(^2\). This potential is shown in Figure 2.4 along with the numeric values.

![Diagram of intermolecular tail-tail attractive interaction potential with numeric values.]

\[ \sigma_1 = 1.24\sigma_H, \sigma_2 = 1.75\sigma_H, V_1 = -1.0\epsilon, V_2 = -0.3\epsilon \]

Figure 2.4: Intermolecular tail-tail attractive interaction potential: $\sigma_H$ is the diameter given in Equation 2.1. $\sigma_1$ is the inner well width defined by the separation distance between the particles centres. $V_1$ is the potential energy associated with the inner well. $\sigma_2$ is the outer well width defined by the separation distance between the particles centres. $V_2$ is the potential energy associated with the outer well.

### 2.2 Hard-Surface Solvent Model for Surfactants

Implicitly modelling the presence of a solvent is useful because it eliminates many particles. This method does come with some disadvantages, for example, curvature will not be able to extensively develop\(^3\) and surfactants cannot escape. This model is used to equilibrate surfactant systems.

\[^2\] More complicated potentials with more steps can be used, [6], but these require more computational resources and therefore are not as efficient.

\[^3\] The staggering of surfactant heads is an example of curvature. This can occur to an extent with this model. Larger scale curvature cannot develop.
the monolayer before it is placed on the solvent surface. It is also used for a preliminary investigation into tilting and phase behaviour of this model.

The solvent is implicitly modelled by restricting the centre of the head group below a particular $z$ value ($z_{wall} - 0.3\sigma$) and restricting the tail groups above a $z$ value ($z_{wall} + 0.3\sigma$)\(^4\). The kinematics are dealt with by simply reversing the $z$ value of the velocity upon interaction with the wall. This interaction is shown in Figure 2.5

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure25.png}
\caption{Hard-wall, implicit solvent model: Head group particles (red) cannot pass above the line whereas the tail group particles (blue) cannot pass below the line. On the right, other particles in the surfactant are not shown for clarity.}
\end{figure}

\subsection{2.3 Explicit Solvent Model for Surfactants}

Curvature is the first stage of collapse and therefore the hard-surface model described above cannot be used for collapse studies. What is needed is a more robust model of the solvent. This can be achieved by explicitly creating solvent particles and assigning appropriate potentials such that a liquid/gas interface is created. The surfactants can then be placed on this surface. In a finite particle number simulation, one such interface alone cannot be created. It is however, possible to create two interfaces\(^5\). To obtain better statistics, both interfaces are used during a simulation. The setup procedure for

\begin{itemize}
\item \textsuperscript{4} The finite thickness (0.6$\sigma$) is needed to maintain order in the monolayer.
\item \textsuperscript{5} This is due to the presence of periodic boundaries.
\end{itemize}
this system is explained in detail in Section 3.3.2. Table 2.3 shows the possible solvent interactions and the interaction potential assigned to each. Each one is described in detail below.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent-Solvent</td>
<td>Double Well</td>
</tr>
<tr>
<td>Solvent-Head</td>
<td>Single Well</td>
</tr>
<tr>
<td>Solvent-Tail</td>
<td>Shoulder</td>
</tr>
</tbody>
</table>

*Table 2.3: A complete list of solvent pair potentials is included in this table.*

### 2.3.1 Solvent-Solvent Double Well Interaction

The solvent must be modelled accurately so the behaviour is similar to an actual solvent like water. Several solvent-solvent interaction potentials were considered, and the criteria for accepting an interaction potential is straightforward. The model must allow the particles to form a liquid-like substance that can maintain a liquid/gas interface (with low gas density) at moderate temperatures. As presented in Chapter 5, the final solvent-solvent interaction potential was chosen as a double well. This interaction is strong enough to create a liquid but also sufficiently long-ranged to allow an interface to be maintained. The potential is given in Figure 2.6 along with the values for the well widths and depths.

### 2.3.2 Solvent-Head Attractive Potential

The solvent-head attraction arises from electrostatic interactions between the polar molecules in the head group and the solvent molecules. To model this, a single-well pair potential is used, this is shown in Figure 2.7 along with the numeric values of the potential.
\( \sigma_{ss1}=1.4\sigma_{ss}, \sigma_{ss2}=2.25\sigma_{ss}, V_{ss1}=-1.0\epsilon, V_{ss2}=-0.3\epsilon \)

**Figure 2.6:** Solvent-solvent attractive interaction potential: \( \sigma_{ss} \) is the diameter given in Equation 2.1. \( \sigma_{ss1} \) is the inner well width defined by the separation distance between the particle centres. \( V_{ss1} \) is the potential energy associated with the inner well. \( \sigma_{ss2} \) is the outer well width defined by the separation distance between the particle centres. \( V_{ss2} \) is the potential energy associated with the outer well.

\( \sigma_{sh}=1.05\sigma_{tt}, \sigma_{sh1}=1.5\sigma, V_{sh1}=-2.0\epsilon \)

**Figure 2.7:** Single well attractive potential: \( \sigma_{sh} \) is the diameter given by Equation 2.1. \( \sigma_{sh1} \) is the well width defined by the separation distance between the particle centres. \( V_{sh1} \) is the potential energy associated with the well.

### 2.3.3 Solvent-Tail Repulsive Potential

The last interaction is the hydrophobic interaction between the tail group particles and the solvent particles. A shoulder potential is used to model this interaction. This is shown in Figure 2.8 along with the numeric values for the potential.
$\sigma_{st_1} = 1.5\sigma, \ V_{st_1} = 1.0\epsilon$

*Figure 2.8:* Repulsive shoulder potential: $\sigma_{st}$ is the diameter given by Equation 2.1. $\sigma_{st_1}$ is the well width defined by the separation distance between the particle centres. $V_{st_1}$ is the potential energy associated with the shoulder.
CHAPTER 3
DMD THEORY AND SIMULATION DETAILS

This chapter describes the simulation details relevant to this study. Section 1 covers the simulation method, discontinuous molecular dynamics (DMD). This includes both the details of the method as well as the time saving techniques used. Section 2 provides a description of the relevant physical parameters measured, and finally, Section 3 presents the simulation details, including system initialization and equilibration techniques.

3.1 DMD Method: Background

As presented in Chapter 1, DMD is a simulation method that can be used as an alternative to MD. DMD was developed to study hard-sphere systems by Alder and Wainwright [1], but has since been extended to include more systems from simple chemical systems [7] and polymers [31; 25; 18] to more complex systems like proteins [32; 33] and molecules, both semi-flexible [9] and rigid [11]. In DMD, unlike MD, the particles feel only impulsive forces; therefore, the trajectories of the particles in these systems can be determined analytically. A DMD simulation progresses as a series of these two-body 'collisions', at which times the appropriate impulsive force is placed on the particles involved in the collision to conserve both energy and momentum. (see Figure 3.1) In contrast to MD where the velocity of every particle is changing every time step, a particle in a DMD simulation retains the same velocity over a longer time range. This results in a speed increase [19; 10] over
conventional MD, which is beneficial when studying long-time phenomena with a large number of particles.

![Diagram of DMD progression algorithm]

**Figure 3.1**: The basic DMD progression algorithm. The arrows on the particles indicate the velocity.

The following sections describe the techniques used to perform a DMD simulation. The most basic concepts are introduced first beginning with periodic boundaries.

### 3.1.1 Periodic Boundaries

To reduce finite size effects in computational simulations, all simulation methods generally use periodic boundaries. The result of periodic boundaries is a seamless connection between opposite sides of the simulation box and therefore, in theory, an infinite size system. This is shown in Figure 3.2.
Figure 3.2: Periodic boundaries allow for a seamless connection between the boundaries of the simulation box. The result is that particles that are far apart in the actual simulation box are close if periodic boundaries are considered. The off lattice box is the periodically corrected area for the red particle. This figure is only in two dimensions but periodic boundaries are typically incorporated in all three dimensions.

Periodic boundaries are implemented by determining the distance, in each dimension, between the two particles under consideration. If the magnitude of the distance in any direction is greater than half the box length, the appropriate correction (adding or subtracting a box length) is made to this component of the separation.

3.1.2 Simulation Box Structure: Cells

It is advantageous in both DMD and MD to divide the simulation box into smaller volumes called sub-cells [3], shown in Figure 3.3. The particles in a given cell are sorted into a linked-list by particle number. When a particles moves from one cell to another the
corresponding lists are updated. The cell’s size depends on the particle density as well as the range of the pair potentials. For dense systems with a potential range between 2.5 and $3.0\sigma$, we find that a cell length of 1.25 and 1.5 reduced units, which corresponds to 2-3 particles per cell, is the most ideal size. This study has a maximum potential of $2.25\sigma$; therefore, the minimum cell length used is $1.125\sigma$, though the actual value of the cell size depends on the configuration of the system.

![Figure 3.3: Example cell structure of a simulation box.](image)

Cells are used over other particle organization methods (i.e. neighbour lists) because of the benefits when considering possible particle interactions in DMD. In DMD, a particle pair only needs to be considered for a collision if the particles are in the same or neighbouring cells\(^1\).

In DMD, cells play a more important role in addition to restricting the number of collision calculations. This subtly arises in DMD and not in MD because DMD is event

---

\(^1\) For the conditions described above, each cell has 124 neighbours. See below in this section. For particles near a periodic boundary, the set of neighbouring cells includes the cells across the appropriate boundary.
based and not time step based. Consider the situation illustrated in Figure 3.4 with two hard spheres. The simulation box on the top does not contain cells whereas the box on the bottom does contain cells. In the upper simulation, the particles are travelling away from each other (because of the periodic boundaries), and no event would be stored. In the future, the particles would overlap (near the centre of the simulation box), this event would be missed. If cells are used then this problem can be remedied by creating a cell crossing event. When the particle enters a new cell the linked list is updated and the particle’s next event is re-calculated, see Section 3.1.3. With this implementation, the event missed when no cells were implemented is determined after the particle moves into another cell. A particle always has a cell-crossing event that is easily predicted by knowing the location of the cell walls and the velocity of the particle.

Figure 3.4: DMD simulation box with and without cells: The upper image is three periodic images of the simulation box without including cells, and the lower image is equivalent except that cells are included.

For basic hard-sphere collisions, the cell structure must meet two conditions to predict all events: the size of a cell must be larger than the particle’s diameter and there must
be at least three cells across the simulation box.\footnote{For simulations involving more than just hard sphere potentials, the size of the cell must be at least the largest potential range. It may be computationally desirable to make smaller cells and search for events in the adjacent 124 cells, not just 26. In this case the simulation box must be at least five cells across and each cell must be at least \(1/2\) of the range of the largest potential.}\footnote{More important than this is that the potential between the discontinuities is constant; therefore, there are no forces exerted on the particles.} If these conditions are met, then events will only occur between two particles if they are in neighbouring cells. This means that events only have to be determined between pairs of particles in neighbouring cells, and all other pairs can be ignored.

\subsection*{3.1.3 Time Calculations and Event Prediction}

The trajectories of particles in a DMD simulation are determined exactly by predicting and processing collisions. This section describes the process for predicting 'collision events' between particles. Since the potentials are discontinuous\footnote{More important than this is that the potential between the discontinuities is constant; therefore, there are no forces exerted on the particles.}, the particles move with constant velocity until specific times, at which point an impulsive force is placed on the particle changing the velocity. In between collision events, the position of a particle at a future time \((t + \Delta t)\) is related to the product of the velocity and the time

\[
\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i \Delta t,
\]

(3.1)

where \(i\) denotes the particle, \(\vec{r}_i(t)\) is the position of particle \(i\) at time \(t\), and \(\vec{v}_i\) is the velocity which, since this is constant between collisions, is not a function of time.

