Depletion and Structural Force Interactions of Bubbles in Aqueous Polyelectrolyte Solutions

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Submitted in total fulfilment of the requirements of the degree of Doctor of Philosophy

February 2016

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and
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Produced on archival quality paper
Abstract

The examination of several different experimental systems presented in this thesis work are linked through their singular aim of investigating the interactions of deformable interfaces, in this case air bubbles, in aqueous polyelectrolyte solutions. Direct force measurements were used to probe depletion and structural force interactions between colliding air bubbles at equilibrium timeframes. In addition, air bubbles were generated without the presence of interface stabilising molecules within a block-and-break microfluidic device to probe the interactions from generation to equilibrium.

Direct force measurements were conducted between interacting bubble pairs in aqueous solutions of polyvinylpyrrolidone (PVP), a neutrally charged polymer, and sodium poly(styrene sulfonate) (NaPSS), a negatively charged polyelectrolyte. The selection of these molecules allowed a comparison between neutral and charged polymers and their influence on the measured force interactions. It was found that for measurements conducted in the presence of PVP, neither a structural force nor a depletion interaction was able to be measured. This was largely due to an increase in solution viscosity with increasing concentration of PVP, which results in an increase in the hydrodynamic fluid flow that subsequently overwhelms any potential presence of a depletion interaction. Also, the polydispersity of the molar mass of the PVP would appear to be responsible for the non-observance of structural forces in this system. This conclusion is based on the results of force measurements conducted in aqueous solutions containing monodisperse NaPSS. Uncharged polymers have also been shown to have a lower osmotic pressure when compared to a charged polyelectrolyte, which decreases the magnitude of the depletion interaction.

The measurements conducted in the presence of NaPSS with the deformable interface of bubbles were shown to be more sensitive to the presence of the polyelectrolytes when compared to similar measurements using rigid interfaces. The study involved the use of both polydisperse and monodisperse molar mass distributions and the experimental factors that were examined were NaPSS concentration, bubble collision velocity and polyelectrolyte molar mass. Structural forces were measured with the use
of a monodisperse sample but only a depletion interaction when the polydisperse molar mass distribution was present. This demonstrates that polydispersity in molar mass results in the structural forces to be smoothed. The dispersity of the various molar mass distributions was manipulated to further investigate the role they play on the observed interactions. The polydisperse samples were dialysed, which removed the low molar mass molecules and the monodisperse samples were blended to create a bidisperse mixture. When the dispersity was decreased through dialysis, structural forces were observed and the bidisperse mixture only allowed the presence of a depletion interaction to be measured. These measurements further highlight the role that molar mass dispersity plays on the observed interactions and shows how these interactions can be manipulated.

These measurements were then compared with an analytical model based on polyelectrolyte scaling theory (depletion interaction) or an empirical model (structural forces) in order to explain the effects of concentration and bubble deformation on the interaction between bubbles. The modelling highlighted that these interactions can be accounted for by polyelectrolyte scaling theory taking into account the structural properties of the polymer in solution in the dilute and semi-dilute polymer concentration regimes. It was also shown in all measurements that depletion and structural forces were overwhelmed by hydrodynamic fluid flow at increase bubble collision velocities.

Bubbles were generated for the first time within a block-and-break microfluidic device. The original design allowed water droplets in oil to be generated and design changes were required to ensure air bubbles could be formed. Block-and-break devices offer the advantage, that the generated bubble sizes are flowrate independent instead of other design types where the bubble size varies with flowrate. Air bubbles were able to be generated in solutions of pure water, NaPSS and sodium dodecyl sulfate (SDS) and their size was shown to be flowrate independent. The microfluidic device designs were modified to allow staged amphiphilic addition of SDS and NaPSS after the bubble was generated in pure water and this has the potential to allow complexity to be increased stepwise throughout an experiment. The combination of both direct force measurements and microfluidic studies allowed bubbles in the presence of aqueous solutions of NaPSS to be studied from generation through to their equilibrium form.
Declaration

This is to certify that:

i. the thesis comprises only my original work towards the PhD except where indicated in the Preface,

ii. due acknowledgement has been made in the text to all other material used,

iii. the thesis is fewer than 100 000 words in length, exclusive of tables, maps, bibliographies and appendices.

Christine Isabel Browne
Preface

All work presented in this thesis study has been conducted during my enrolment as a PhD student at The University of Melbourne. Figure 3.7 in Chapter 3 was taken by Doug Mair and Figure 3.5 in Chapter 3 was taken with the assistance of Dan Smith. Adrian Sulistio and Joel Scofield completed the dispersity measurements with the use of gel permeation column presented in Chapter 5 as part of Table 5.1. The custom Matlab computer code used in Chapter 7 for the automated image analysis was designed and written by Christopher Bolton. The results generated by the automated image analysis are included in Figures 7.7 through to Figure 7.10.
Acknowledgements

The undertaking of a PhD is a long and windy journey that could not be completed without the support and patience of others. There are many people that have helped steer me through this path and without them the fact that I am now able to write the acknowledgements for my thesis would not have been possible.

I must begin by thanking my supervisors Ray Dagastine and Franz Grieser for their support and encouragement not only over the past four years during my PhD, but also the times during undergraduate and Honours that I worked with them. During this time they have provide many opportunities and a safe space to allow me to grow as a scientist. My skills, not only in the lab but also in science communication, have improved immensely and it is only due to the supportive and encouraging environment they have set-up that I have been able to achieve these things. Also a thank you to Rico Tabor, who when I started my PhD was wonderful in teaching me all things AFM. Throughout the years his advice has been spot on and presented in a clear, concise manner that I quite often return to many months or even years later.

Universities are places filled with many, many people and there are a few special ones that have been great during my PhD. It is always nice to have a great research group and I thank all the members, past and present, for their support and the fun times. It has been fun to share an office with Chris and Chris, not only due to the confusion over names but that they have been a constant when many other people have come and gone. It’s always great to have a chat and discover that the person sitting next to you has the same struggles with their own work. I thank Marta for her patience in helping with my training on the AFM and when the cry of ‘I got liquid in the head’ would arise. I also thank her for her many chats, tea and swimming sessions over the years.

Also to the many people who gave Uni a nice social aspect as well. I have especially enjoyed the lovely mornings with the ‘Buenos dias Brunetti’ club. I would also like to thank Lauren, Katelyn and Anna for their friendship and ability to provide useful advice when it was most required. The ‘stalwarts’ of the PFPC seminars have also provided enjoyment over the years.

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The people I have worked with down at the Melbourne Centre for Nanofabrication (MCN) have also played a vital role in the completion of this work. I have received hours of training on various instruments and their friendly faces made the trip down to Clayton worthwhile. A special thank you must go to Dan Smith for his advice with a many processing issue within the cleanroom.

Throughout this journey I sadly had to say goodbye to two strong and loving women who in many ways have shaped who I am, my Nana, Mary Isabel Drew and my aunty, Jennifer Anne Drew. My Nana believed that being educated, well-read and showing compassion for others were the most important things in life. Even though she did not get the opportunity to go to University herself, mainly due to the era in which she was born, she was the person you wanted on your trivial pursuit team as there was no way you were going to beat her. Her belief in education led her to be a librarian later in life and once she retired she volunteered at the local school working with children who needed extra support in learning to read. She believed in the power of education and the riches that it can bring to a person’s life. My Aunty was a fighter. She had previously been diagnosed with leukaemia and told she had 3 more months with us. 11 years later, the reason for her death was not this disease, though it had tried with all its might to get her during the intervening years. Her motto for life was “It’s another day, I’m still here and today will be great.” A great motto to live by and when things are getting tough, something I like to remind myself.

I must also thank my poor suffering parents, Heather and Greg who are currently dealing with their two children completing PhDs. Their patience, support and constant encouragement with anything that I have attempted in life has been amazing. I’m sure they are thankful for my upcoming submission so they now only have one set of conversations about experiments, writing and general challenges faced in a PhD. Also my brother, Richard, whom I have spent many hours discussing the ups and downs experienced in the field of science over lunch or whilst out for a ‘cache.

A special thank you must go to Amy Hein, someone who I met at kindergarten and is essentially my sister. I say thank you for all the crazy, insane and just plain hilarious messages of encouragement and love that you have sent me over the past four years. It is always the small things, such as the endless stories and hours of amusement you have provided with all the silly things that happen in daily life that mean the most and
always put a smile on my face. Thank you for still being at my side after this journey and I hope our friendship continues for many, many, many years to come.

Friends from school and undergraduate times, Guiding and guitar lessons have made contributions to my life outside of my studies. I know that at times I have been down the PhD hole, speaking incoherently about science (or not speaking at all) but I’m ready to stick my head up and experience life, study free. Finally, this thesis could not have been written without the driving beats and melodies of Taylor Swift, Tina Turner, Metallica, and U2 just to name a few.
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Chapter 1 - Thesis Overview

This chapter will present the main themes and outcomes of this thesis study.
1.1 Introduction to the Thesis

The interaction of bubbles and droplets are of vital importance in many practical and industrial applications. The beneficiation of mineral ores, such as those carrying gold via froth flotation in the mining industry or the use of dissolved air flotation to aid the removal of particulates from water during treatment rely on the interactions of the material and bubbles. Bubbles also provide a textural element to foods such as soft drinks, chocolates, whipped cream or foamed milk. Understanding the fundamental aspects of the interaction between bubbles during various inherent or applied conditions allows improvement in processes and ultimately lowers the costs of manufacture/production to the involved industries.

Bubbles, droplets, particles and surfaces have been studied for many years with the use of various techniques. Bubbles are able to rise in liquids, attract each other and coalesce or repel each other, dissolve or expand in solution, undergo cavitation, create foams and have particles or molecules adhere to their interfaces. Due to the various ways they can behave in solutions the possibilities for investigation are numerous.