A collision event between particles \(i\) and \(j\) will occur at a future time, \(t_{c,ij}\), when the separation distance between the two particles satisfies the following condition,

\[
|\vec{r}_i(t + t_{c,ij}) - \vec{r}_j(t + t_{c,ij})| = \sigma_{ij},
\]

(3.2)
where $\sigma_{ij}$ corresponds to the separation distance between the particles associated with a discontinuity in their interaction potential. For example, for hard-core collisions, $\sigma_{ij}$ is simply the average diameter of particles $i$ and $j$ given by Equation 2.1.

By solving Equation 3.2 and using Equation 3.1 for the position of the particles, one may obtain the collision time, $t_{c,ij}$, for this particular event. $t_{c,ij}$ is given by the following equation. This calculation is shown in its entirety in Appendix A.

$$t_{c,ij} = \frac{-b_{ij} \pm \sqrt{b_{ij}^2 - v_{ij}^2 C_{ij}}}{v_{ij}^2},$$

(Equation 3.3)

where $t_{c,ij}$ is the time until the next interaction between particles $i$ and $j$, $v_{ij}$ is the relative speed of particle $i$ with respect to particle $j$, $C_{ij}$ is a measure of the separation distance between the molecules\(^4\), and $b_{ij}$ is the projection of $\vec{v}_{ij}$ onto $\vec{r}_{ij}$. The choice of sign in Equation 3.3 depends on the value of $C_{ij}$. If $C_{ij}$ is negative then the positive root is chosen, while if $C_{ij}$ is positive then the negative root is used. This selects the soonest, positive, real collision time from the 2 solutions of the quadratic. A complex root signifies no collision and is ignored.

In principle, the collision times for each particle $i$ with its neighbours (i.e. particles in the same and neighbouring cells) must be calculated in order to determine the soonest-to-occur event. Such a calculation can be computationally costly, so it is advantageous to establish a filtration scheme to eliminate those events that one knows a priori will never occur (without requiring a collision time calculation). Depending on the type of event, a decision tree may be constructed to assist in the prediction of events. The decision trees are shown for hard-core, bonded, and square-well interaction potentials in Figures 3.5, 3.6, and 3.7, respectively. Parameters used in the trees are described above. As a reminder, since $b_{ij}$ is the projection of $\vec{v}_{ij}$ onto $\vec{r}_{ij}$, it is negative when particles are approaching

\(^4\)For a core collision, $C_{ij} = r_{ij}^2 - \sigma_{ij}^2$ where $r_{ij}$ is the relative separation of particle $i$’s centre with respect to particle $j$’s centre, and $\sigma_{ij}$ is the average diameter of particle $i$ and $j$ (Equation 2.1).
each other, and positive if particles are receding from each other. In the following trees, accompanying each path is a graphical representation of the particles. The equations use the relative position and velocity of particle \( i \) with respect to particle \( j \). Therefore particle \( j \) is stationary. The double well is simply an extension of the square-well decision tree and therefore is not shown.

\[
\frac{b_{ij}^2}{\sigma_{ij}^2} > \frac{v_{ij}^2}{r_{ij}^2 - \sigma_{ij}^2}
\]

**Figure 3.5:** Hard-core collision, event decision tree: If the particles are moving away from each other (\( b_{ij} \) positive), no event will occur. If the particles are moving toward each other, there is a possibility of an event. This event will occur if the condition shown is true; otherwise, no event will occur. \( \sigma_{ij} \) is the average of the particle diameters (Equation 2.1). Refer to Figure 2.2 for potential parameters.
Figure 3.6: Bond-collision event, decision tree: Separation distance of particles is always between $\sigma_1$ and $\sigma_2$. If the particles are moving away from each other then an event will happen when the separation distance is at $\sigma_2$. If the particles are moving towards each other, two things are possible: (1) if the condition shown is met, an event will occur involving the two particles when the separation distance is $\sigma_1$; (2) if the condition fails, the particles will pass by each other and will be moving away ($b_{ij} > 0$), and an event will occur involving the two particles at $\sigma_2$. Refer to Figure 2.3 for potential parameters.
Figure 3.7: Square-well collision event decision trees, one tree with $b_{ij}$ negative and the other with $b_{ij}$ positive. In both cases ($b_{ij}$ positive and negative), if the particles are closer than $\sigma_1$ (in the well) then the decision logic is identical to Figure 3.6, with the exception of the parameter values. If the particles are outside the well, then the decision logic is identical to Figure 3.5, with different parameter values as provided in Figure 2.7.
3.1.4 Event Storage in Binary Trees

Once all valid events for all particles have been predicted, the particle with soonest-to-occur event must be chosen. For a many-body system, the number of events can be quite large, and considerable computational effort must be invested to sort these events in order of occurrence. To deal with this potential bottleneck, Rapaport [24] devised an efficient event-list structure based on a binary tree. Memory overhead and event deletion speed are comparable for both binary tree and linked-list data structures. However, it is much faster to insert events into the binary tree, where, as a function of particle number, an insertion for binary trees scales as $O(\log(N))$ compared to $O(\frac{N^2}{2})$ for linked list data structures.

As mentioned in Section 3.1.2, every particle will have either a cell crossing event or a collision event, where this event is the soonest-to-occur event for that particle. The soonest-to-occur event is stored as $i$’s next event and is sorted into the tree by comparing the event time to that of the head node in the tree. For detailed insertion rules refer to Appendix B which includes an example of an event binary tree.

When the velocity of particle $i$ changes, $i$’s next event is no longer valid and must be recalculated\(^5\). The old event must be removed (see [28] for removing techniques for binary trees) and the new event re-sorted (again, see Appendix B). In order to determine the next event to occur in the entire system, the leftmost node of the binary tree is found and the event performed. The leftmost node is easily found by cascading down the binary tree, always to the left, until no left daughter node exists.

\(^5\) Any particle that was involved in a future collision with $i$ no longer has a valid event. See Section 3.1.5, on Collision Lists, for a remedy to this problem.
3.1.5 Collision Lists

Each particle is assigned a number to identify it. At any given time, only one future event is stored for each particle (either cell-crossing or collision event). In the case of collision events, the particle with the lower number stores the event between the particles. Here we use $i$ and $j$ as labels for the particles, where $i < j$. This permits a reduction of the number of events to be calculated for a given particle with its neighbours by, on average, 50% as it is useless to calculate events with particles that have a lower index. Additionally, this ensures that two particles will never store the same event. This serves to lessen the number of event deletions in the binary tree, as only one copy of an event is in storage.

To introduce collision lists [24], the following example is useful to consider. Particles $i$, $j$, and $k$ all are storing a collision event with particle $l$. Particle $l$ is storing a collision event with particle $m$ but the time until this event ($l$ with $m$) is less than the collision times stored with particles $i$, $j$, and $k$. This is shown in Figure 3.8 with all of the velocities relative to particle $l$ and times indicated.

After the collision between particle $l$ and $m$, the events stored with particles $i$, $j$, and $k$ are all invalid because particle $l$’s velocity has changed, and therefore needs to be recalculated. To eliminate the need to check all particles in the neighbouring cells (up to 200 particles on average) with an index lower than $l$ to see if their future event is invalid, a collision list is maintained for every particle. $l$’s collision list is a list of all particles whose future event is with $l$. In this example, the particles in $l$’s collision list are $i$, $j$, and $k$; therefore, when $l$’s velocity changes it is now easy to know which other particles in the system must recalculate events, only the particles on $l$’s collision list. On average, the number of particles in a collision list is less than one.

\footnote{This is less than one due to cell crossing events.}
Figure 3.8: Collision list example scenario. Velocities are relative to particle \( l \). The letters are particle labels whereas the numbers are arbitrary collision times, with \( t_{lm} < t_{(i,j,or \ k)_l} \). For an explanation, see text.

3.1.6 Local Times

The DMD method is an event driven algorithm whereby a simulation proceeds as a series of events, not time steps like in a MD simulation. Since each event involves only one or two particles, only the particles involved in the collision must have their positions updated. In a typical MD simulation, all particles have their position and velocity updated, which involves force calculations at each step.\(^7\)

However, since particles move with constant velocity in between collision events, even greater computational savings can be obtained by deferring position updates for particles until their next event or event prediction [13]. In practice, how this is managed is that local times are assigned to each particle based on their last position update. A particle’s ‘local clock’ is only updated with the running simulation clock, or ‘global clock’ when it

---

\(^7\) The time scales of a DMD event and a MD time step are generally different, the exact time saving depends and many properties such as density and the choice of pair-potentials.
is involved in the **prediction** of an event or actually **participating** in an event. A graphical representation of this is shown in Figure 3.9.

![Figure 3.9: Local times](image)

**Figure 3.9:** Local times: Instead of a particle’s position being updated every event, the only time a particle’s position needs to be updated is when it is involved in the prediction of an event or actually participating in an event. In this diagram, Events 2 and 3 do not involve the particle; therefore, updating its position requires extra computations. Event 4 does involve the particle in question and therefore its position must be updated before the velocity is changed.

### 3.1.7 Event Processing

Once the events have been predicted, the soonest-to-occur event must be dealt with. If the event is a cell crossing, the particle is moved from its old cell list to the cell list in the new cell and the particle’s next event is calculated. The velocity of the particle does not change. Otherwise the event is a collision event and the particles involved are advanced forward so that their positions coincide with the time of the collision. Upon collision, the velocities of the particles are updated according to the following collision rules that are derived from the equations for conservations of energy and linear momentum.

For a simple hard-core interaction, with no change in potential, the change in the velocity of the particle \( i \) is as follows,

\[
\Delta \vec{v}_i = \frac{-2\mu_{ij}\vec{r}_{ij}b_{ij}}{m_i\sigma_{ij}^2},
\]  

(3.4)
where $\mu_{ij}$ is the reduced mass of the two colliding particles, $m_i$ is the mass of particle $i$, and $\sigma_{ij}$ is the location of the discontinuity. At the time of collision, $\sigma_{ij}^2$ should be identical to $|\vec{r}_{ij}|^2$ but, due to round-off error that is limited by machine precision, there will, in practice, be slight differences, $\sigma_{ij}^2$ is replaced with $|\vec{r}_{ij}|^2$ to counter-act this.

For other types of interactions involving square-wells or repulsive shoulder potentials, the energy conservation equation is modified and, hence, the change in velocity for a particle accordingly differs,

$$\Delta \vec{v}_i = \frac{\vec{r}_{ij}\mu_{ij}b_{ij}}{\sigma_{ij}^2m_i} \left( \sqrt{1.0 - \frac{2\Delta U \sigma_{ij}^2}{\mu_{ij}b_{ij}^2}} - 1 \right),$$

(3.5)

where $\Delta U$ is the change in the potential. In both of these cases (Equations 3.4 and 3.5) the change in the velocity of particle $j$ is defined through conservation of momentum as

$$\Delta \vec{v}_j = -\Delta \vec{v}_i.$$  

(3.6)

A special case must be considered when dealing with a positive change in potential. If the change in potential is larger than some particular value, then the pair cannot pass the discontinuity in the potential. This occurs when

$$1.0 < \frac{2\Delta U |r_{ij}|^2}{\mu_{ij}b_{ij}^2},$$

(3.7)

the collision is changed to a hard sphere-like collision, where the changes in the velocity are defined by Equation 3.4.
3.2 Thermodynamic and Structural Properties

The following section discusses some of the details involved in measuring thermodynamic quantities in a DMD simulation; it begins with some basic discontinuous molecular dynamic concepts such as reduced units.

3.2.1 Reduced Units

In S.I. units, many quantities of interest are very large and many are very small, especially when compared to other units. For example, the length scales used in a typical DMD simulation are on the order of angstroms ($1 \times 10^{-10} m$), time scales are on the order of picoseconds ($1 \times 10^{-12} s$), temperatures are on the order of 100 K ($1 \times 10^2$), masses are on the order of atomic mass units ($1 \times 10^{-27}$) and velocities are typically quoted in $10^{-5}$ centimeters per second ($1 \times 10^{-7}$), here the number in brackets is the S.I. unit order of magnitude. Reduced units are used in DMD simulations for several reasons, the most obvious being that mentioned above, the simplicity of having different scales (length, time, and temperature) on the same order of magnitude. Reduced units are also useful in reducing round-off error that can arise when numbers of largely different magnitudes are used together in computations (addition and subtraction etc). The reduced units used in this study are given below:

$$
\sigma^* \approx 3 \text{ Å} \\
m^* = 18 \times (1.66 \times 10^{-27} \text{ kg}) \\
\epsilon^* \approx 1694 \text{ J/mol}
$$

(3.8)

The value of $\epsilon^*$ is chosen so that a reduced temperature of $1.34 T^*$ is equivalent to 273K.

$^8$ See Section 5.1.2.
From these assignments, most quantities of interest can be determined, such as time, temperature, surface tension, density, and pressure [3];

\[
t = \sigma^* \sqrt{\frac{m^* N_A}{\epsilon^*}} t^* = (0.99 \text{ ps}) t^*, \quad (3.9)
\]

\[
T = \frac{\epsilon^*}{R} T^* = (207.3 \text{ K}) T^*, \quad (3.10)
\]

\[
\gamma = \frac{\epsilon^*}{(\sigma^*)^2 N_A} \gamma^* = (31.26 \text{ mN/m}) \gamma^*, \quad (3.11)
\]

\[
\rho = \frac{m^*}{(\sigma^*)^3} \rho^* = (1.107 \text{ g/cm}^3) \rho^*, \quad (3.12)
\]

and

\[
P = \frac{\epsilon^*}{(\sigma^*)^3 N_A} P^* = (1028 \text{ atm}) P^*, \quad (3.13)
\]

where \(t^*, T^*, \gamma^*, \rho^*\) and \(P^*\) are the unit-less simulation quantities of time, temperature, surface tension, density and pressure, respectively; \(R\) is the gas constant and \(N_A\) is Avogadro's number. To convert reduced units to real units, one multiplies the simulation output (2 time units for example) by the corresponding factor (0.99 ps), to get the actual time, 1.98 ps in this case.

### 3.2.2 Temperature Equilibration

An important quantity to measure in discontinuous molecular dynamic simulations is the kinetic temperature, which may be used to estimate the thermodynamic temperature of the system.\(^9\)

The reduced kinetic temperature can be approximated using the equipartition theorem, which states, for a classical system of particles, that each degree of freedom contributes

\(^9\)In this study we freely interchange kinetic temperature with the thermodynamic temperature, as both are equivalent in the thermodynamic limit or after sufficient ensemble averaging.
\( \frac{k_B T}{2} \) to the total average kinetic energy. In reduced units, each degree of freedom contributes \( T^* \) to the total reduced kinetic energy. This can be solved for \( T^* \), the reduced kinetic temperature:

\[
KE^* = \sum_i \frac{1}{2} m^* |\vec{v}_i|^2 \approx \frac{3}{2} N T^*, \tag{3.14}
\]

\[
T^* = \frac{1}{3} \langle m^* |\vec{v}|^2 \rangle_N. \tag{3.15}
\]

where \( N \) is the total number of particles, and the average is over all particles \( (N) \). The kinetic temperature is an instantaneous measure of the kinetic energy in a system. These DMD simulations were performed in the NVE ensemble, where \( N \) denotes constant particle number, \( V \) denotes constant volume, and \( E \) denotes constant energy. The temperature is not constant in these simulations. The thermodynamic temperature \( (T^*) \) can be obtained by averaging the kinetic temperature over the course of the simulation.

For this study, a system is defined to be equilibrated at a temperature of \( T^* \) if, for an extended period, the reduced temperature does not change by more than 5\%. Fluctuations exist in the temperature because of the ensemble chosen. To obtain the optimal configuration of a system of particles, it is not sufficient to equilibrate the particles only at the desired temperature because the system may be get 'trapped' in a meta-stable minimum instead of the global minimum. To circumvent this, annealing cycles are used. An annealing cycle is a process where the system of particles is heated to high temperatures and then cooled down slowly to the desired temperature. This process allows the system to settle into the optimal configuration. A typical annealing cycle used in this work where the desired final temperature is \( T^*=1.0 \) would be: \( T^*=2.75, T^*=2.5, T^*=2.25, T^*=2, T^*=1.75, T^*=1.5, T^*=1.25, T^*=1.0 \).
The exception to this is when a combined surfactant-solvent simulation is being studied, two pre-equilibrated systems are placed together to form a surfactant/solvent system as described in Section 3.3.2. Equilibration at the desired temperature is performed but not an annealing cycle. Even though both systems begin at the desired temperature, the interactions at the interface cause minor fluctuations in the kinetic temperature, and equilibration ensures that the temperature remains the same. This equilibration phase is short compared to a solvent or surfactant equilibration phase with annealing involved.

### 3.2.3 Pressure

For a system of $N$ particles, the instantaneous pressure is given by

$$V P_{\alpha,\beta} = \frac{N}{3} \langle m v_{\alpha} v_{\beta} \rangle + \langle W_{\alpha,\beta} \rangle,$$

(3.16)

where $\alpha$ and $\beta$ are one of $x$, $y$, or $z$, and $\langle W_{\alpha,\beta} \rangle$ is the internal virial [3] and is defined as

$$\langle W_{\alpha,\beta} \rangle = \sum_{i=0}^{N-1} \sum_{j=i+1}^{N} r_{ij,\alpha} f_{i,\beta},$$

(3.17)

where the sum is taken over all particle pairs, $r_{ij,\alpha}$ is the $\alpha$ component of the separation distance between particles $i$ and $j$ at the time of measurement and $f_{i,\beta}$ is the $\beta$ component of the force on particle $i$ at the time of measurement. An instantaneous value of the pressure can not be obtained with this formula, ensemble averaging is needed, especially in DMD.

$$\langle W_{\alpha,\beta} \rangle = \frac{1}{t_{obs}} \sum_{collisions} r_{ij,\alpha} \Delta p_{i,\beta},$$

(3.18)

where $t_{obs}$ is the time over which the sum is carried out. $\Delta p_{i,\beta}$ is the change in the $\beta$ component of particle $i$’s momentum at the time of collision, whereas, $r_{ij,\alpha}$ is the $\alpha$
component of the separation distance between particles $i$ and $j$ at the time of the collision. As mentioned above, an instantaneous value of $W_{\alpha,\beta}$ is not possible especially in DMD, and its true value is obtained by averaging over many collisions. The pressure tensor and the internal virial are symmetric tensors: that is, $\langle W_{\alpha,\beta} \rangle = \langle W_{\beta,\alpha} \rangle$. The total pressure can be expressed as

$$P = \frac{1}{3} [P_{xx} + P_{yy} + P_{zz}]$$

(3.19)

and for an isotropic system

$$P_{\alpha,\beta} = P \delta_{\alpha,\beta},$$

(3.20)

where $\delta_{\alpha,\beta}$ is the Kronecker delta function which equals unity if $\alpha = \beta$ and 0 if $\alpha \neq \beta$.

### 3.2.4 Surface Tension

When studying interfaces, Equation 3.20 is invalid since the system is not isotropic. In a situation like this, it is desirable to study the surface pressure, which gives insight into the stability of the surface. To obtain the surface pressure the surface tension is needed, as seen in Equation 1.1. Surface tension arises from an imbalance in the forces at a surface. If a collection of molecules form two interfaces (see Figure 3.10) then the resulting surface tension at each interface is determined by Equation 3.21, [2]

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} [P_N(z) - P_T(z)] dz,$$

(3.21)

where $\gamma$ is the surface tension, and the $\frac{1}{2}$ is to account for the two interfaces. Here it is assumed that both interfaces behave similarly and therefore have equal surface tensions. $P_N(z)$ and $P_T(z)$ are the normal and tangential components of the pressure tensor defined in Equations 3.22 and 3.23;
Figure 3.10: Two solvent/air interfaces. All simulation box boundaries are periodic.

\[
PT(z) = \frac{1}{2} [P_{xx}(z) + P_{yy}(z)],
\]

(3.22)

\[
P_N(z) = P_{zz}(z),
\]

(3.23)

where

\[
P_{aa}(z) = \langle \rho(z) \rangle k_B T \frac{1}{A} \left[ \frac{1}{t_{\text{obs}}} \sum_{\text{collisions}} r_{ij,a} \Delta p_{i,a} \frac{1}{|z_{ij}|} \Theta \left( \frac{z - z_i}{z_{ij}} \right) \Theta \left( \frac{z_j - z}{z_{ij}} \right) \right]
\]

(3.24)

and where \( A \) is the area of the \( xy \) plane, \( t_{\text{obs}} \), \( r_{ij,a} \) and \( \Delta p_{i,a} \) are defined in Equation 3.18, and \( \Theta(z) \) is the Heaviside function, \( \Theta(z) = 0 \) if \( z < 0 \), \( \Theta(z) = 1 \) if \( z > 0 \). The product of these two Heaviside functions produces a step function with a width of \( |z_{ij}| \) which has a value of 1 if the \( z \) value corresponds to a position between the particles (taking into account periodic boundaries) and 0 otherwise. In practice, the simulation box is divided in the \( z \) direction into \( N \) thin slabs of width \( \Delta z \) and \( P_{aa}(\text{Slab}_k) \) is computed where \( k \)
is between 1 and N. If the line connecting two particles passes through \( \text{Slab}_k \), then the contribution is made to \( P_{\alpha\alpha}(\text{Slab}_k) \). The total \( P_{\alpha\alpha}(\text{Slab}_k) \) is given by,

\[
P_{\alpha\alpha}(\text{Slab}_k) = \langle \rho(\text{Slab}_k) \rangle k_B T - \frac{1}{A \Delta z} \left[ \frac{1}{t_{\text{obs}} \text{collisions}} \sum r_{ij,\alpha} \Delta p_{i,\alpha} \frac{z_k}{|z_{ij}|} \right],
\]

where \( z_k \) is the magnitude of \( z_{ij} \) located in \( \text{Slab}_k \).\(^{10}\)

A simple way of obtaining a value for the total surface tension in a system is using the following expression,

\[
\gamma = \frac{L_z}{2} \left[ P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right],
\]

where \( P_{\alpha\alpha} \) is defined in Equation 3.16 and \( L_z \) is the length of the box in the \( z \) direction. Since the pressure components in this equation are scaled by the volume, the effect of \( L_z \) is simply to change this scale factor to the area of the \( xy \) plane. The factor of \( \frac{1}{2} \) is for the two interfaces [20]. Equation 3.26 is useful when calculating the total surface tension of a system. The disadvantage of this equation is that the surface tension contributions can no longer be looked at as a function of \( z \). Computationally, this equation is more efficient because it does not require the pressure contributions to be divided among many different bins.