One important aspect for many applications involving bubbles is how the bubbles will interact with each other during a collision. These interactions are dependent on the surface forces present and on the deformation of the bubble interface. Solution additives influence whether the bubbles are attractive or repulsive in their interactions. Structural and depletion forces are a particular focus of interest due to their presence when additives such as polymers, polyelectrolytes and surfactants are added to aqueous solution. Attractive depletion forces are important in allowing a dispersed phase to be flocculated and then resuspended in solution with a change of solution conditions. Due to this ability to flocculate and redisperse colloidal particles structural and depletion forces are of interest within the sphere of industrial applications.

1.2 Objectives and Outcomes

The overall theme of the studies within this thesis is to investigate the deformable interface of air bubbles in a variety of different solution conditions. First, direct force measurements were conducted with the atomic force microscope (AFM) to determine
and investigate the interaction forces between a pair of bubbles when they come into close contact. The second method that was utilised was generating bubbles with a diameter of less than 100 micrometres within a microfluidic device. These two different types of measurements have the ability to probe bubble interactions at two distinct time points. The microfluidic device investigates the time from bubble generation to the equilibrium state of the bubble interface whereas the direct force measurements probe more deeply the equilibrium timeframe interactions.

Within the AFM studies conducted in this thesis depletion and structural forces were investigated with the use of different polymers. First, an attempt was made to measure these using polyvinylpyrrolidone (PVP), an uncharged polymer. Previous work had indicated that depletion forces are potentially present in solutions with this polymer\textsuperscript{23}. Direct force measurements were conducted between bubbles in solutions of PVP, but a depletion force was unable to be measured with this system. This was due to the increased solution viscosity obscuring the depletion interaction as the hydrodynamic fluid flows in the system are increased and also due to the lower osmotic pressure when compared to a polyelectrolyte\textsuperscript{24}. This led to the next study with a polyelectrolyte and was conducted with sodium poly(styrene sulfonate) (NaPSS).

There are numerous studies reported in the literature conducted with NaPSS demonstrating the presence of structural and depletion forces between approaching surfaces at concentrations where solution viscosity does not overwhelm the forces of interest. Previous AFM studies that have used NaPSS as the structuring colloid have focused on measurements involving rigid interfaces. There has been one study reported that investigated the interactions of NaPSS between colliding droplets as a model system for sugar beet pectin\textsuperscript{25}. The research detailed in this thesis characterises the interactions between colliding air bubbles with varying polyelectrolyte concentration, molar mass and collision velocity.

These studies were also expanded to investigate the effect of dispersity of molar mass by using both commercially available polydisperse and monodisperse samples. The dispersity of the molar mass plays a large role on whether a depletion or structural force is measurable. When a polydisperse sample was used only a depletion force was present and a structural force returned with the use of a monodisperse sample. The
study was extended further with the polydisperse sample undergoing dialysis and two different monodisperse molar masses combined to create a bidisperse molar mass.

Due to the time taken between generating a bubble to undertaking a direct force measurement another technique was required to investigate the effect of polyelectrolytes on a newly created bubble interface. This work was conducted by generating bubbles within a microfluidic device. A block-and-break type microfluidic device was designed and fabricated to generate bubbles with a diameter under 100 micrometres. The bubbles were generated in water, sodium dodecyl sulfate (SDS) and NaPSS and the use of these solute molecules was due to the different time scales of absorption to an air-water interface. It is known from work reported in the literature that SDS undergoes a greater rate of absorption to the air/water interface than NaPSS and this study allowed these effects to be investigated.

1.3 Chapter Summaries

A list and brief description of the material presented in the chapters within this thesis are presented below.

Chapter 2 - Literature review: The relevant literature is presented to give this thesis study context within the broader colloid and interface science area. It begins with a presentation of the theoretical knowledge of various aspects important in colloid science. It then continues to explain the current state of direct force measurements with AFM and the generation of bubbles in microfluidic devices. A more detailed explanation of structural forces and the measurement of them is also included.

Chapter 3 - Experimental methods: The experimental methods for both the direct force measurements with the use of AFM and the fabrication of the microfluidic devices are described in this chapter. The techniques presented here are used throughout the subsequent chapters.

Chapter 4 - Direct AFM force measurements between air bubbles in aqueous polyvinylpyrrolidone solutions: A brief discussion of measurements conducted with aqueous polyvinylpyrrolidone solutions and the reasons that depletion forces were unable to be measured is presented.
Chapter 5 - Direct AFM force measurements between air bubbles in aqueous polydisperse sodium poly(styrene sulfonate) solutions: Presentation of the direct force measurements conducted between colliding air bubbles in aqueous solutions of polydisperse NaPSS solutions is shown in this chapter. The experimental variables of polyelectrolyte concentration, collision speed and molar mass is discussed.

Chapter 6 - Direct AFM force measurements between air bubbles in aqueous monodisperse sodium poly(styrene sulfonate) solutions: In a similar fashion to Chapter 5 direct force measurements between colliding bubbles is presented using monodisperse NaPSS. Focus is on the same experimental variables as in Chapter 5 and includes a discussion of the effects of the molar mass dispersity and its role on the subsequent interactions between colliding bubbles.

Chapter 7 - Formation of an air bubble within a microfluidic device: This chapter focuses on the fabrication of microfluidic devices aimed at generating bubbles with a diameter of less than 100 micrometres without the presence of a surfactant or similar surface stabilising molecule. This work also focuses on the generation of bubbles in SDS and NaPSS solutions to explore the effects these molecules have on the interfaces of newly created air bubbles.

Chapter 8 – Summary and conclusions: This chapter summarises the material presented in this thesis study and highlights the important outcomes.

1.4 List of Publications

A list of publications that have been produced from the work presented in this thesis are:


The relevant literature is presented to give this thesis context within the broader colloid and interface science area.
Chapter 2

2.1 Introduction to Colloidal and Surface Forces

The study of colloidal and surface forces is of considerable relevance with respect to understanding their influence in a wide range of applications where the presence and stability of colloidal particles or droplets are vital. For example, suspension of colloidal particles present as ore in mineral processing needs to be able to be separated, processed and eventually some fraction stored as a waste product. Emulsions and foams form the basis of food products such as ice cream, salad dressing and chocolate. It is not only important to control the interactions between these droplets to maintain product stability, but the size and the distribution of them to have a suitable overall product texture and quality. Further understanding and knowledge of the fundamental interactions between particles, droplets and bubbles can be expected to improve the formulation and manufacture of the many varied practical applications of colloidal systems.

2.2 Types of Surface Forces

Various surface forces are present between colliding bubbles, droplets, particles or surfaces. In these interactions the surface chemistry along with the solution additives influences the final outcome of the colliding species. The forces discussed here can either be repulsive or attractive, and they dominate various length scales from angstroms to micrometres.

2.2.1 Electric Double Layer Force

The electric double layer (EDL) force comes about due to the presence of a surface charge, as a result of either the dissociation of an ionisable group on a surface, or the adsorption of a charged species to a neutral surface. The first description of an EDL was by Helmholtz, in which the electric field was limited to a molecular layer from the surface\textsuperscript{26}. This described the basic features of the charged surface, but did not account for the capacitance effect of an EDL. Gouy-Chapman determined that the EDL was also affected by the thermal motion of ions in solution\textsuperscript{27}. This thermal motion causes the counter-ions to move away from the surface which forms a diffuse charge layer.

The current model of an EDL consists of three main sections the Stern or Helmholtz layer, diffuse layer and bulk solution and is shown in Figure 2.1. Due to the surface
charge oppositely charged ions in solution are more likely to be attracted to the surface and form what is referred to as the Stern or Helmholtz Layer\textsuperscript{28}. In this layer the counter-ions are transiently bound to the surface to balance the charge imparted by the surface and creates a region with an increased concentration of counter-ions\textsuperscript{28}. In the diffuse layer the counter-ions and co-ions undergo thermal motion, which is able to be described by the Poisson-Boltzmann equation\textsuperscript{29}. Both the Stern and diffuse layers are required to neutralise the effect of the charged colloidal interface.

**Figure 2.1.** Schematic of the EDL interaction showing the Stern layer, diffuse layer and the bulk solution. The Debye length is equal to the sum of the distances of the Stern and diffuse layers. The EDL potential is the highest at the colloidal interface and decreases to zero in the bulk solution.

### 2.2.1.1 Poisson-Boltzmann Equation

The Poisson-Boltzmann equation allows the electrostatic potential ($\psi$) to be related to the volume charge density ($\rho_e$) near a charged interface. The equation relies on several assumptions regarding the diffuse ions, which are that the ions are point charges, that there are no specific ion interactions, the dielectric constant for the solvent does not
vary through the EDL and the charge on the surface is evenly distributed. The Poisson
equation is shown as Equation 2.1.

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho_e}{\varepsilon \varepsilon_0} \tag{2.1}$$

where $\psi$ is the electrostatic potential, $x, y, z$ are the distance in the respective plane
from the interface, $\rho_e$ is the volume charge density, $\varepsilon$ is the dielectric constant of the
solution and $\varepsilon_0$ is the permittivity of a vacuum.

To simplify the presentation of the Poisson-Boltzmann equation it is generally taken
that the interface is planar and therefore the differential equations in the $y$ and $z$ axis
will be zero. The Boltzmann equation, shown as Equation 2.2, describes the diffusion
effect of the ions.

$$n_i = n_i^0 \exp(-W_i/k_B T) \tag{2.2}$$

where $n_i$ is the number density of each type of ion, $n_i^0$ is the bulk ion number density
defined by each type of ion per unit volume, $W_i = z_i e \psi$, $k_B$ is the Boltzmann constant and $T$ is
the temperature.

The volume charge density is a summation of all ions present of either sign in the
electrolyte solution in a unit volume and is shown as Equation 2.3.

$$\rho_e = \sum_i n_i z_i e \tag{2.3}$$

where $z_i$ is the charge number for of a particular type ion and $e$ is the charge on an
electron.

The three previous equations can be combined to form the Poisson-Boltzmann
Equation, shown as Equation 2.4.