3.2.5 Radial Distribution

To study the structural features of a given system, one typically employs the structure factor or radial distribution function. These quantities allow one to determine the arrangement of molecules and to distinguish between solid, liquid, and gas-like phases. The radial distribution function, \( g(r) \), simply stated, is a measure of the probability, given a

\(^{10}\) This value, \( z_k \) is usually equal to \( \Delta z \) except at the end points where the particle is located part way though a particular slab.
reference molecule which is located at a particular site, that another molecule is located a distance \( r \) away from this reference molecule. This function is normalized so that a value of 1 corresponds to the density of the system. The radial distribution function is defined according to,

\[
g(r) = \frac{\rho_c(r)}{\rho(r)},
\]

(3.27)

where \( \rho(r) \) is the radial density of particles averaged over all origins\(^{11}\) and \( \rho_c(r) \) is the radial density of particles averaged over all origins with the restriction that a particle exists at that origin. The calculation of \( g(r) \) is done in practice by binning the separation distances of all particles into different shells with an inner radius of \( i\Delta r \) and an outer radius of \( (i + 1)\Delta r \) where \( i \) is the shell number between 0 and 500 and \( \Delta r = \frac{L}{2 \times 500} \).

The total number of particles in each shell is then normalized by dividing by the average number of particles that would exist in that shell based on the average density. The radial distribution cannot extend passed half of the smallest side length because periodic boundaries begin to affect the distribution. If the system is non-isotropic, this will also affect the radial distribution function.

### 3.2.6 Tilt Parameters

To measure the structure and extent of tilting of the surfactants in the monolayer it is useful to measure the \( x, y, \) and \( z \) components of the surfactant tail vector. These three quantities are defined as the difference in each direction between the last tail group and the head group and are shown in Figure 3.11

\[
\theta \quad \text{and} \quad \phi \quad \text{are determined by using the appropriate trigonometric identities:}
\]

\[
\theta = \arctan \left( \frac{\sqrt{r^2_{x,N} + r^2_{y,N}}}{r_{z,N}} \right)
\]

\[\text{(3.28)}\]

\(^{11}\)This is simply the density of the system \((N/V)\), since it is independent of \( r \).
Figure 3.11: Surfactant parameters: $r_x$, $r_y$, and $r_z$ are measured for all surfactants and averaged over particle number giving $r_{x,N}$, $r_{y,N}$, and $r_{z,N}$. These numbers can then be used to obtain various tilting angles like $\theta$ and $\phi$ shown in this figure.

$$\phi = \arctan \left( \frac{r_{y,N}}{r_{x,N}} \right)$$

(3.29)

3.3 Simulation Details, Setup, Progression and Monitoring

As eluded to in Chapter 1 and described in Chapter 2, there are many different ways that one can model a Langmuir monolayer. For each one of these ways, several solvent models may be explored. This study uses a coarse-grained surfactant model and two different solvent representations. The justification and description of these two models is given in Chapter 2. This section presents the simulation details of each model including the initial setup, equilibration procedures, and production run details.

3.3.1 Hard-surface Solvent Model Simulations

Initialization

A surfactant is added to the system by first creating a head particle and placing it on a 2-D
hexagonal lattice below the location of the wall (see Section 2.2). The first tail particle is placed directly above the head particle at a distance of 0.75σ_{ht}. This tail particle is above the hard-wall. Nine other tail particles (for a total of 10) are then placed at increasing z values, incrementing by 0.75σ_{tt} = σ_{lt,tt} each time. Each particle is given a random velocity in each direction. This process is continued until all the desired surfactant molecules are added. An example resulting configuration is shown in Figure 3.12. The velocities are then scaled to achieve the desired kinetic temperature and adjusted so that the centre of mass velocity is zero. The simulation box is periodic in the x and y direction to reduce finite size effects. The box and particle placement is also designed to have a continuous transition across the boundary, which is essential in high-density simulations.

![Figure 3.12: Example surfactant configuration, this system contains 196 molecules with a density of 9.6 Å² per molecule. The left image is a top view whereas the right image is a side view.](image)

For hard-surface simulations of different densities performed in this study, the simulation box’s cross-sectional area was held constant at 1882 Å². The number of particles was varied from 140 to 196. This was done so that at low densities, with the explicit solvent model that goes to even lower densities, the amount of solvent particles would not be large.

**Equilibration**

This systems were then equilibrated using the following annealing cycle: 2.71 T*, 2.43 T*, 2.14 T*, 1.86 T*, 1.57 T*, 1.29 T*, 1.0 T*. For a more complete description of an annealing cycle and temperature equilibration see Section 3.2.2. This process lasts for,
on average, 1000 reduced time units, but depends highly on density.

**Production Runs and Averages**

For the hard-wall solvent model, the production runs where simulation data is collected are continuations of the equilibrated systems. The each simulation was run between 25 and 50 CPU hours, the number reduced time units simulated in this time frame varies depending on the density and the temperature. For a system run at a temperature of $T^* = 1.0$ and a density of $11.76 \, \text{Å}^2/\text{molecule}$, the number of reduced time units per CPU hour was 385. This simulation was run on a Pentium 4 Xeon, 3.06 GHz computer.

Data is sampled at two intervals. The first interval is short (every $1 \times 10^5$ events) and the tasks performed at this interval include equilibration checks, radial distribution samples, and kinetic energy measurements\(^{12}\). The second interval is longer (every $2 \times 10^6$ events). In this interval all of the necessary thermodynamic quantities are determined and outputted to a file. These are listed below along with the use of each one, all values are given as intensive, i.e. they are independent of the number of particles.

- **Instantaneous kinetic energy** and **Instantaneous potential energy**: These are used to check energy conservation. After equilibration, these should always add to a constant value and show no systematic change over time.

- **Average kinetic energy** and **Temperature**: These quantities are equal to within a multiplicative factor of $\frac{2}{3}$. The temperature, after averaging over the course of a run, represents the thermodynamic temperature ($T^*$) of the system.

- **Average tilt components** ($r_{x,N}$, $r_{y,N}$, and $r_{z,N}$): These values are the average\(^{13}\) $x$, $y$, and $z$ components of the surfactant tail vector defined in Figure 3.11. They can be used to find the important tilt angles (Equations 3.28 and 3.29).

---

\(^{12}\) Kinetic energy measurements are made in the short interval because an average is needed for the pressure calculations. If the instantaneous kinetic energy is used to estimate the temperature, the pressure, and therefore surface tension, will show large fluctuations.

\(^{13}\) Average is taken over all surfactant molecules at the time of the interval.
**Particle positions and velocities:** Each particle’s position and velocity is printed to a file. These can be used to determine diffusion properties and velocity-velocity auto-correlations or create graphical representations of the surfactants over time.

### 3.3.2 Explicit Solvent Model Simulations

**Initialization and Equilibration**

Simulations with solvent particles are performed in two parts. First, the surfactants at the desired temperature and density are initialized and equilibrated using the procedures in the previous section. The simulation box has a cross-sectional area of $2298\text{Å}^2$. A configuration file is created with the positions and velocities of all the particles.

The solvent is also prepared separately. For typical simulations, and unless otherwise stated, the number of solvent particles used was 2925. These particles are placed on a $15\times15\times13$ rectangular lattice with side dimensions, of $47.94\text{Å} \times 47.94\text{Å} \times 41.55\text{Å}$ where the $41.55\text{Å}$ is in the $z$ direction. The actual simulation box has a height (in the $z$ direction) of $191.76\text{Å}$, and therefore the solvent particles are located in a slab-like configuration, centred in the simulation box. This is the same size simulation box as the surfactant molecules are prepared in, which allows for seamless integration of the two systems. Periodic boundaries are in all directions. Velocities are assigned randomly and like the hard-surface model are scaled to the appropriate kinetic temperature and adjusted for zero centre-of-mass motion.

The initial density of the solvent slab is irrelevant due to the equilibration procedure. The first annealing cycle heats the solvent to a temperature so that it completely fills the simulation box, and therefore the initial configuration is lost. As the system is cooled down in the annealing process, the solvent begins to collect into a liquid. In the temperature range of interest, most of the particles have once again collected into a slab configuration while the rest compose a gas in the remaining volume. At appropriate temperatures, the
two liquid/gas interfaces are clearly discernible, see Chapter 5. This process takes 2000 -
3000 reduced time units and 10 CPU hours for each desired temperature. It is only done
once for each temperature under investigation. After equilibration, a configuration file is
created with the positions and velocities of all the solvent particles. Simulation data were
obtained on a Pentium 4 Xeon, 3.06 GHz computer.

The two configuration files are combined by positioning the slab of surfactants at the
two liquid/gas interfaces. This is accomplished by duplicating the monolayer and inverting
the \( z \) values of one copy in order to ‘flip’ the monolayer. The first head in each layer is
then used as a reference and the entire monolayer is shifted to the appropriate liquid/gas
interface.\(^{14} \) The \( z \) value of the interface is chosen by determining where the density
drops to \( \frac{1}{2} \) of the liquid value. This process will result in overlapping particles (surfactant
and solvent) and therefore careful steps must be taken to eliminate these overlaps. The
system is designed such that these overlaps will be eliminated over time and cannot re-
occur. The new potentials between the solvent particles and the surfactant particles will
result in minor fluctuations immediately after the combination of the systems, but since
both are equilibrated at the desired temperature, the equilibration process is simplified.
The system is equilibrated (not annealed) once again at the desired temperature. This
process lasts around 100 reduced time units for a system with 115 surfactant molecules,
this takes longer for more molecules and shorter for less.

**Production Runs and Averages**

For the single-site solvent model, the production runs where simulation data is collected
are continuations of the equilibrated systems. The each simulation was run for 55 CPU
hours. The reduced time steps simulated in this period varies depending on the number
of surfactant molecules and the temperature. For systems run at a temperature of \( T^* \)

\(^{14} \) So that the tails point away from the surface.
= 1.62, the number of reduced time units per hour for a system of 115 molecules and solvent is 45. This data was obtained on a Pentium 4 Xeon, 3.06 GHz computer.

Similar to the hard-wall model, data is sampled at two intervals. The first interval performs the same tasks as the hard-wall model with the exception that radial distribution samples are not taken. During the second, longer interval all of the necessary thermodynamic quantities are determined and directed to a file. These are listed below along with the use of each one. All values are given as intensive, i.e. they are independent of the number of particles. All measured quantities in the hard-wall model are monitored here as well, with the exception of the tilt angles. These quantities are not included in the list below.

**Pressure tensor components** \((xx, xy, xz, yy, yz, \text{ and } zz)\): These are measured in order to obtain the surface tension.

**Pressure tensor components** \((xx, yy, zz)\) as a function of \(z\): These allow the surface tension contributions to be analyzed as a function of \(z\).

**Density distributions**: The density of the solvent, heads, and tails is measured as a function of \(z\). This data allows for the determination of the interface locations.
In order to obtain the proper phase behaviour and collapse dynamics of our model Langmuir monolayer, it was important to establish an appropriate model for the solvent. The most extreme possible model for the solvent treats the solvent as a continuum producing an effective field for the surfactants. The simplest continuum model treats the sub-phase as a hard-surface, whereby molecules cannot detach from or penetrate below the surface. Such models are good for examining tilt behaviour, which is the focus of this chapter. A less drastic continuum model employs so-called Fermi-like step functions, which permits penetration of the surfactants into the sub-phase, while also allowing surfactants to leave the surface [22].

4.1 General Tilting Behaviour

At medium pressures and lower temperatures, the surfactants tilt to minimize the surface energy. As discussed in Chapter 1, the two main types of tilting are NN, where the surfactant tails tilt towards their nearest neighbour, and NNN where tilting is in the direction of the next nearest neighbour. The optimal packing of the head groups on the surface is expected to be hexagonal; however, due to the orthorhombic distortions of the hexagonal lattice that occur upon tilting, the resulting lattice becomes rectangular. There is an expansion in the head-group spacing in the direction of tilt and a contraction of the
head-group spacing in the direction perpendicular to the tilting direction. At high pressures and lower temperatures, the monolayer will be in an untilted phase. Although there is no tilting in this phase, the underlying lattice still exhibits an orthorhombic distortion; this is due to the backbone structure of the tail.

The simulations presented in this chapter are performed in the NVE ensemble with constant particle number, volume, and energy. As explained in Section 3.3.1, the size of the simulation box is held constant with each simulation having a different number of molecules arranged in a hexagonal geometry. As such, the simulation box had fixed geometry (hexagonal); which, in general, would have a symmetry that would be incommensurate with the underlying head-group lattice symmetry. These effects are minimized for larger systems, but still will affect the thermodynamics and phase behaviour of the system. In particular, it is possible for the system to become trapped in metastable states, where the monolayer adopts tilting structures of mixed composition. Associated with such metastable structures is the development of defect lines. To compensate for this problem, it is preferable to perform simulations in the constant particle number, constant surface pressure and constant temperature (NIIT) ensemble, where the surface pressure is held fixed while both the area and shape of the simulation box are allowed to varied. This ensemble was not used due to the challenges of implementing such an ensemble within the DMD framework. Refer to Chapter 6 for a discussion on this issue.

At higher temperatures for all pressures, the entropy of the system dominates the thermodynamics and the surfactants will adopt configurations that tend to maximize the free volume available to the chains. Hence, the chains will on average be untilted and have random configurations, meaning that at higher temperatures, the system is driven from an ordered to a disordered phase. It is important to note that this phase, while untilted, is different than the high pressure, low temperature phase that is both untilted
and ordered. At sufficiently high pressures, this transition from tilted to untilted may result in an ordered, untilted phase. This phase, the hexatic phase, has hexagonal symmetry.

4.2 Tilting Results

To explore such tilting transitions, one can employ the order parameters discussed in Chapter 3, namely $\langle \theta \rangle$ and $\langle \phi \rangle$. $\theta$ measures the tilt of the surfactant tail, and $\phi$ measures the azimuthal angle in the $xy$ plane (see Figure 3.11). Since the simulations were performed on a hexagonal lattice, which as discussed above is incommensurate with the underlying head-group lattice, it is difficult to discern the tilt-direction (NN or NNN) from a histogram of $\phi$. As such, visual inspection of different configurations (that were generated during a simulation) was used instead to determine the tilt direction.

Figure 4.1 shows the variation in tilt angle with surfactant concentration. As expected, low tilt angles are observed for simulations performed at high density whereas larger average tilt angles are observed at lower densities. With this model for the surfactants, the system exhibits tilting in the NN direction. A top view of the simulation (196 molecules) looking down onto the $xy$ plane is shown in Figure 4.2.

Figure 4.3 shows the relationship between tilt angle and temperature for five densities. This data supports the two trends discussed above in Section 4.1. At low temperatures, as the density is increased ($((a) \rightarrow (e))$ the system is driven to an untilted phase, the tilt angle, $\theta$, changes from $\approx 40^\circ$ in (a) to $18^\circ$ in (e). The other trend that this data shows is the transition from tilted to untilted as the temperature is increased. This is due to entropic effects: as the surfactants untilt they increase the available volume, and thereby increase the entropy. Visual inspection of the low temperature simulations confirms that these systems are ordered and tilted in the NN direction. While the high density system (curve (e) and Figure 4.2) is uniform over the simulation box, this is not the case for
Figure 4.1: Average tilt angle vs. surfactant concentration: The temperature of this system is 1.0 T*; data is obtained by keeping the area constant and changing the number of particles from 100 surfactants at high area per molecule to 196 at the low area per molecule.

the lower density systems where the tilt angle is large and leads to a greater mismatch between the system box and the underlying head-group lattice. The effect on the system is thought to be small and only significantly noticeable on a small percentage of the surfactant molecules present.

In Figure 4.3, two noticeable transitions in the tilt angle can be observed for some of the curves. The first transitions occurs between 1.3 and 1.4 T* in each of the curves (b) through (e). There is evidence of this transition in curve (a), but better statistics are need before this is confirmed. As confirmed by visual inspection, these transitions are not transitions in tilt direction (i.e. NN → NNN of NNN → NN); rather they are believed to be abrupt changes in the head-group lattice structure (NN → NN’), this type of behaviour very interesting and has be theoretically predicted in Reference [22].

The second transition in tilt angle occurs in three of the five curves. This transition, confirmed by visual inspection, is from tilted (NN) to untilted. At the highest density, corresponding to curve (e), the system transits to an ordered phase because of both the
higher temperature and density. This phase is thought to be the **hexatic phase**, where the underlying head group lattice is hexagonal. The configuration is shown in Figure 4.4. To confirm this phase, structural properties must be determined such as the radial distribution function of the head groups.

The other two curves that show tilt angle transitions at higher temperatures are curves (a) and (b). Unlike the high density curve, these transitions are from an ordered tilted phase (NN) to a disordered untilted phase, which is confirmed by visual inspection, and shown in Figure 4.5.

The lack of a second discontinuous transition in curves (c) and (d) is interesting. In curve (d), the transition from tilted to untilted appears to occur continuously. This behaviour is unlike the lower densities, curves (a) and (b), and unlike the higher density curve (e). The final state, (ordered or disordered) can not be obtained with the data below 3.0 T*. The final curve, (c), appears to be a coexistence between tilting behaviour seen in (d) and the untilted (disordered) behaviour seen in (a) and (b). This is confirmed
Figure 4.3: Tilt angle vs. Temperature, the surfactant concentration of this system is (a) 13.44 Å²/molecule (140 molecules), (b) 12.55 Å²/molecule (150 molecules), (c) 12.14 Å²/molecule (155 molecules), (d) 11.76 Å²/molecule (160 molecules), and (e) 9.6 Å²/molecule (196 molecules).

by Figure 4.6, where the instantaneous tilt angle\(^1\) is plotted versus the instantaneous temperature\(^2\). The two loci of points in this phase-like diagram correspond to two different surfactant states, one where the surfactants are untilted (disordered) and one with the surfactants tilted (NN). The difference in the temperature of these two configurations is due to energy conservation; when the surfactants tilt the resulting potential energy is lower and therefore the temperature is higher. A possible cause of this behaviour is a poor equilibration procedure, but this can be ruled out because the systems switch between states (untitled and tilted) multiple times over the course of the simulations.

When tilted, all surfactant monolayers simulated here had NN tilting of the surfactants. Theoretical investigations of low-temperature tilting behaviour [22] predict that NNN

\(^1\) Here instantaneous means the average tilt angle of all the surfactants for one configuration.

\(^2\) Again, instantaneous refers to one measurement of the temperature, see Section 3.2.2.
Figure 4.4: Hexatic phase, 2.7 T*: The Langmuir monolayer phase is untilted and ordered on a hexagonal lattice. This image shows both a top and a side view. This curve has a concentration of 9.6 Å²/molecule, and a temperature of 2.7 T*.

Figure 4.5: Low density untilted, disordered phase. This curve has a density of 13.44 Å²/molecule, and a temperature of 2.7 T*.

tilting should be more favourable in high density situations. To see if NNN tilting could be obtained for a high density monolayer, the width of the outer well in the tail-tail interaction potential was increased to 2.25σ instead of the value of 1.75σ_{tt} listed in Figure 2.4. This effectively increases the attraction between tail particles. For a simulation
Figure 4.6: Instantaneous tilt angle vs. instantaneous temperature. The surfactant density of this system is 12.14 Å²/molecule (155 molecules), and the untilted phase is disordered.

with this potential and a density of 9.6 Å²/molecule (196 molecules) NNN tilting was observed and is shown in the top view image looking down onto the $xy$ plane in Figure 4.7.
Figure 4.7: A simulation snapshot showing NNN tilting, the view is looking onto the \(xy\) plane. The tails are clearly pointing in the NNN direction. The number of molecules is 196, giving a concentration of 9.6 \(\text{Å}^2\)/molecule. The width of the outer well in the tail-tail interaction potential was increased from 1.75\(\sigma\) to 2.25\(\sigma\) to achieve this tilting configuration. The temperature in this simulation was 1.0 \(T^*\).
Although the hard-surface solvent model is sufficient to explore tilting behaviour in these model Langmuir monolayers, the model is inadequate for capturing the true dynamics and non-equilibrium properties associated with buckling and collapse. There is no mechanism in this model to allow the development of curvature at the surfactant/solvent interface. To address this issue, we have employed a single-sphere model for the solvent where each sphere represents a single water molecule with a size of $\sigma = 3 \text{ Å}$, which sets the length scale for the study. As alluded to in Chapter 2, the original model chosen for the solvent was a simple single-well pair potential between hard spheres. An additional well was needed in order to approximate the properties and behaviour of water. This potential was presented in Chapter 2 along with the interaction parameters.

Before combining this explicit solvent with the surfactant molecules, separate simulations were performed in order to test the robustness of our solvent model.

### 5.1 Explicit Solvent Model

#### 5.1.1 Phases

The general phase behaviour of a simple solvent is shown in Figure 5.1. While Figure 5.1 is not to scale, the location of $\rho^*$ roughly corresponds to the density used in this study and is equal to the number of particles divided by the total volume, $0.195 \left( \frac{\text{particles}}{\sigma^3} \right)$. At this
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Figure 5.1: Simple solvent phase behaviour: In this temperature vs. density phase diagram $g$ denotes the gas phase, $l$ denotes the liquid phase and $s$ denotes the solid phase. For areas in coexistence, the appropriate phases are indicated.

密度，取决于所选择的温度，系统将要么处于三种相中的一种：气相（例如 $T_3$）、气液共存（例如 $T_2$）或气固共存（例如 $T_1$）。其他相（固相、液相和固液共存）不进行研究，因为它们不适用于本研究，而且对于所选择的密度来说，这些相在图上不可达。尽管我们的目的在于研究此模型溶剂的一般相态性质，我们特别感兴趣的是气液共存区域的部分，因为这对于进行与完整朗缪尔单层的模拟是有意义的。我们研究了气固共存和气相，以便更好地理解溶剂模型并获得气液共存区域的温度极限。

2925溶剂粒子被放置在由15粒子×15粒子×13粒子构成的四维格子上，并被置于一个长方体模拟箱的中央（47.94 Å × 47.94 Å × 191.76 Å），见图5.2。如前所述，这对应于密度为0.195（粒子/σ^3）。初始，溶剂被加热至高温（4.0 $T^*$），系统行为类似气体，如图5.3所示。图5.3中的不连续性是由于图中标记的步长不连续性造成的。图5.3中的不连续性是由于图中所标记的步长不连续性造成的。
potential located at $1.4\sigma_{tt}$ and $2.25\sigma_{tt}$. At distances greater than the largest well width there is no structure seen, as can be expected from a gas.

As the temperature is reduced the solvent begins to collect into more liquid-like drops to reduce the free energy of the system. At sufficiently low temperatures ($1.4 \ T^*$ to $1.9 \ T^*$) the majority of particles collect in one region (density $\approx 0.8$) and a small percentage form a large low density gas (density $\approx 0.01$), these two regions are in coexistence. At these temperatures, the slab is in the liquid phase as confirmed in the radial distribution function shown in Figure 5.4. There exists short-range order in the system as demonstrated by the four distinct solvent shells, yet the long-ranged positional order expected in a solid does not exist. The number of particles in the slab is large compared to the number of particles not in the slab, therefore these particles do not significantly affect the radial distribution function. Figure 5.5 shows an experimental radial distribution function of liquid water.
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Figure 5.3: Gas phase radial distribution function: This gas phase simulation was performed at a temperature of 4.0 $T^*$. The density is $0.195 \left( \frac{\text{particles}}{\sigma^3} \right)$, this is high for a gas and is to be considered when drawing conclusions from this figure.