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{\varepsilon \varepsilon_0} \sum_i n_i^0 z_i e \exp\left(-\frac{z_i e \psi}{k_B T}\right) \tag{2.4}$$

If two assumptions are made, this form of the Poisson-Boltzmann equation can be simplified into the more usable form of the Debye-Hückel approximation. If it is
assumed that a single symmetrical electrolyte is present (1:1) and that the electrical or potential energy is small when compared to that of thermal energy \(|z \psi_0| \leq k_B T / e \approx 25\) of the ions, Equation 2.4 can be expanded into the form shown as Equation 2.5.

\[
\frac{\partial^2 \psi}{\partial x^2} = -\frac{1}{\varepsilon \varepsilon_0} \left[ \sum_i n^0_i z_i e - \sum_i n^0_i z_i^2 e^2 \left( \frac{\psi}{k_B T} \right) \right]
\]

(2.5)

For electroneutrality to occur in the bulk solution the first summation must equal zero and therefore gives Equation 2.6.

\[
\frac{\partial^2 \psi}{\partial x^2} = \sum_i n^0_i z_i^2 e^2 = \kappa^2 \psi
\]

(2.6)

where

\[
\kappa = \left( \frac{e^2}{\varepsilon \varepsilon_0 k_B T} \sum_i n^0_i z_i^2 \right)^\frac{1}{2}
\]

(2.7)

The inverse of Equation 2.7 is more commonly known as the Debye length and is a measure of where the diffuse layer of an EDL and the bulk solution meet. For a 1:1 electrolyte, such as NaCl, the Debye length, expressed in units of nanometres, can be calculated with Equation 2.8.

\[
\kappa^{-1} = 0.3041 \frac{1}{\sqrt{C}}
\]

(2.8)

where C is the concentration (mol/L) of the 1:1 electrolyte.

2.2.1.2 The Interaction of Charged Interfaces in Solution

The above description allows the ion charge distribution to be determined within the EDL of one charged interface. In the case of interface and colloidal science, the main areas of interest are the interactions that occur between various interfaces. When two charged interfaces are approaching each other in solution the EDL associated with each individual surface begin to influence each other. Once the distance between the two surfaces is a sufficiently small distance and the EDL layers begin to overlap, this is referred to as weak overlap. The overlap of the two EDLs between approaching
surfaces creates an electrostatic repulsion. The form of the Poisson-Boltzmann equation shown as Equation 2.6 no longer holds under these conditions and the full solution is required. The two boundary conditions required to solve the full Poisson-Boltzmann equation are constant surface charge and constant potential and are maintained by the system. The full derivation of the solution will not be shown here as it has previously been shown in literature. Using these boundary conditions along with the linear superposition approximation assumption the EDL potential at weak overlap between two infinite half spaces can described as:

\[
V_{\text{EDL}} = \frac{64k_B T n^0}{\kappa} \tanh \left( \frac{e \psi_{oi1}}{4k_B T} \right) \tanh \left( \frac{e \psi_{oi2}}{4k_B T} \right) e^{-\kappa h}
\]

(2.9)

where \( V_{\text{EDL}} \) is the EDL potential energy, \( n^0 \) is the bulk ion number density, \( \psi_{oi} \) is the surface charge and \( h \) is the separation.

2.2.2 van der Waals Forces

The van der Waals (vdW) forces are attractive in nature and come about due to the dipole moments and collective interactions between molecules. These interactions are the main cause of destabilisation of a dispersed phase in solution. There are three separate components that can contribute to the vdW interaction; Keesom, Debye and London interactions.

Keesom or orientation interactions are between two molecules that both have a permanent dipole moment and examples of molecules would be water or carbon dioxide. When the dipole moments are aligned the maximum attractive force will occur and subsequently when the dipole moments are oppositely aligned the maximum repulsive force will be present. The alignment of the dipole moments will fluctuate with time and space due to thermal energy of the solution, though thermodynamically alignment of the dipole moments is preferred as this lowers the free energy and thus an attractive force is present. The Debye or induction interaction is between a molecule with a permanent dipole moment, that induces a dipole within a neighbouring molecule. In the same way as the Keesom interactions align, the dipole moments of the molecules involved in a Debye interaction will align in to minimise their free energy and an overall attractive force will be present.
London or dispersion interactions are described by quantum mechanical perturbation theory and come about due to fluctuations in the electron distribution cloud and thus, this originates from induced dipole moments of molecules, not permanent dipole moments of molecules. The fluctuations occur at a frequency of $10^{15}$-$10^{16}$ Hz$^{26}$ and induce a temporary dipole within the molecules surrounding the first molecule. The constant fluctuations of the electron cloud create waves of induced dipoles through the system of interest. The potential energy of the vdW force between molecules decays with distance as an inverse sixth power and is shown as Equation 2.10$^{26,28}$.

$$W_{AB}(D) = -\frac{C_{AB}}{D^6}$$  \hspace{1cm} (2.10)

where $W_{AB}(D)$ is the potential energy between two molecules, $C_{AB} = C_{Keesom} + C_{Debye} + C_{London}$ is the total contribution of the various components of the vdW force and $D$ is the distance between molecules.

The interactions between macroscopic size objects and not individual molecules are of interest to the field of colloid and surface science and these are described as long range vdW forces. The first derivation of the vdW force for macroscopic objects was by Hamaker$^{32}$ and is shown as Equation 2.11.

$$W(h) = -\frac{A_H}{12\pi h^2}$$  \hspace{1cm} (2.11)

where $W(h)$ is the vdW interaction between two flat half spaces, $A_H$ is the Hamaker constant and $h$ is the separation of the flat half spaces.

The derivation was based on the assumptions that the interactions were pairwise additive and non-retarded in nature$^{28}$. The potential energy decays with the inverse of separation squared and allows the vdWs force to act over longer range distances (order of tens to a hundred of nanometres)$^{27}$. The pairwise additivity does not hold when large numbers of molecules are present, as the polarisability of the electron density cloud of a molecule is influenced by all the neighbouring molecules and not just an individual molecule. The increased number of molecules also causes the assumption of the interaction being non-retarded to break down. The influence of the electron density fluctuations moves from molecule to molecule at the speed of light, $c$, and therefore the time of propagation through the field is approximately $D/c^{30}$. Molecule 1 causes
alignment of the dipole moment of molecule 2 and in turn molecule 2 reflects its position back to molecule 1. If the distance is sufficiently small the dipole moment of molecule 1 will be in the same position as it was originally and the free energy of the system will remain at a minimum. When the distance between the molecules becomes larger and molecule 1 no longer has the same alignment when molecule 2 reflects its dipole moment position back the free energy cannot be minimised and causes the force to no longer be non-retarded. The retardation of the dipole interaction propagation decreases the range or length scale that the vdW force influences.

To overcome the problem of the pairwise summation required for the Hamaker method Lifshitz theory\textsuperscript{33,34} was developed and treats the material as a continuous media using properties such as refractive index, dielectric constant and spectroscopy data over decades of frequency to construct the dielectric function of the material. This is a complex method that requires advanced knowledge of quantum field theory and statistical mechanics along with the properties of the materials to be known over a large frequency range\textsuperscript{28,30}. Due to this complexity the use of this theory did not become popular in colloid science until simplifications were made in the derivation\textsuperscript{35,36}. The calculation for the Hamaker constant of two surfaces of the same material with a different material separating them is shown as Equation 2.12\textsuperscript{37}.

\[
A_{123}(L) = -\frac{3}{2} k_B T \sum_{n=0}^{\infty} \frac{1}{r_n} \int_{r_n}^{\infty} x \ln\left\{ [1 - \Delta_{13} \Delta_{23} e^{-x}] \times [1 - \bar{\Delta}_{13} \bar{\Delta}_{23} e^{-x}] \right\} dx,
\]

\[
\Delta_{jk} = \frac{\epsilon_j s_k - \epsilon_k s_j}{\epsilon_j s_k + \epsilon_k s_j}, \quad \bar{\Delta}_{jk} = \frac{s_k - s_j}{s_k + s_j},
\]

\[
s_k^2 = x^2 + \left( \frac{2\xi_n L}{c} \right)^2 (\epsilon_k - \epsilon_3),
\]

\[
r_n = \frac{2L \xi_n \sqrt{\epsilon_3}}{c}, \quad \xi_n = \frac{2\pi n k_B T}{h}, \quad \epsilon_k = \epsilon_k(i\xi_n),
\]

where \(c\) is the speed of light, \(h\) is Planck’s constant divided by \(2\pi\) and \(\xi_n\) are sampling frequencies of the dielectric function \(\epsilon_k(i\xi)\).

Hamaker constants and Hamaker functions for vdW interactions are available in literature\textsuperscript{26,28,29,38} and the sign of the value is indicative of whether the interaction is
attractive (positive) or repulsive (negative). For interactions involving air bubbles it is usually expected that two bubbles colliding in water will experience an attractive vDW force and a bubble approaching a silica surface will undergo a repulsive interaction\textsuperscript{28,39}.

### 2.2.3 DLVO Theory

Derjaguin, Landau, Verwey and Overbeek (DLVO) theory describes the overall interaction between colloids as the sum of the EDL and vDW forces between them, as demonstrated in Figure 2.2. The overall interaction is a function of surface potential, electrolyte concentration, dielectric spectra of the materials (as it relates to the Hamaker function) and the separation as these affect the magnitude and range of EDL and vDW forces that are present.

![Energy Interaction Graph](image)

**Figure 2.2.** A schematic of the relationship between the EDL, vDW forces contributions to the DLVO interaction between two colloidal objects. The DLVO interaction is the total of the EDL and vDW interactions.