Figure 5.4: Liquid phase radial distribution function: This liquid phase simulation is performed at a temperature of 1.88 $T^*$.

Due to the simplicity of this work’s model, differences are expected. Given this, the radial distributions are in qualitative agreement. Note $1.0\sigma = 3.0 \text{Å}$

For lower temperatures ($T < 1.35T^*$) the slab collapses via a first-order transition into the solid phase, this is confirmed by the radial distribution function shown in Figure 5.6.
From this figure, it is clear that the system was in the solid phase due to the sharp peaks and sustained long-ranged positional order. As with the gas-liquid coexistence, the gas density at this temperature was sufficiently low so as to not affect the radial distribution function.

Figure 5.5: Experimental liquid water radial distribution function for oxygen-oxygen. Image obtained from [16].

Figure 5.6: Solid phase radial distribution function: This solid phase simulation was performed at a temperature of 1.31 T*.
The particular arrangement of particles in these simulations caused unwanted effects in the liquid and solid radial distribution functions. These are, (a) incorrect normalization due to densities that depend on the system configuration, and (b) the decreasing trend in the radial distribution functions as the separation distance increases. Normally a simulation is carried out with a fixed density. This density corresponds to the liquid portion of the phase diagram over the range of temperatures being studied and therefore the particles are uniformly distributed throughout the box. This density ($\rho$ in the radial distribution function, Equation 3.27) serves as a normalization for the radial distribution function. For this system, the density used for normalization was 0.195 ($\frac{\text{particles}}{\sigma^3}$) but when the system was in coexistence (gas-liquid or gas-solid), this constant did not properly normalize the data. For example, a liquid slab with a 'local' density of 0.8 ($\frac{\text{particles}}{\sigma^3}$) is roughly 4 times as dense as the 'global' average; therefore, the radial distribution function is 4 times too large for all separation distances, as can been seen in Figures 5.4 and 5.6. The other effect ((b) above), was the result of the finite thickness of the slab. The particles at the interfaces have fewer neighbours than particles near the centre, and this effect is more evident as the separation distance approaches the half-width of the slab because, at this point, not only are particles near the interface affected but also particles near the centre of the slab. This leads to a downward trend of the radial distribution function as the separation distance is increased. This is evident in Figure 5.4, but is hard to notice in Figure 5.6 because of the positional ordering at large distances.

The effects noted above could be corrected for if the local densities could be determined. This was not implemented here because the radial distribution functions were only used to determine the phase of the system, not other quantitative properties.
5.1.2 Liquid-Gas and Liquid-Solid Coexistence

While the local densities were not used to correct the radial distribution functions, they were used to determine part of the phase diagram of our system. The density distribution of a $1.88 \ T^*$, liquid-gas system as a function of $z$ is seen in Figure 5.7. This curve can be represented mathematically by Equation 5.1. This equation, in part, naturally arises in the van der Waals theory of surface tension [8]. The measured density distribution can be fit with this equation to obtain an approximation for both the gas density and the liquid/solid density, as well as to obtain other useful parameters relating to the width of the slab.

\[
\text{PD}(z) = \frac{1}{2} [\rho_l + \rho_v] - \frac{1}{2} [\rho_l - \rho_v] \tanh \left( \frac{z - z_o}{d} \right),
\]

where $\rho_l$ is the liquid density, $\rho_v$ is the vapour density, $z_o$ is the value of $z$ corresponding to the average density, and $d$ is related to the width of the interface or, as it is more commonly known as, the Gibbs-dividing surface [2].
By plotting both the gas and liquid/solid densities for temperatures in the range of $1.31T^*$ to $2.35T^*$, a coexistence curve (similar to Figure 5.1) can be constructed for this particular model (Figure 5.8). Of interest in this figure is the region near $2.5T^*$, which corresponds to the critical point of this model. Simulations in the vicinity of this temperature can be difficult to obtain due to large amount of liquid evaporation near this temperature. At the critical temperature, the size of each phase is macroscopic and cannot be simulated with the current method. At a temperature of $1.34T^*$; it can also be seen that the density of the solvent jumps by 0.064 reduced units, this signifies the liquid to solid transition of the slab. This data was obtained by using an equilibrated liquid-gas coexistence configuration at $1.8T^*$ and raising/lowering the temperature to the desired point for measuring. A hysteresis effect is likely to occur near both phase transitions (gas-liquid coexistence to gas and gas-liquid coexistence to gas-solid coexistence); this is not investigated\(^1\) by slowly raising the temperature of a solid configuration to see when melting occurs, or lowering the temperature of a gas configuration to see when condensation occurs.

While this model does not fully represent water and all its properties at different temperature ranges\(^2\), we assume that, the solid-liquid transition that is observed at $1.34T^*$ corresponds to a real temperature of 273 K. Using this as a reference temperature, we deduce that one reduced temperature unit is equal to 203.7 K. From the reference value of the temperature, $\epsilon$ is determined to be 1694 J/mol (Equation 3.10).

Figure 5.9 compares the phase diagram obtained in this work to that obtained with a more detailed water model (simple point charge (SPC)), (refer to Refs. [2] and [12]). The critical point is higher for the more detailed water model due to hydrogen bonding, which raises the critical point of fluids.

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\(^1\)There are problematic issues with doing this in a simulation using the current method.

\(^2\)This is not the purpose of this study, an approximate representation is sufficient.
Figure 5.8: Liquid-gas coexistence: The coexistence region for this particular solvent model is represented in the temperature vs. density phase space. This phase diagram does not include any pure liquid phase, pure solid phase, or liquid-solid coexistence data as these phases were not investigated.

Figure 5.9: Temperature-density phase diagram: A comparison between current model and data obtained from Ref. [12] (Boxes), where simulations were performed using GEMC (Gibb’s Ensemble Monte Carlo) and an SPC water model, the solid line is the coexistence seen in Figure 5.8 with appropriate unit conversions.

The accepted experimental values for water are given in Ref. [12] and occur at even higher temperatures, with the critical temperature of 647.3 K. The GEMC simulations with an SPC water model from Reference [12] cautiously estimate a critical temperature for their model of 587K, while the model used in this study has a critical temperature of
≈ 500K. It is important to note that the Langmuir monolayer collapse simulations carried out with this model were performed over a temperature range for which the coexistence curve agrees will with Ref [12].

The surface tension of the liquid slab can be determined at each temperature based on Equation 3.21, which is shown below again for reference.

\[
\gamma^* = \frac{1}{2} \int_{-\infty}^{\infty} [P_N^*(z) - P_T^*(z)] dz, \quad (5.2)
\]

where \( P_N^*(z) \) and \( P_T^*(z) \) are the pressure tensor components (normal and tangential, respectively) as a function of \( z \) position calculated from Equations 3.23 and 3.22, respectively. The surface tension results are shown in Figure 5.10, along with results from Ref. [2]. Note that the surface tension at high temperatures is much lower than the experimentally accepted values and other model results, which again shows that the liquid’s surface is not stabilized at high temperatures with this model.

![Surface tension vs. Temperature](image)

*Figure 5.10: Surface tension vs. Temperature. The line through the open squares represents a quadratic fit to the points. Closed squares are results from Ref. [2], where the SPC/E water model was used. The experimentally accepted curve falls through the closed squares.*
In addition to the scalar value of the surface tension, the positional dependent surface tension contributions are a useful quantity to observe as they quantitatively show where contributions to the surface tension are being made, as a function of $z$. For a temperature of $1.88 \, T^*$ the difference in the pressure tensor components (argument of integral in Equation 5.2) as a function of $z$ position is shown in Figure 5.11, along with the solvent particle distribution. It is clear from this figure that contributions to the surface tension occur only at the interface between the liquid and the gas, as expected.

**Figure 5.11:** Positional dependant surface tension contributions: Surface tension contributions (solid line, not to scale), the integral of which is the surface tension (Equation 3.21). In addition the particle distribution as a function of $z$ (dashed).

### 5.2 Collapse Phenomena of a Model Langmuir Monolayer

In this section, we examine the behaviour of a model Langmuir monolayer utilizing the explicit solvent model investigated in Section 5.1. In particular, we focus on the phenomenon of collapse that occurs at surface pressures well beyond the equilibrium spreading pressure. The most straightforward way to study this phenomenon is to examine the change in surface pressure as the cross-sectional area is decreased at fixed temperature. Changes in the slope of the resulting pressure isotherm indicate phase transitions, whereas plateaus
correspond to coexisting phases. At sufficiently low areas, there is a peak in the isotherm corresponding to the collapse pressure, $\Pi_c$, followed by a plateau at even lower areas. This method is used in experiments, and included here for reference is the experimental isotherm for stearic acid that was presented in Chapter 1. This isotherm has the characteristics described above.

![Experimental pressure isotherm of stearic acid](image)

*Figure 5.12: Experimental pressure isotherm of stearic acid. Collapse occurs around 22 Å²/molecule [21]. 1 dyne/cm equals 1 mN/m.*

The measurements made in this section were made by placing a layer of surfactants (previously equilibrated on a hard-surface) onto the equilibrated water slab discussed in Section 5.1. As discussed in Chapter 2, the heads interact with the solvent particles through a single square-well potential and the tails interact with the solvent particles via a soft repulsive shoulder potential that models the hydrophobic nature of the tail groups. Details of these potentials can be found in Section 2.3. At low densities, far from collapse and after the surfactant slab equilibrates with the solvent, a typical particle distribution is similar to that shown in Figure 5.13.
5.2.1 Pressure Isotherms

In order to construct pressure-area isotherms, the surface pressure must be calculated from the surface tension through Equation 1.1. The values of the surface tension for a bare solvent interface are given in Table 5.1. This number is needed when calculating the surface pressure. The surface tension of the interface decreases as molecules are added (i.e. density increases) since solvent particles at the air/solvent interface may now interact with the head groups thus lowering the surface energy. It is noted that the tail groups contribute a small amount to the surface tension of the system, but the majority of the contribution to the surface tension is still concentrated at the solvent/surfactant interface. Pressure isotherms, similar to Figures 1.4 and 5.12 can be constructed for various temperatures. These are shown in Figures 5.14 through 5.16 for temperatures 1.46, 1.62, and 1.88 $T^*$, respectively. These isotherms are shown in real units using the conversions presented in Chapter 3 for a better comparison to Figures 1.4 and 5.12.
<table>
<thead>
<tr>
<th>Temperature ($T^*$)</th>
<th>Surface Tension ($\gamma_w$) ($\gamma^*$) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.46</td>
<td>2.69 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>84.1 ± 0.9</td>
</tr>
<tr>
<td>1.62</td>
<td>2.25 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>70.3 ± 0.6</td>
</tr>
<tr>
<td>1.88</td>
<td>1.38 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>43.1 ± 0.3</td>
</tr>
</tbody>
</table>

Table 5.1: Bare solvent interface surface tension both in reduced units ($\gamma^*$) and S.I. units (mN/m) at various temperatures.

Figure 5.14: Pressure isotherm at $T^* = 1.46$. The dashed line indicates the spreading pressure which is determined from the surface tension of a bare interface and is numerically equal to 84.1 mN/m. The solid line is a linear interpolation between the points.

These isotherms qualitatively reproduce the general features observed in experiments on Langmuir monolayers (See Figure 5.12, especially in comparison with Figure 5.16). A small non-zero surface pressure is found at large areas per molecule, but then drastically changes near the critical density; this effect is seen in all three isotherms. At the temperature of 1.46 $T^*$, the fluctuations in the pressure evident in the 40 - 70 A$^2$/molecule range are suggestive of van der Waal loops and the liquid-condensed (LC) - liquid-expanded (LE) coexistence region but note that the errors are purely representative of the deviation in

---

3 Monolayers composed of more realistic (and chemically detailed) surfactants change the structure of the pressure isotherms. Other properties such as pH of water or the presence of proteins also have an affect on this. Stearic acid is a relatively simple surfactant molecule and therefore makes an interesting comparison with this model.
Figure 5.15: Pressure isotherm at $T^* = 1.62$. The dashed line indicates the spreading pressure which is determined from the surface tension of a bare interface and is numerically equal to 70.3 mN/m. The solid line is a linear interpolation between the points.

Figure 5.16: Pressure isotherm at $T^* = 1.88$. The dashed line indicates the spreading pressure which is determined from the surface tension of a bare interface and is numerically equal to 43.1 mN/m. The solid line is a linear interpolation between the points.

the surface tension of one simulation. Therefore, these errors do not provide a satisfactory measure of the actual error. A more accurate estimate would require multiple simulations with different initial conditions to be performed. At higher temperatures, $(1.62 \ T^*)$, the fluctuations appear to change into a smooth plateau. This plateau is characteristic of
monolayers undergoing the LE-LC phase transition, but must be explored in detail before any conclusions are made. At even higher temperatures, there are fluctuations in the surface pressure at high areas per molecule ($> 50 \, \text{Å}^2$/molecule, Figure 5.16), due to instabilities in the monolayer.

On a closer examination of the high-density regions in Figures 5.14 though 5.16, it can be seen that the surface pressures of the two low temperature (1.46 $T^*$ and 1.62 $T^*$) isotherms do not level off in the same fashion as the surface pressure of the 1.88 $T^*$ isotherm. One possible explanation for this behaviour is that the system is metastable at high densities and therefore, at low temperatures the system cannot collapse (as seen in Figure 5.16). This persistent metastable state could be the result of the surfactant model. If the tail groups are too rigid then this may prevent curvature from developing to the extent needed for collapse. As an attempt to see if the rigidity of the tail group plays a role in this possible metastability, the intramolecular interactions were modified from the form presented in Chapter 2 to purely hard-sphere interactions. A pressure-area isotherm was generated at a temperature of 1.62 $T^*$, which may be seen in Figure 5.17.

Comparing Figure 5.17 with Figure 5.15 we see the effect of the modified tail potential is to induce collapse (i.e. the system moves away from the metastable state at lower densities). This allows us a more thorough look at collapse because the density range of the collapse is more inline with the simulated densities. At 1.62 $T^*$, the surface pressure reaches a peak at $18 \, \text{Å}^2$/molecule and then, upon a further reduction in the area/molecule, plateaus at a surface tension of zero. This process is explained further in the next section.
Figure 5.17: Pressure isotherm examining a modified intramolecular tail-tail interaction: The temperature is 1.62 T* and the intramolecular tail-tail interactions are all hard-sphere interactions based on a 1σ* interaction distance. The dashed line corresponds to the spreading pressure (70.3 mN/m). The solid line is a linear interpolation between the points.
5.3 Buckling of Langmuir Monolayers

As seen in Figures 5.16 and 5.17, the surface pressure peaks at low concentrations and then drops back down to lower values as the concentration is lowered further. This is a sign of monolayer collapse. Two system configurations for two particular densities are presented in Figure 5.18. These two images represent configurations from the simulations used to construct Figure 5.17. The concentrations are 18.4 Å²/molecule (top of surface pressure peak) and 15.9 Å²/molecule (collapsed system), for the left and right images respectfully.

![Figure 5.18](image)

*Figure 5.18: A side profile of two systems with different concentrations. The temperature of this system is 1.62 T* with an initial surfactant concentration of (a) 18.4 Å²/molecule and (b) 15.9 Å²/molecule. System (a) is metastable with respect to collapse, where system (b) has collapsed.*

By examining the time dependence of various measured quantities, more information about monolayer collapse can be obtained. Figure 5.19 shows the surface tension as a function of time for the modified surfactant model at an initial concentration of 15.9 Å²/molecule and a temperature of 1.62 T*. It is apparent that the system began in an unfavourable configuration (high surface pressure) and then transformed to one where the surface tension is zero. The high curvature state shown in Figure 5.18(b) is the final
configuration. This effect was also observed at high density in simulations with the original model at 1.88 T^*.

Figure 5.19: Surface tension as a function of time. The temperature of this system is 1.62 T^* with an initial surfactant concentration of 15.9 Å^2/molecule. The surface tension levels off at a value of zero within error, the final configuration of the system in shown in Figure 5.18(b).

The spread in the data values in Figure 5.19 is the result of the finite size of the system, as well as the short sampling time. With time-dependant quantities like the surface tension, the time interval between samples must be small so that the actual value does not change significantly over the time range. In DMD, this is a problem because many collisions (Equation 3.18) are needed to determine the surface tension accurately. The graph is in qualitative agreement with Figure 1.9, shown again here for reference in Figure 5.20.

The change in the surface tension seen in Figure 5.19 is the result of a structural change in the monolayer (Figure 5.18(b)). As the surface pressure increases, curvature develops at the surfactant/solvent interface in order to reduce the surface energy. This behaviour is also seen in Ref. [20], with the noticeable exception that in the present study the surfactant molecules do not evaporate into the gas, and therefore there is no
Figure 5.20: Surface tension of a water/surfactant system versus time for a collapsing monolayer. The system started in an unstable configuration and collapsed to a stable system through the expulsion of surfactant molecules into the air. Figure adapted from [20], the system has a cross-sectional area of 4900 Å².

mechanism to allow the monolayer to relax back to a flat profile corresponding to the mechanically stable equilibrium state.

There are several explanations for why surfactants do not leave the surface of the solvent. The pair potentials between the solvent and surfactant particles and the potential between intermolecular tail particles are two possible explanations and are discussed below. Another possibility is that surfactants under these conditions do not leave the surface, but collapse through other mechanisms, namely those suggested in Ref. [29]. This is also investigated below.

Potentials

The head-solvent interaction potential may be too strong and therefore, at these temperatures and pressures, there is insufficient energy to cause to head groups to leave the interface into the air. This possible cause was investigated in two different ways. The first simulation was run with a shallower head-solvent well; the results were quantitatively different but did not result in surfactant molecules leaving the surface during collapse.
width of the head-solvent well was also shortened. This resulted in surfactants escaping the surface at very low densities where this effect is not expected. A combination or modification of these changes could be explored to fully test the head-solvent interaction. This would include testing a double-well potential for the head-solvent interaction similar to the current solvent-solvent interaction potential.

The intermolecular tail-tail interaction may also be too strong and keep the surfactant molecules from escaping the surface. As seen in Figure 5.18(b), the tail particles at the vacuum/surfactant interface are only surrounded on one side by other tail particles. If the surfactants were to leave the surface, this configuration is ideal because there is less of a potential energy barrier for the surfactants to overcome. Since this does not happen, the tail-tail interaction may be too strong and is worthy of further investigation.

Other Collapse Mechanisms

As presented in Figure 1.8, a possible collapse mechanism is through the formation of large amplitude folds followed by a tri-layer. Figure 5.18(b) shows a possible 'seed' of one of these large amplitude folds, but due to the size of the box, there are not enough surfactant molecules to allow for any further formation. The size of the simulation box also results in the fold being supported by itself in the next periodic image. These two finite size effects prompted a larger simulation to be carried out with 13520 solvent molecules and 484 surfactant molecules. This system is almost 300% larger in cross-sectional area. Several configurations from this simulation are shown in Figure 5.21. Due to the size of this simulation, pressure isotherms were not calculated but surface tension measurements were made at the highest density over the course of the simulation, the progression of the surface tension is shown in Figure 5.22.

The final configuration for the large simulation can be seen in the right-most image in Figure 5.21. Unlike Figure 5.18(b), the fold does not interact directly with its periodic
CHAPTER 5: LANGMUIR MONOLAYERS ON AN EXPLICIT SOLVENT

Figure 5.21: Lateral profiles from a simulation with the large system size. The temperature of this system was 1.62 $T^*$, with an initial surfactant density of 13.6 Å$^2$/molecule. The left-most image is taken at 0 ps, the middle image is after 83 ps, and the final image is after 680 ps, well after the surface tension has reached 0. This simulation has 13520 solvent molecules and 484 surfactant molecules.

Figure 5.22: Surface tension as a function of time. The temperature of this system was 1.62 $T^*$ with an initial surfactant density of 13.6 Å$^2$/molecule. The surface tension levels off at a value of zero within error. This simulation has 13520 solvent molecules and 484 surfactant molecules for a total of 18844 particles.

This fold does not 'fall' over to form a tri-layer but is consistent with another mechanism Ybert et al. propose which is multi-folds. This collapse mechanism consists of many folds 1-2nm in vertical extent that are extended macroscopically perpendicular to the direction of compression. In order to elucidate the actual mechanisms occurring in this system, even larger simulations must be performed, possibly in the NIIT ensemble where
the surface pressure can be controlled. Such simulations would include approximately 80000 particles.

There is an increase in the collapse rate between Figure 5.19 and 5.22. These two systems were simulated at different concentrations. Since the initial configurations for the large system simulations is a higher density, the monolayer is further from equilibrium and a faster collapse is expected. However, simulations performed for the smaller system at the same density as the large system of 13.6 Å²/molecule were found to have collapsed also on the order of 400 ps, therefore this difference is still present and seems to arise because the different system sizes. The collapse time with the large system is more in agreement with the results from Nielsen et al., [20]. Such comparing must be done with caution, as the systems are different in the surfactant and solvent representations.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

Langmuir monolayers have been studied for over a century. They have applications in many areas ranging from biological systems to material science. The surfactants that compose the monolayers are simple in design: they have a head group which is attracted to the water and a tail group which is repelled by the water. Despite this simple structure, monolayers have a rich phase diagram with many different structural features. Non-equilibrium dynamics, in particular, collapse of Langmuir monolayers is an area of increasing interest both experimentally, [29; 26] and with computer simulations [20; 14]. Langmuir monolayers are an essential part of biological structures such as cell membranes and lung alveoli. Common processes of these structures - aiding in the transportation of molecules in and out of cells and exhalation of air for example - rely on collapse dynamics of monolayers to be successful. It is the goal of research in these areas to understand these collapse dynamics and processes.

This thesis used a simple hard-surface surfactant model to investigate Langmuir monolayer structure at high densities. Explicit solvent was used to study phase coexistence. The combination of these models, surfactants and explicit solvent, was used to examine the phenomenon of collapse in monolayers. These model systems were studied using the DMD formalism.
6.1 Hard-Surface Simulations

Simulations of Langmuir monolayers were performed utilizing the hard-surface model for the solvent. With this primitive model, we were able to study certain structural phenomena present in Langmuir monolayers such as tilting transitions. As expected, the magnitude of the tilt angle decreased with both increasing temperature and decreasing density. First-order phase transitions were seen. These transitions were not only in tilt directions (NN to untilted (ordered, hexatic), and NN to untilted (disordered)) but also in the head-group lattice structure (NN to NN’). This behaviour (NN to NN’) has been theoretically predicted at low temperatures [22] but never seen in simulations to date. It was found that by changing the tail-tail intermolecular interaction potential both nearest neighbour and next-nearest neighbour tilting can be achieved. As expected, the magnitude of the tilt angle decreased with both increasing temperature and decreasing density. Several results of this model are still puzzling such as tilt-phase coexistence.