For colloids with a high surface potential they will remain dispersed in solution at low electrolyte concentrations in a thermodynamically stable state. As the electrolyte concentration increases the surface potential is effectively screened and creates a secondary minimum in the interaction energy profile. If the colloids are unable to overcome the primary energy barrier they can remain in the secondary minimum or dispersed within solution (kinetically stable)\textsuperscript{28}. 
If the surface potential is lowered, the energy barrier is also lowered and in this case slow coagulation of the colloid is possible. Rapid coagulation will occur if the energy barrier drops below a critical interaction energy determined by the size of the particles, the particle number density and the thermal energy of the particles from Brownian motion\(^{30}\). For some systems with EDL and vDW forces, this can occur with a decreased surface potential, an increase electrolyte concentration, or from changes in temperature. If the surface potential goes to the point of zero charge (e.g., at the isoelectric point of a mineral oxide), the EDL force is no longer present and only the vDW force is operating. In this case the surfaces experience an attractive force. As the literature has grown since the advent of DLVO theory other forces have been included as additive components into DLVO theory including steric forces, depletion or structural forces\(^{28,30}\).

2.2.4 **Structural and Depletion Forces**

Structural forces arise in a solution due to structuring of smaller colloids such as surfactant micelles\(^{40,41}\), nanoparticles\(^{42,43}\), solvent molecules\(^{44}\) or polyelectrolytes\(^{45-47}\). This solution structure leads to oscillatory forces at small separation when the smaller colloid is confined between large interacting colloids such as silica particles, bubbles, droplets or surfaces.

![Figure 2.3: A schematic of a typical structural force profile as two larger colloids approach each other with a diagram of the molecules layers.](image-url)
During confinement the smaller colloids form layers that lead to a repulsive interaction as demonstrated in Figure 2.3. As the surfaces approach further a layer of the smaller colloids are expelled from the thin film to the bulk solution. In this process an osmotic pressure difference is established between the thin film and bulk solution and an attractive force occurs between the surfaces. This process of colloid structuring and expulsion, and the subsequent force oscillations continue until the last layer of molecules.

Depletion forces are closely-related to structural forces, which can often be thought of as the low concentration limit of a structural force and occur when the smaller colloid is excluded from the thin film, as shown at point 7 in Figure 2.3. Depletion forces were first described by Asakura and Oosawa and occur when the approaching surfaces are closer than half the characteristic length scale of the depletant. In the case of a spherical depletant, the characteristic length scale is the diameter and therefore, half of this distance is the radius. Due to volume exclusion, when the depletants are excluded from the thin film the osmotic pressure difference causes an attractive force between the interacting surfaces.

### 2.3 Other Considerations in the Measurement of Surface Forces

#### 2.3.1 Derjaguin Approximation

The Derjaguin approximation is a scaling of forces based on geometric arguments that allows for the derivation of a useful analytic relationship to connect the interaction energy between infinite half spaces to the forces between varieties of surfaces with curved geometries. For example, the approximation shown as Equation 2.13 below calculates the total force between two spheres as related to flat surfaces. In this work we use the Derjaguin approximation to move between the geometries of plate-plate, plate-sphere and sphere-sphere arrangements.

\[
F_R = 2\pi \left( \frac{a_1 a_2}{a_1 + a_2} \right) \int_0^\infty F_a(D)\, dD = 2\pi \left( \frac{a_1 a_2}{a_1 + a_2} \right) W(D)
\]

where \( F_R \) is the force between two spheres, \( a_1 \) and \( a_2 \) is the radius of the spheres, \( F_a(D) \) is the force between two flat plates, \( W(D) \) is the potential energy between two flat plates and \( D \) is the separation distance between two spheres at their closest point. If
the experimental orientation is that of a flat plate and sphere the above equation reduces to Equation 2.14.

\[ F_R = 2\pi a W(D) \]  

\( (2.14) \)

The Derjaguin approximation only holds when the separation between the interacting surfaces (\( D \)) is much lower than the radius of the spheres (\( a_1 \) or \( a_2 \))\textsuperscript{29}.

### 2.3.2 Disjoining Pressure

The disjoining pressure is described as the change in the pressure within a film and the bulk phase between two interacting surfaces\textsuperscript{52,53} as shown in Equation 2.15\textsuperscript{29}.

\[ \Pi(h) = P_{film} - P_{bulk} = -\frac{dV}{dh} \]  

\( (2.15) \)

where \( \Pi(h) \) is the disjoining pressure, \( P_{film} \) is the pressure in the film, \( P_{bulk} \) is the pressure in the bulk, \( V \) is the interaction energy and \( h \) is the separation of the surfaces.

As the disjoining pressure is related to the interaction energy each component that contributes to the overall disjoining pressure can be determined separately and then summed as shown in Equation 2.16\textsuperscript{29}. When discussing the interaction response of deformable interfaces the use of disjoining pressure instead of force can be easier. This is due to the analysis often requiring a normal stress balance that includes both the internal Laplace pressure of the bubbles or droplets and the pressures in the intervening film between the interacting species that arise from surface forces\textsuperscript{54}. Therefore, one can describe a total disjoining pressure as:

\[ \Pi_{tot}(h) = \Pi_{EDL}(h) + \Pi_{vdW}(h) + \Pi_{dep}(h) + \Pi_{other}(h) \]  

\( (2.16) \)

where \( \Pi_{tot}(h) \) is the disjoining pressure, \( \Pi_{EDL}(h) \) is the EDL pressure component, \( \Pi_{vdW}(h) \) is the vdW pressure component, \( \Pi_{dep}(h) \) is the depletion pressure component and \( \Pi_{other}(h) \) is any other component contributing to the disjoining pressure including hydrodynamic drainage effects\textsuperscript{55-58}.

### 2.4 Direct Force Measurements

Various techniques have been developed in the past to measure the forces of interaction between both rigid and deformable interfaces. Some of the most common
methods are surface forces apparatus (SFA)\textsuperscript{59-61}, total internal reflection microscopy (TIRM)\textsuperscript{62-64} and atomic force microscopy (AFM)\textsuperscript{65-67}. Typical experimental arrangements for SFA are measurements conducted between two rigid, molecularly smooth interfaces, such as mica\textsuperscript{68} and with TIRM a sphere and flat plate. Using either TIRM or SFA to examine the interactions of two deformable interfaces is quite difficult. Measurements conducted between a droplet and a flat interface with the use of TIRM have been conducted, but the analysis of the experimental data requires that the droplet does not deform to provide a quantitative interaction result\textsuperscript{69,70}. The SFA has been successfully modified to examine the interaction of a single deformable mercury drop and a flat surface by incorporating a large capillary with a radius of several hundred micrometres\textsuperscript{71-76}. Horn and co-workers have an established literature in this area and more recently have produced several studies using a single bubble and a flat interface\textsuperscript{77,78}. Much earlier work by Fletcher and co-workers\textsuperscript{79-81} developed what was referred to as the liquid SFA which contained two large liquid capillaries but the separation resolution was quite limited compared to the work of Horn and co-workers.

The advent of AFM being used to study deformable interfaces, notably for droplets and bubbles with radii of 30 to 50 micrometres, has inspired several groups to develop more recent AFM-like devices for much larger bubbles or drops. Notably, the work of Zhenghe Xu’s group, which has developed several different instruments to probe the force between a bubble or droplet of almost half a millimetre and a similar sized rigid particle\textsuperscript{82-87}. They have developed an interesting set of literature relevant to particle attachment of bubbles and droplets using the analysis methods developed for AFM measurements with deformable interfaces. Frostad and co-workers have recently developed an instrument, a cantilevered-capillary force apparatus, which effectively is a scaled-up version of an AFM\textsuperscript{88}. This instrument allows the interactions between two drops with radii of an approximate range of 50 to 70 micrometres to be examined and further probe scaling relationships to predict coalescence times between drops.

These larger scale measurements are also reminiscent of more classical capillary drainage studies\textsuperscript{7,89-92}, but the incorporation of force measurements instead of, or in addition to separation measurements has changed the type of information accessible from these measurements and has been driven by the advent of the AFM. To determine the force interactions present in those of structural forces between deformable
interfaces, at the relevant nanometre length scale where these force are present, the use of the AFM is required. Another advantage of the AFM is that the bubbles and droplets used in these studies are at a length scale that is relevant to emulsions or foams, which allows fundamental studies to link well with industrial or commercial research problems.

2.4.1 **Atomic Force Microscope**
The AFM was originally designed by Binnig, Quate and Gerber in 1986\(^6\). The original purpose for the AFM was to take topographical scans of insulating (or non-conductive) materials, by passing a sharp tip (referred to as a cantilever) across a surface to construct a three-dimensional image of the surface. The tip is raster scanned across the surface and the force between the tip and the surface is controlled by the feedback loop with the controller and this is dependent on the mode of operation, whether it is contact, tapping/intermittent contact, or non-contact modes. The advantage of this instrument is that a three-dimensional rendering of the surface is possible without destroying the sample. As the interaction between the tip and surface are dependent on surface chemistry, variations across a surface can also be detected and due to this effect direct force measurements is possible with the AFM.

2.4.2 **Beginning of Direct Force Measurements**
Direct force measurements are a specific type of measurement that is conducted on the AFM where the cantilever is now driven in the normal direction towards and then subsequently away from the surface instead of being raster scanned across the surface\(^9\). During this process the cantilever responds to the force interaction between the tip, surface and fluid medium, and the position and deflection of the cantilever are measured\(^9\). The data are able to be converted into a force verses distance plot, referred to as a force curve. The force curves are able to determine the types of surface interaction and magnitude, but with the use of a standard AFM cantilever with a sharp tip, that often possess a poorly defined or unknown geometry\(^9\) and as well as significantly variability of the surface chemistry\(^9\) of the tip means in practice that quantitative studies are difficult\(^9\).

To overcome this problem of the unknown geometry, glass microspheres with a radii ranging from 2 to 5 µm have been attached to the end of an AFM cantilever\(^6,10\). Around the same time measurements were also conducted with large diameter spheres.
with a diameter of approximately 120 µm\(^{101}\). This method is commonly known as the ‘colloidal probe technique’ and typically conducted with the smaller microspheres, approximately 2 to 20 µm\(^{102}\) in diameter. In these initial studies force curves were measured between the glass sphere and a flat silica surface with solutions of NaCl and various solution pH (from pH 2.0 through to 10.0) and the results agreed well with DLVO theory along with other techniques that measured forces at the time\(^{66,100}\). The size and type of the microsphere can be changed from that used in the original measurements and these parameters can be varied to explore different experimental parameters\(^{103}\). It is difficult to optically attach particles smaller than 1 µm in diameter onto the tip, but a previous study placed nanoparticles of colloidal gold approximately 10 to 40 nm on a cantilever\(^{104}\). The measurements conducted do not agree well with DLVO theory where this is likely due to a breakdown in the validity of the Derjaguin approximation constraints on the geometry.

2.4.3 Deformable Interfaces

In many applications of colloidal science deformable interfaces of bubbles and droplets are of interest, so the progression for the AFM as a force measurement technique onto systems containing a deformable interface was an important one. This involved a modification of the colloidal probe technique discussed above, where a droplet or bubble was fixed to the substrate and the rigid probe on the cantilever was retained. Even though the exact separation of the probe and bubble or droplet interface could no longer be measured due to the deformation of the interface, it opened up many new possibilities for further investigation.

The first AFM measurement that involved a deformable interface was completed by Butt\(^{105}\), where a colloidal probe of diameter of 7 to 20 µm was used to study the interactions between an air bubble in water or a water droplet in air fixed to a substrate. Subsequently, further measurements with an air bubble affixed to a substrate were undertaken\(^{106-108}\). Along with affixing air bubbles to the substrate, oil droplets were used as the deformable interface\(^{109-115}\). These measurements also began to explore dynamic interactions and the description of experimental results when compared to expected theory\(^{114,115}\).

The next advance in direct force measurements was that a droplet was attached to the end of a cantilever and measurements were conducted between a droplet pair\(^{54,116,117}\).
This work was conducted between n-decane droplets in various concentrations of SDS aqueous solutions and was the first demonstration of not only equilibrium measurements between droplets, but also dynamic measurements\textsuperscript{54,116}. It showed that fluid drainage or hydrodynamic forces coupled to the EDL and vdw\textsubscript{s} components of the force and through the use of modelling determined the droplet profiles under various conditions.

The transition to bubble-bubble measurements began with a measurement of air bubbles in solutions of 1 mM NaNO\textsubscript{3} and 10 mM SDS\textsuperscript{118}. This work demonstrated that measurement of bubble-bubble interactions was possible with the use of an AFM, the surface tension of the bubbles could be varied by the addition of SDS and that dynamic interactions produced similar responses as previously demonstrated with droplets. The use of custom made cantilevers that have a gold disc at the end to anchor the bubble allowed more reliable results to be gained and therefore the experimental results were able to be modelled with theory for a bubble-plate system\textsuperscript{55,56}. This was extended further with modelling of a bubble-bubble experimental arrangement\textsuperscript{119}.

Since this original work further studies have been undertaken and focus on various aspects of the interactions between bubble pairs. Bubbles generated in different gases and in solutions of various pH were measured to determine the surface charge of the interface and determine the stability of these various systems\textsuperscript{120}. Stability of bubble pairs in solutions of salts, alcohols\textsuperscript{15} and peptide surfactants\textsuperscript{121} have also been studied and also the interactions between an air bubble and oil droplet\textsuperscript{122}.

Aside from bubble-bubble interactions the AFM has the ability to measure forces between a bubble anchored on the cantilever and various surfaces. Both repulsive van der Waals\textsuperscript{39} and attractive hydrophobic\textsuperscript{123} force interactions have been studied between air bubbles and different surfaces or surface coatings. This has been taken further where the flat plate was a sample of sphalerite mineral and allowed investigation into a froth flotation process used in mineral processing\textsuperscript{124}. The focus of flotation processing in the minerals industry means that colloidal probe measurements with air bubbles are still ongoing and have a role to play in industrial applications. These studies allow the three phase contact angles, bubble-particle separation and effects of hydrodynamic and detachment forces on attached particles in the presence of the surface active chemicals used in industry to be measured\textsuperscript{125-130}.
Combining the AFM with other microscopy techniques to visualise the interactions whilst they are undergoing has also allowed more information to be gained. Confocal fluorescence microscopy has been utilised to visualise the collision of two droplets during a direct force measurement and recently the AFM was combined with reflection interference contrast microscopy (RICM) to observe the thin film between a bubble and surface. The interference pattern of the bubble and interacting surface allows the radial profile of the bubble to be directly measured. Due to the experimental arrangement a bubble pair could not be measured with combined AFM and RICM.

**2.4.4 Modelling Deformable Interfaces**

Due to the separation of the droplet or bubbles being unknown as a result of interfacial deformation, modelling of the experimental results is required to determine the separation and thin film profile during the direct force measurement. For this modelling the Chan-Dagastine-White (CDW) model was developed as it is derived from the augmented Young-Laplace equation. The original presentation of the model was for a particle attached to the cantilever and a droplet affixed to a substrate. The CDW model allowed the experimental results to be compared to theory and accounted for the interfacial deformation. This model was then expanded to allow the interactions between bubble/droplet pairs or a bubble and flat plate. Further discussion and presentation of the CDW model for two bubbles is shown in the Experimental Methods Chapter (Chapter 3).

The experimental verification of the model has been ongoing and an example is the use of a combined AFM and confocal fluorescence microscopy, which allowed the interactions between droplets to be monitored visually. This allowed the measured separation from the confocal measurements to be compared to the modelling of the experimental direct force measurement results. Combining an AFM measurement with RICM, the thin film thickness and radial profile of the bubble was able to be directly measured and allowed further verification of the deformable interface modelling.

The introduction of dynamic direct force measurements led to a need for a model to account for velocity of the droplets and bubbles during a collision. Various studies have been undertaken which utilise the model to compare the experimental and theoretical results and the use of modelling allowed the determination of one component of the total interaction measured. The measurement of a bubble...
against a deformable substrate, in this case poly(dimethyl siloxane) (PDMS), has led to a combination of an analytical and finite element modelling technique. Comparing experimental results to those predicted by theoretical approaches continues to expand to allow various experimental conditions to be explored and quantified.

2.5 Measurement of Depletion and Structural Forces

As depletion and structural forces deviate from DLVO theory, there has been much interest in the study of these forces. The first measurement was conducted by Horn and co-workers with a liquid crystal between sheets of mica on the SFA. Subsequently, the work was continued with the use of an organic solvent, octamethylcyclotetrasiloxane (OMCTS). After these measurements conducted on structural force interactions with the use of SFA, depletion interactions were attempted to be measured in the presence of polymers and polyelectrolytes. It was not possible to measure a depletion interaction and the authors surmised that the force of interest was below the detection limit of the experimental apparatus.

Due to the difficulties in completing the measurements with the use of techniques such as SFA, depletion interactions were also studied in various other ways. The stability of colloid silica particles in a solution containing dissolved polymers, as the polymer induced depletion flocculation that could be monitored over time. Other methods to study the stability of colloidal dispersions were by constructing phase diagrams, completing shear stress measurements to understand the rheology of the suspension and different light scattering techniques. Whilst these techniques provide insight into the stability and time scales of depletion flocculation, the interactions occurring between the particles are not probed directly.

To probe the depletion and structural force interactions directly, techniques such as SFA, AFM, TIRM and thin film balance were required. Measurements conducted on the SFA with the use of a cetyltrimethylammonium bromide micelle system showed that between two sheets of mica the period of oscillation was approximately that of a micelle. Compression of lamellar phases of sodium dodecyl sulfate (SDS) and 1-pentanol or the ionic liquids of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C₄mim][NTF₂]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄mim][BF₄]) were also shown to exhibit a
structural force between the two rigid interfaces of mica. Studies utilising TIRM\textsuperscript{175-178} showed that due to the higher sensitivity to the measured force, lower concentrations and different structuring molecules could be measured. Studies have continued on structural force interactions with SFA\textsuperscript{179} and TIRM\textsuperscript{180,181}, though as the experimental arrangements require two rigid interfaces this limits the ability to study deformable interfaces.

The disjoining pressure and thin film thickness between two air interfaces can be measured with the use of a thin film balance. This measurement requires a stable thin film and therefore attractive force types are not able to be measured. Some of the first measurements conducted in which structural forces were measured were with surfactant micelles\textsuperscript{182,183}, as the surfactant stabilises the thin film interface. Studies into the effects of polyelectrolytes on the thin film have also been conducted, but require surfactant to avoid coalescence of the two interfaces\textsuperscript{184-188}. The presence of more than one structuring colloid leads to complex results and it is difficult to interpret the contribution of each to the force response.

Direct force measurements have become an important technique with which to measure structural forces. The arrangement of an AFM experiment allows both rigid and deformable interfaces to be used in the study of structural forces. The measurement of depletion and structural forces with the use of AFM has been studied for some time and some of the earliest examples are the measurement of OMCTS\textsuperscript{189} and PDMS\textsuperscript{190}. The measurement of PDMS was also able to, determined theoretically, by polymer theory the chemical potential. Further measurements of these forces with the use of a rigid interface have been extensive and include polyelectrolytes\textsuperscript{45-47,191-200}, nanoparticles\textsuperscript{42,43,201-203}, surfactant micelles\textsuperscript{40,204,205} and the effects of combining structuring colloids\textsuperscript{206-209}.

The use of bubbles and droplets in the study of structural forces has led to some interesting observations as a consequence of the deformation of the interface. The deformation leads to an increased sensitivity of the forces imparted on the bubbles and droplets during a measurement\textsuperscript{210}. The increased sensitivity allows measurements to be conducted that would be difficult with the use of a rigid interface. The structural forces of micelles, nanoparticles and a micro-emulsion have been studied with deformable interfaces\textsuperscript{25,48,127,211}. The concentration and size of the structuring molecules influence
the interaction as does the shape\textsuperscript{212}. Numerous studies, both with deformable\textsuperscript{213} and rigid interfaces\textsuperscript{83,84}, have shown that measurements conducted with non-spherical colloids have more than one important length scale and this influences the interaction between macromolecules.