6.2 Explicit Solvent Model

One of the main objectives of this thesis was to examine collapse phenomena which occur in Langmuir monolayers. One mechanism of collapse occurs through the development of curvature at the interface. Unfortunately, the hard-surface continuum model of the solvent is insufficient to capture such phenomena, and a more realistic solvent model is required.

Simulations with pure solvent at a density of 0.195 particles/\(\sigma^3\) were performed to test the solvent model. In the region of interest, the system phase separated into liquid and gas and allowed a liquid-gas coexistence curve to be constructed for this model. This curve agrees well with experiment and more detailed water models (SPC) in the temperature range of interest. Although, this coexistence curve differs from the exper-
imental curve for water in that water can maintain a liquid at higher temperature, this is due to hydrogen-bonding present in water but not explicitly included in this model. At sufficiently high temperatures, all the particles exist as part of a gas, whereas at low temperatures the particles form a solid. Radial distribution functions were calculated for all three of these phases. These functions, with the exception of the gas phase, suffered from inherent problems due to the non-isotropic density of the system. Hysteresis effects are not investigated, but are most definitely present near the phase transition regions of this model. Collapse simulations were performed at temperatures above the liquid-solid transition and well below the liquid-gas transition. This was based on the assumption that any hysteresis in the solvent model would not be evident at these temperatures and therefore would not affect the collapse dynamics.

6.3 Pressure Isotherms and Collapse of Langmuir Monolayers

A layer of surfactants which had been equilibrated on a hard-surface were deposited at the air/solvent interface of a slab that had also been previously equilibrated. Pressure isotherms were examined at three different temperatures. The temperatures were above the liquid-solid transition temperature and below the liquid-gas transition temperature found in Chapter 5.

Two models of intramolecular tail-tail interactions were investigated. The first model had intramolecular potentials that maintained some rigidity in the surfactant tail groups. With this model, collapse was seen at high pressures in that some form of curvature developed at the surfactant/solvent interface for all temperatures. Only at the highest temperature (1.88 $T^*$) did the surface pressure reach a peak and then fluctuate about the zero surface tension region. The intramolecular tail-tail potential was modified so that the interactions between tail particles were purely repulsive. Since the tails were no longer
rigid-like, changes in the monolayer’s structure could occur more easily with this modified interaction, as is seen through collapse at lower densities. At a temperature of $1.62 \, T^*$ we see the surface pressure reaches a peak at a high density of surfactant molecules; this system is metastable with respect to collapse. At even higher densities, a zero surface tension region is reached, this collapse is due to the development of high curvature.

While the results show collapse at high densities, they suggest that a modification to the potentials, most likely the tail-tail interaction potential, could be made so that the monolayer has the ability to return to a stable configuration by expelling individual surfactant molecules into the vacuum. Collapse occurs in several of the pressure isotherms studied in this work. The collapse is seen dynamically in Figures 5.19 and 5.22 where the latter is a simulation where the size of the simulation box was increased to examine finite size effects. These surface tension versus time curves are similar to those presented in Reference [20]. Configuration snap-shots are shown of two collapsed monolayer simulations (one small system simulation and one large system simulation). These snapshots suggest that collapse may be occurring through the Ries mechanism where large columns of surfactants form and then fold over to form tri-layers or through a multi-fold collapse mechanism where many small folds (1 - 2 nm in height) form as the pressure is increased. If this is the case, the current tail-tail interaction potentials may be sufficient to model this type of collapse. However, larger simulations are needed to investigate this further.

6.4 Future Considerations

6.4.1 Hard-Surface Solvent Model

With the current hard-surface model of Langmuir monolayers there are still unanswered questions: the behaviour of curve (d) in Figure 4.3 is puzzling, and while both NN and NNN tilting is observed, transitions between these tilting types has not yet been seen with
this model. It is possible that further investigation with the 'NNN potential' will reveal this, although another modification to the intermolecular tail-tail interaction potential may be required to allow these transitions to occur.

In reality, for energetic reasons, surfactant tails adopt an all-trans conformation. Hence, the atoms along the surfactant backbone tend to lie in a plane, which we can call the backbone plane of the surfactant. At low temperatures, the backbone plane of the surfactants will be arranged so as to be optimally packed together. Depending on the pressure and temperature, the direction of this packing can be in either the NN or NNN direction. In addition, there exists a herringbone phase, whereby the backbones pack in a Herringbone fashion at a relative orientation of 90°. A more detailed model, effectively modelling angular potentials is needed to achieve these structures. To fully eliminate the possibility that finite size effects are causing unrealistic behaviour in the hard-surface model of Langmuir monolayers, simulations need to be performed in the NIIT ensemble. This system is discussed in relation to collapse studies further on in this section.

6.4.2 Explicit Solvent Model

The obvious next step to improve upon the explicit solvent model is a more detailed description of the water molecule by including the hydrogen atoms and possibly the electron pairs as pseudo-particles. With a model like this, hydrogen bonding is now possible to simulate. Preliminary simulations into such a model were performed using two different DMD approaches:

i) **Fully flexible model**: The fully flexible DMD model of water uses all of the same techniques as the DMD model described in this thesis. In these preliminary investigations, electron pairs were modelled as particles with a mass equal to that of hydrogen. To model hydrogen bonding, electron pairs and hydrogen atoms on different molecules were
modelled with attractive short-range potentials, and like pairs (hydrogen - hydrogen and electron pair - electron pair) were treated as repulsive at short distances due to electrostatic repulsion. To maintain the shape of the water molecule strict bond potentials were required between all intramolecular pairs (10 in total). Initial simulations with this model failed to produce a stable air/water interface at the appropriate density. Further investigation of the oxygen-oxygen interaction is needed to produce a suitable set of potentials.

ii) Rigid DMD model: The water model discussed above, which accounts for hydrogen bonding, requires 10 intramolecular interactions to maintain the water molecule’s shape. These intramolecular interactions occur at a frequency almost an order of magnitude greater than that for the intermolecular events, yet do not contribute significantly to the relevant dynamics of the system. Hence, much computational effort was expended in non-essential dynamics and presented a computational bottleneck to studying the important dynamics. To circumvent this computational bottleneck, a rigid-body water model was explored, where the bonds within the water molecule are fixed. The oxygen was located at the centre of mass and the two hydrogen atoms and the two electron pairs form the four points of a tetrahedron each located a distance of $1.0\sigma$ away from the oxygen. While this spherically symmetric model is inexact, it allows for a simplification in the solution of the equations of motion for this rigid-body system. Recently, a solution for any rigid-body, including asymmetric molecules, has been provided within the DMD framework [10]. While the essential DMD framework remains intact, the determination of collision times and collision rules requires significant modification. The collision times are determined numerically instead of analytically, and when two particles have a collision, all particles on the corresponding molecules are affected (10 individual particles all together).

A downside of a more realistic solvent model is the mismatch in the level of coarse-graining between the solvent and the surfactant molecules. Without fully modelling the
surfactant molecules (which includes the incorporation of hydrogen bonding between the head-group and water and more complex tail-tail interaction potentials) the some benefits of the realistic water model would be lost.

6.4.3 Collapse Studies

More work must be done with the current model to fully understand what mechanisms are being observed, and whether it is possible to observe other collapse pathways. Any future collapse studies would benefit from all of the aforementioned improvements, particularly the ability to perform simulations in the N\_II\_T ensemble. We suggest that a DMD-MC hybrid system be used to allow for simulation box size changes. Overlapping particles would occur when the simulation box is contracted in any one direction and, these overlaps can be handled the same way as the overlaps present in this work when the equilibrated solvent model is combined with the equilibrated surfactant layer. Using this technique, simulations could be performed where a stable monolayer is compressed to higher densities and eventually to a collapse transition.
APPENDIX A

TIME CALCULATIONS

The following is the derivation of Equation 3.3. This equation predicts the time when the two particles $i$ and $j$ will be at a separation distance of $d$. The derivation begins with transferring the particles to the reference frame of particle $j$; that is,

\[ \vec{r}_{ij}(t) = \vec{r}_j(t) - \vec{r}_i(t), \quad (A.1) \]

and

\[ \vec{v}_{ij} = \vec{v}_j - \vec{v}_i, \quad (A.2) \]

where $\vec{r}_i$ is the position of particle $i$ and $\vec{v}_i$ is the velocity of particle $i$. Note that $\vec{v}_i$ is independant of time between collisions.

If the two particles will be at a separation distance of $d$ then the following equation will be true at that time,

\[ |\vec{r}_{ij}(t + t_{c,ij})| = d \quad (A.3) \]

where $t_{c,ij}$ is the future (or past) time at which the two particles will be at a separation of $d$. Since the particles move with respect to each other at a constant rate, Equation (A.3) can be written as
\[ |\vec{r}_{ij}(t) + \vec{v}_{ij} t_{c,ij}| = d \]  

(A.4)

To solve for the time, both sides of Equation (A.4) are squared to obtain

\[ \vec{r}_{ij} \cdot \vec{r}_{ij} + [2\vec{r}_{ij} \cdot \vec{v}_{ij}] t_{c,ij} + [\vec{v}_{ij} \cdot \vec{v}_{ij}] t_{c,ij}^2 = d^2. \]  

(A.5)

Since \( \vec{r}_{ij} \cdot \vec{r}_{ij} = r_{ij}^2 \), \( \vec{v}_{ij} \cdot \vec{v}_{ij} = v_{ij}^2 \), and defining \( \vec{r}_{ij} \cdot \vec{v}_{ij} = b_{ij} \), Equation A.5 can be solved for \( t_{c,ij} \) using the quadratic equation.

\[ t_{c,ij} = \frac{-b_{ij} \pm \sqrt{b_{ij}^2 - v_{ij}^2 C_{ij}}}{v_{ij}^2} \]  

(A.6)

where \( C_{ij} = r_{ij}^2 - d^2 \). This is Equation 3.3.
There are four different types of nodes in a binary tree. Each node is a site for storing an event. At the top of every binary tree, there is a head node. A parent node is a node that has nodes stored below it. A left daughter node is a node that is the left linking node of a parent. Finally, a right daughter node is a node that is the right linking node of a parent. A left or right daughter node may or may not have nodes stored below it and therefore may also be a parent node. This simple structure is shown in Figure B.1.

The binary tree is organized so that left daughter nodes have an event time that is less than their parent node, and right daughter nodes have an event time that is longer than their parent node. When an event is being inserted into a binary tree, first the time is compared to the time of the head node. If the time is shorter, the process is continued with the left node. If the time is longer, the process is continued with the right node. When the destination node (left or right daughter node) does not exist after comparing.
times, the event is inserted at this location. An example of a binary tree is shown in Figure B.2. The top number in each node is the particle number, whereas the bottom number is the time of that particle’s next event.

![Sample binary tree storing events](image)

*Figure B.2: Sample binary tree storing events. A left child of a node always has a smaller time, whereas the right always has a larger time. The top number in each node is the particle number, whereas the bottom number (the sorted number) is the time of that particle’s next event.*

If an event (particle number 8) with a time of 6.0 time units were to be inserted into this tree the process would be as follows: 

1. 6.0 is larger than 1.5 and therefore go right: 
2. 6.0 is larger than 2.4 therefore go right: 
3. 6.0 is less than 9.3 and therefore go left: 
4. since no node exists left of the parent, create a new node with particle number 8 and event time of 6.0 time units.

For deletion of elements from a binary tree see Ref. [28].
BIBLIOGRAPHY