2.5.1 Modelling of Depletion and Structural Forces

Modelling of depletion and structural interactions has also been ongoing alongside experimental research and the aim of this work was to further the understanding and quantify the role various colloids play when in confinement\textsuperscript{214}. The results that can be gained from modelling are very detailed and complex, and can predict not only force interactions, but also density profiles of molecules in solution\textsuperscript{215-224}. Over time the modelling of these forces has been simplified to allow for an easier comparison of experimental results to theory\textsuperscript{225-229}. The experimental results of measurements conducted using SFA\textsuperscript{146}, AFM\textsuperscript{25,230}, TIRM\textsuperscript{180,181} and stability studies\textsuperscript{163,168,169,231} have been confirmed and described theoretically.

Through modelling it has been shown that the magnitude of a depletion interaction decreases when either the aspect ratio\textsuperscript{232} or the polydispersity of the depletant increases\textsuperscript{233-236}. Another study demonstrated that molecules of an uncharged polymer do not distribute themselves in solution under confinement in the same manner as charged polyelectrolytes\textsuperscript{237}. Both systems exhibit a depletion zone in proximity to the confining wall, but the density profile of the uncharged polymer remains constant in the bulk solution and the polyelectrolyte has an oscillatory profile. The effects of interface deformation in droplets in the presences of depletants has also been studied and are able to predict the contact angle formed between interacting colloids\textsuperscript{238} and the interaction energy of the thin film between colliding droplets\textsuperscript{239}.

2.5.2 Structural Forces and Polyelectrolytes

Polyelectrolytes are polymers that have a counter ion i.e., Na\textsuperscript{+}, Li\textsuperscript{+}, Ca\textsuperscript{2+}, etc., which dissociates when dissolved into a solvent, which is commonly water. The charge dissociation means that the viscosity of the solvent does not increases as rapidly as with other polymer additives. As polyelectrolytes dissolve readily into water they are common in industrial settings such as mineral and water treatment flotation, where the interactions between bubbles are vital in the operation of the process.
There are numerous reviews\textsuperscript{50,214,240-245} within the literature regarding the force response involving polyelectrolytes and interacting surfaces. The study of the interactions of polyelectrolytes between deformable interfaces without the presence of a surfactant to provide kinetic stability to the interface has previously not been possible with the thin film balance. Deformable interfaces in the presence of polyelectrolytes have previously been measured\textsuperscript{25} with the use of AFM and provide an opportunity to avoid the use of a surfactant that is required to stabilise the interfaces in the thin film balance. The polyelectrolyte used throughout this thesis study was sodium poly(styrene sulfonate) (NaPSS) in order to link in with the main previous studies conducted with rigid interfaces on the AFM\textsuperscript{45-47,191,192} or TIRM\textsuperscript{176,177}. Interestingly, structural forces with the polyelectrolytes of NaPSS or poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) have not been shown with the SFA and it is proposed that this is due to the lower sensitivity and drift of the instrument when compared to AFM\textsuperscript{242}.

\subsection*{2.5.3 Polyelectrolyte Scaling Theory}

Polyelectrolyte scaling theory has been developed and presented by de Gennes\textsuperscript{246} and allows trends to be described across both concentration and molar mass variations\textsuperscript{247-250}. Scaling theory allows predictions of the interactions during concentration and molar mass changes. These scaling laws are dependent on whether the polyelectrolyte is in the dilute, semi-dilute or entanglement regime.

Within the dilute regime the molecules are able to maintain their own space within the solvent and form in a space-filling lattice. The space between the molecules is the characteristic length, $\xi$, that corresponds to the period of oscillation of the structural force. The characteristic length is dependent on the concentration of the polymer such that $\xi \sim c^{-\frac{1}{3}}$. As the concentration increases the molecules can no longer maintain their own space and start to interact with each other and form a cross linked network, which is referred to as the overlap concentration, $c^*$. The overlap concentration is dependent on the number of monomer units that consist within an individual polyelectrolyte molecule and this calculation is shown in the Appendix 10.1. With an increase in monomer units the molecules become larger and the overlap concentration decreases.

At higher concentration than $c^*$, an increase in concentration, increases the number of cross links in the 3D mesh like structure that forms. The period of oscillations is now
dictated by the distance between the cross linking points with this form, $\xi \sim c^{-1/2}$. A further increase in concentration will lead to a point of entanglement, $c_e$, of the molecules and concentrations larger than this are in the entanglement regime. At this point the concentration of polyelectrolyte has increased sufficiently that the motion of the individual molecules are constrained by the presence of the other molecules. The entanglement concentration is approximately $10^3 \leq c_e/c^* \leq 10^4$ in a solution with no additional electrolyte and $c_e \approx 10c^*$ in a high electrolyte solution. In this regime a large increase in solution viscosity occurs and has not been investigated in previous structural force studies.

As the $c^*$ of a polyelectrolyte is dependent on the size of the polymer coil the addition of electrolyte or adjustment of the solution pH leads to changes in the $c^*$ of polyelectrolytes within solution. The size of the polyelectrolyte molecule in solution or radius of gyration is dependent on the charged species within the polymer. The addition of electrolyte or adjustment of the solution pH leads to screening of the charged groups within the polymer chain. This screening leads to compaction or a decrease in the size along with the polyelectrolyte becoming more flexible within solution and therefore leads to an increase in the $c^*$ of the polyelectrolyte.

### 2.6 Microfluidic Devices

Studies involving the use of microfluidic or ‘lab-on-chip’ devices are broken into two major categories of fundamental droplet and bubble studies or creating microreactors with the potential to improve fields such as medical testing, food products, and pharmaceutical products. The size of microfluidic devices is a driving factor for the use in these areas, as small amounts of reactants can be used to create products or used in testing procedures, but the size also changes the flow regime of the fluids from that of typical industry processing used currently. Fundamental studies to further the development of droplet and bubble generation and handling are vital in improving the potential practical applications of the technology.

The formation of droplets and bubbles within a microfluidic device is dependent on the surface chemistry of the device channels and this can be varied easily with the use of well-established techniques such as photolithography or etching methods. The use of photolithography allows complicated channel designs to be easily designed and
manufactured with the use of graphical imaging software. The generation of droplets and bubbles with devices has been studied and characterised extensively. These generation methods typically fit into different flow type regimes, discussed in the next section.

There are a vast number of applications for microfluidic devices that require a reliable generation of drops or bubbles and they range from biological areas where polymerase chain reactions and protein crystallisations can be achieved with the use of a single device, right through to the fundamental studies of coalescence events and interfacial properties of emulsions. They also have the potential to contain chemical reactions in the generated droplets or the emulsions can be used as templates for the fabrication of microparticles. Though the size of these devices mean that a small volume of liquid can be used in these types of applications scaling of the technology needs to occur so it would be relevant on an industrial scale and this is currently ongoing.

Microfluidics offers the ability to generate and then subsequently complete a study of interest within the one device. This offers the advantage of the measurement remaining contaminant free which is vital in fundamental studies on interfacial effects. Along with interactions between two bubbles the stability and packing of foams has also been studied and the resultant foam is dependent on not only the volume fraction of the emulsion, but the aspect ratio of the channel. Currently bubbles have been readily generated in the present of surfactant or similar stabilising molecules. Bubbles generated in solutions of pure water are possible within a t-junction device but the size of the bubbles is flowrate dependent. Currently in the literature no bubbles are generated in a microfluidic device, where the size is flowrate independent without the presence of surfactant or similar surface stabilising molecule.

### 2.6.1 Bubble and Droplet Formation

There are various typical design types used for bubbles and droplet formation in microfluidic devices. The generation of bubbles and droplets fit into three main categories of the fluid flow types of crossflow, flow-focusing or co-flow, though various other types are also available. A detailed description of the device types for bubbles and droplets has previously been presented. Therefore only a brief description will be presented here and schematic images are shown as Figure 2.4.
Figure 2.4. Schematic images of various microfluidic designs which are able to generate droplets or bubbles. The gas (or dispersed) phase is shown as white and the water (or the continuous) phase is shown as blue. In all images the flow direction is left to right. a) crossflow t-junction device. b) Flow focusing device. c) Co-flow device. d) Block-and-break device. e) Both a top and side view of a step emulsification device.

2.6.1.1 Crossflow (t-junctions)

A t-junction device is a relatively simple design which relies on a crossflow arrangement of the dispersed and continuous phases. Typically the dispersed phase enters through the bottom of the junction and the continuous phase flows across the top at a 90 degree angle. The size of the generated emulsions is dependent on the flowrate ratio of the dispersed and continuous phases and calibration of this system is required to generate a known size emulsion. Due to the simple design, numerous studies have been involved in the characterisation of the devices constructed from various substrates. The influence of the aspect ratio of the channel, the symmetry of the junction, flowrate regime and break off mechanism have been studied. Modelling of the emulsion generation process has been extensive and
Chapter 2

gives researchers the ability to design a t-junction device easily\textsuperscript{289,291,309-312} for various other studies that have interest in colloidal and surface chemistry areas\textsuperscript{313-316}.

2.6.1.2 Flow Focusing

The flow focusing design has the dispersed phase in the middle channel of three and the other two channels with the continuous phase\textsuperscript{317}. The continuous phase channels meet perpendicularly with the dispersed phase and there is an orifice downstream of the intersection point\textsuperscript{318}. As the break off of the emulsion in this design is driven by viscous forces that the continuous phase places on the dispersed phase, the size of the droplets or bubbles is highly dependent on the flow regime that the device is operated under\textsuperscript{319-322}, as well as geometry driven\textsuperscript{323-328}. Another study removed the channels between the dispersed and continuous phases and showed that generation of an emulsion was possible with flow focusing\textsuperscript{329}. Care in balancing the pressure between the two streams was required to ensure an emulsion was generated. Work has been completed to demonstrate that generation of monodisperse emulsions is possible, but due to the break off mechanism used, an interface stabiliser such as a surfactant is required\textsuperscript{288,330-332}. In a similar fashion to that of t-junction devices various studies have focused on modelling the droplet or bubble formation to aid improving further designs\textsuperscript{333-339}.

2.6.1.3 Co-flowing

A co-flow arrangement within a microfluidic device involves the dispersed and continuous phase flowing down a channel in the same direction\textsuperscript{340}. The break off of the droplet or bubble is due to the dispersed phase having an attractive interaction with the channel wall. The size of the generated emulsion is dependent on the ratio of the dispersed and continuous phases. Currently, the work on this design type has been limited and the generated emulsions are still flowrate dependent, requiring significant calibration for a required size.

2.6.1.4 Step Emulsification

This type of design is more complicated than the others described above due to formation of the emulsion occurring when the dispersed and continuous phases pass over a ‘step’ or rapid height change in the channel height\textsuperscript{341}. As the device is no longer
planar in design, the fabrication process of the device is no longer achievable solely with the rapid prototyping method involving photolithography and PDMS molding\textsuperscript{342,343}. Prior to the change in the channel height a t-junction allows both the dispersed and continuous streams to be injected into the main channel. The size of the generated emulsion is dependent on the height of the shallow channel and the flowrate ratio of the dispersed and continuous phases. Care must also be taken to be in the correct flow regime as with a higher flowrate ratio the device will enter the jetting regime and with a low ratio an emulsion will form at the t-junction\textsuperscript{344}.

2.6.1.5 \textit{Block-and-break}

A block-and-break generation device creates a pressure balance that allows droplets to be generated of a size determined via the device geometry rather than fluid flowrates\textsuperscript{345}. The block-and-break design is a t-junction with a bypass channel and this extra channel allows a pressure balance to be set up between the start of the generation zone and the end. Due to this pressure balance the formed droplets will have the same volume as the channel volume contained in the generation zone. Currently there is only one paper in the literature for this design type, where the focus was on droplet generation\textsuperscript{345}. The authors showed that the droplets formed where consistently of the same size even when the flowrate of the dispersed phase was varied. This design shows promise in being a way to generate droplets and bubbles on a microfluidic device with minimal calibration of the emulsion size compared to flowrates.

2.6.1.6 \textit{Other Techniques}

Success has also been brought about with devices that incorporate fine glass capillaries such as capillary microfluidic devices\textsuperscript{346-354}, capillary t-junction devices\textsuperscript{355-358} and the combination of both by incorporating a capillary in a microfluidic device\textsuperscript{359,360}. Microfluidic devices fabricated with the use of photolithography have the advantage of being reproducible when compared to devices utilising glass pulled capillaries. The glass capillaries in these devices are usually placed by hand under a microscope and it would be difficult to manufacture an exact replica of the design. Even though these devices have this shortcoming, they have provided another avenue to generating monodisperse emulsions.
It has been shown that monodisperse\textsuperscript{350-353} and double\textsuperscript{349} or even triple\textsuperscript{354} emulsions are possible with the use of glass capillaries in a co-flow arrangement. Careful selection of the size of the capillaries allows alignment of the capillaries, though the construction of these devices still remains difficult. Due to the dimensions of the capillaries used, over time they become contaminated by solution additives that precipitate out of the solutions that are being used. Glass capillaries in a t-junction flow arrangement have also been shown to be able to generate monodisperse foams with bubbles of approximately 8 $\mu$m in diameter\textsuperscript{355-358}. These devices have the same fabrication issues as the other co-flow glass capillaries, though this is slightly mitigated by the use of a perspex block to hold the capillaries in place.

Incorporating a glass capillary into a PDMS fabricated t-junction device has allowed bubbles with a diameter of 10 $\mu$m to be generated\textsuperscript{359}. The capillary was used to inject the gas phase into the device and due to the constriction of the channel width at the tip smaller amounts of gas were injected when compared to a standard PDMS device. It was shown that the bubble size was dependent on the gas and liquid flowrates, the spacing between the end of the capillary and the device channel wall, and inner diameter of the glass capillary.

### 2.6.2 Other Effects of Microfluidic Channels on Fluid Flow

Typically syringe pumps are used to inject the desired fluid into a microfluidic device. These pumps offer the ability to program the flowrate to achieve the desired flow patterns on the device. The major drawback of these pumps is the large volume of liquid required to fill the channels and tubing entering the device, which creates difficulty in applying sharp changes of the flowrate. It has also previously been shown that typically used syringe pumps have difficulty in maintaining a constant flowrate and create oscillations due to the piston drive mechanism\textsuperscript{361}. This effect becomes exacerbated with the use of a compressible fluid, such as gas. One way to overcome these problems is to use a system where the fluids are driven by pressure instead of a syringe pump\textsuperscript{292,362-364}. These studies have demonstrated that more precise control of the flowrate can be maintained, though they introduce further complexity in the operation of the devices.

The channels in microfluidic devices are orders of magnitude smaller than typical pipes around which classical fluid dynamic theory has been established. This creates
issues where typical friction factor values no longer hold within these devices and the pressure changes down a channel are also influenced by the compressibility of materials such as PDMS\textsuperscript{365,366}. Work has been ongoing to determine the friction factor values or the hydraulic resistance\textsuperscript{367-373} to allow researchers to design future devices with ease, though this is a laborious task due to the numerous combinations of channel materials, dimensions and aspect ratios.
Chapter 3 - Experimental Methods

This chapter will outline and discuss the experimental materials and methods used throughout this thesis.
3.1 Introduction

The experimental methods used in this thesis study were direct force measurements utilising an AFM and the fabrication and use of microfluidic devices. These experimental methods are described in detail below.

3.2 AFM Measurement Methods

As discussed in Chapter 2 the AFM was originally designed in 1986 by Binnig, Quate and Gerber\textsuperscript{65} for the use of imaging surfaces. Since the invention and subsequent commercialisation of the AFM, a number of improvements in the instrument and the imaging modes available for operation have been developed. In addition, the extension of AFM to measure the interaction forces between surfaces has improved greatly due to the ability to functionalise the cantilever tip or attach a colloidal probe to the tip, where both scenarios offer a range of force responses between interacting surfaces to be determined. These improvements have laid the ground work for the extension of the AFM from being able to measure the interactions between rigid interaction surfaces to be able to quantitatively measure the interactions between deformable interfaces such as bubbles and droplets.

\textbf{Figure 3.1.} Schematic of an AFM instrument showing the cantilever, laser, photodiode, sample, stage and direction of travel with use of the z piezo.
As shown in Figure 3.1 the cantilever, laser, photodiode, z piezo distance actuator and the computer controlled (not shown) are the main components required to measure the force response of two interacting surfaces. The laser is reflected off the back of a cantilever and this signal is then received by the photodiode. The photodiode measures the change in signal position of the laser, which changes when the cantilever deflects in response to changes in the applied force acting on the cantilever change in the surface interactions.

**Figure 3.2. Left.** An example of piezo translation versus voltage signal response of the AFM cantilever during a direct force measurement. Schematic in the zero force and constant compliance regions demonstrate the cantilever position and the response of the laser on the photodiode. **Right.** After converting from the electrical signals captured by the computer controller this is an example of the resultant separation versus force plot. The force is determined with the use of the detector sensitivity and the calibrated cantilever spring constant.

At distances sufficiently far from the surface the cantilever does not react to any externally imparted forces and does not deflect as shown in Figure 3.2. As a result of this no change is detected in the photodiode. Once the distance between the cantilever and surface is sufficiently close that they are now able to interact, the cantilever will deflect in response. Once the cantilever and surface are in contact the cantilever will continue to deflect as the piezo continues to move and this region is referred to as constant compliance. The determination of the force from the voltage signal is discussed later.
The nature of force interactions is dependent on the change in separation, $\Delta D$, of the two interacting bodies. This value is calculated with the use of Equation 3.1 shown below.

$$\Delta D = \Delta z - \Delta d - \Delta s$$  \hspace{1cm} (3.1)

where $\Delta z$ is the change in piezo translation, $\Delta d$ is the change in deflection of the cantilever and $\Delta s$ is the substrate deformation.

### 3.2.1 Materials

#### 3.2.1.1 Chemicals

All solutions were prepared with Milli-Q purified water with a resistivity of 18.2 M$\Omega$.cm at 25 °C. Poly(sodium 4-styrene sulfonate) (NaPSS) with a molar mass (as designated by the manufacturer) of 70,000 and 200,000 g/mol (30 wt% in H$_2$O solution) were used as received from Sigma Aldrich and is shown as Figure 3.3. Poly(styrene sulfonic acid) sodium salt (NaPSS) with a molar mass (as designated by the manufacturer) of 500,000 g/mol was sourced from Alfa Aesar. Poly(styrene sulfonic acid sodium salt) (NaPSS) with a molar mass of 6800 and 77,000 g/mol was sourced from Fluka or Sigma Aldrich and used as received. The manufacturer supplied dispersity values for the NaPSS with a molar mass of 6800 g/mol was 1.06 and for the 77,000 g/mol was 1.02. Polyvinylpyrrolidone (PVP) with average weighted molar mass of 29,000 and 360,000 g/mol were sourced from Sigma Aldrich. Sodium hydroxide (>99%) was used as received from VWR International and nitric acid (70%) from ACI Labscan. n-Propanol (99.5%) was purchased from BDH and 1-decanethiol (96%) was received from Sigma Aldrich. Ethanol (100%) was purchased from Chem Supply.

Dialysis was undertaken with dialysis tubes with a molar mass cut off (MMCO) of 1 kDa and 14 kDa and these were sourced from Sigma Aldrich.
Figure 3.3. **Left.** Chemical structure of NaPSS. **Right.** The overlap concentrations, \( c^* \), were calculated according to the method outlined in Dobrynin et al.\(^{248} \) based on the supplier specified molar mass denote the transition from the dilute to semi-dilute regimes for the various molar masses used in this study. A sample of these calculations are shown in Appendix 10.1.

### 3.2.1.2 Glassware Cleaning

All glassware used in these experiments was soaked in a 10% Ajax surfactant solution for 1 hour followed by a 10% nitric acid solution for a minimum of 1 hour. Following each step the glassware was rinsed thoroughly with Milli-Q water.

### 3.2.2 Direct Force Measurements

Direct force measurements were conducted using an Asylum MFP-3D atomic force microscope (Asylum Research, Santa Barbara, California) mounted on an inverted microscope (Nikon Ti-2000) to allow for bubble alignment. In this thesis study measurements were made between either two bubbles or a rigid particle and a flat surface (referred to as a plate). A schematic diagram of a measurement between two bubbles is shown in Figure 3.4. In all direct force measurements regardless of type the AFM is set to drive the cantilever towards the interacting surface and the user has control of a certain number of experimental parameters. These parameters are the drive velocity, the overall deflection of the cantilever (or applied force) and the distance that the cantilever travels. By changing these parameters in a systematic way, the variations in the interactions between the surfaces being probed can be studied over a wide range of conditions.
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Prior to a direct force measurement it is important to calibrate the detector sensitivity and cantilever spring constant. The calibration of the detector sensitivity determines the relationship between the response of voltage change on the photodiode in comparison with the deflection in the z direction of the cantilever. A force measurement is conducted in the fluid medium that is being utilised and the gradient of the constant compliance region (where $\Delta d = \Delta s$) is the detector sensitivity. In the case of a measurement between two bubbles this is conducted on an unloaded cantilever against a rigid surface, such as a glass slide. The cantilever needs to be unloaded as the deformation of the bubble interfaces does not allow for an accurate sensitivity to be measured. This calibration is dependent on the cantilever, the position of the laser on the cantilever and the fluid medium present and therefore must be measured each time one of these variables changes. It is also important to check this calibration regularly throughout the course of a set of experiments to ensure this value remains constant.

3.2.3 Spring Constant Determination

Accurate determination of the cantilever spring constant is vital as it is used to change the measured photodiode response to a force via Hooke’s Law as shown in Equation 3.2. Cantilevers can be manufactured to have different spring constant values by varying the shape, size and/or material. Spring constants vary with cantilevers manufactured not only from different silicon wafers, but also across a single silicon wafer. It is therefore important to measure each cantilever’s spring constant for accurate determination.\(^{374}\)
\[ F = KVD_S \]  \hspace{1cm} (3.2)

where \( F \) is the force, \( K \) is the measured spring constant, \( V \) is the voltage signal from the photodiode and \( D_S \) is the deflector sensitivity (gradient of the constant compliance region of a rigid interface force curve).

The spring constants were determined in this work with the use of the Hutter and Bechhoefer \(^{375}\) (Thermal) method. This method is easily applied with the use of the MFP-3D AFM operating software. The advantage of this method is that it is non-destructive and determination of the spring constant is relative fast. Other methods available for spring constant determination are briefly described below, but were not used in this thesis study.

The Cleveland method\(^{376}\) involves adding a known mass to the end of the cantilever and measuring the resonance frequency. The change in resonance frequency with respect to the change in mass allows the spring constant of the cantilever to be determined. Due to the mass being added to the cantilever this technique can only be done after a measurement has been completed and the cantilever is no longer required as it renders the cantilever unusable.

The Sader method\(^{377,378}\) is a non-destructive method in which the resonance frequency of the cantilever (without the added mass of the Cleveland method) is measured. Calculations are then completed to determine the spring constant, which assume the cantilever is rectangular in shape and a homogenous material. Benchmark studies for silicon rectangular cantilevers have shown accuracy comparable to the Thermal Method\(^{379,380}\). There are methods utilising factors to convert to non-rectangular shapes but require a further series of calibration methods and computational description of the hydrodynamic drag function for the cantilever\(^{381}\). The conversion to various shaped cantilevers can lead to errors as large as 250 percent\(^{382}\) in the measured spring constant for some cantilever materials.

Another method is the reference cantilever method\(^{383}\) in which a cantilever with a known spring constant is used in conjunction with the cantilever for which the spring constant is being measured. The deflection response of the two cantilevers is measured and the unknown spring constant can then be inferred. This method can propagate
errors through subsequent measurements and it is vital that the detector sensitivity is
determined with a high degree of accuracy\textsuperscript{384}.

3.2.4 Cantilever Preparation

3.2.4.1 Rigid Interface Measurements

For measurements conducted between rigid surfaces, 5 µm or 25 µm diameter silica
particles (Thermo Scientific) were attached to V shaped (MLCT C Triangular
Cantilever, Bruker Corporation) cantilevers as shown in Figure 3.5. A small volume of
particles were dispersed in Milli-Q water and then pipetted onto the glass microscope
slide that had been placed in an ozone cleaner for approximately 10 minutes prior to
use. The water used to disperse the particles was left to evaporate in a laminar flow
hood to leave the particles spread across the slide. The slide with dispersed particles
was then placed on the AFM microscope stage. The particles were attached to the
cantilevers with epoxy glue (The Original Super Glue Corporation) by dipping the end
of the cantilever in a small part of the glue. A suitable particle was then found on the
microscope slide and the tip was brought down onto the particle. The cantilever was
then left for a minimum of 24 hours to dry before being used for a measurement.

\textbf{Figure 3.5}. A SEM image of a V shaped cantilever with an attached particle
(approximately 25 µm diameter) for a rigid interface direct force measurement (Image
taken with the help of Dan Smith, Melbourne Centre for Nanofabrication).

Prior to use the 5 µm diameter particles were reverse imaged on a spiked grating
(TGT1, NT-MDT)\textsuperscript{385} to ensure they were attached correctly and had smooth surfaces
as shown in Figure 3.6. Reverse imaging occurs when the sample, in this case the
spiked grating, is sharper than the tip of the cantilever. This causes an image of the cantilever to be gained instead of the sample. Reverse imaging allowed a topographical profile of the area of the particle interacting during the rigid direct force measurements to be determined. Due to the repetitive pattern of the spiked grating the particle attached to the cantilever is imaged multiple times over the course of the imaging process. The spring constants for these measurements varied between $0.009 \pm 0.002$ N/m and $0.016 \pm 0.003$ N/m.

**Figure 3.6.** AFM reverse images of 5 µm diameter borosilicate particles attached to cantilevers. **Left:** a particle that has an irregular surface and is not suitable for direct force measurements. **Right:** a particle that has a regular surface and would be suitable for direct force measurements.

### 3.2.4.2 Bubble Measurements

Custom made cantilevers were used in experiments for direct force measurements conducted between bubbles and the fabrication of these are described in Appendix 10.2. These cantilevers have the approximate dimensions of $480 \mu m \times 50 \mu m \times 2 \mu m$ with a gold disc of diameter of $45 \mu m$ located at the end.$^{55,119}$

The cantilever was treated with 1-decanethiol in ethanol$^{119,386}$ for approximately 15 minutes to aid in bubble attachment. Following this, a layer of chromium (approximately 5 nm), followed by gold (approximately 10 nm) was applied to the back of the cantilever via a sputter coater (Emitech K575X). This ensures the laser has a suitable reflectivity off the back of the cantilever into the photodiode of the AFM. The order of these steps ensures 1-decanethiol is not present on the back of the
cantilever thereby preventing bubble attachment to this surface. These cantilevers had measured spring constants between 0.095 ±0.01 N/m and 0.21 ±0.02 N/m.

![Image of a custom made silicon cantilever](image)

**Figure 3.7.** A SEM image of a custom made silicon cantilever. This is the underside of the cantilever and shows the gold at the end that facilitates bubble attachment (image taken by Douglas Mair, Melbourne Centre for Nanofabrication).

### 3.2.5 Generation of Bubbles for Direct Force Measurements

The generation of suitably sized air bubbles for use in direct force measurements is completed ultrasonically\(^{118}\), though it requires careful preparation of the surfaces within the experiment. For the measurement an Asylum Research fluid cell that is designed and supplied with the MFP-3D AFM was used. The fluid cell has replaceable round glass discs that fit into the bottom of the cell. For the bubbles to attach to the glass surface upon ultrasonic generation the glass was made hydrophobic by boiling the clean glass discs in n-propanol for 4 hours prior to use\(^{387}\). The glass rounds and beaker used for the surface modification process were cleaned with the glassware cleaning procedure described previously. To ensure this was conducted safely it was conducted in a laboratory fume hood and the n-propanol was boiled with the presence of a small amount of boiling chips.
Figure 3.8. An image of the ultrasound transducer (generator is not shown) showing the glass vessel, transducer and clamp.

The bubbles were ultrasonically generated (Undatim Ultrasonics D-reactor) with a power of 25 W and frequency of 515 kHz. An image of the transducer arrangement is shown as Figure 3.8. The transducer was connected to the generator so that the ultrasound wave could be imparted to the solution. The glass vessel was clamped to the transducer and filled with Milli-Q water to ensure the transducer did not overheat during operation. Once the vessel was filled with water the AFM fluid cell with the desired NaPSS solution within was placed on top of the vessel. Previously, bubbles have been generated ultrasonically in pure water\textsuperscript{118,121}, but it was found that bubbles could be generated and subsequently attached to the cantilever within the desired aqueous NaPSS solutions. This approach offers the advantage of not having to generate bubbles in water and subsequently adding the desired solution to the fluid cell. This also minimises the risk of contamination of the experiment through the use of additional laboratory equipment and lowers the risk of liquid damage to the AFM. The ultrasound generator was operated for approximately 30 seconds or until bubbles were present on the glass surface of the fluid cell.

Once bubbles were generated the fluid cell was placed into the AFM. The bubbles were able to be visualised with an inverted optical microscope (Nikon Ti-2000). Once
a suitable bubble was found the area of the gold disc of the custom made cantilever was lowered onto the bubble. When the cantilever was raised the bubble was then attached to the cantilever as shown in Figure 3.9.

![Figure 3.9](image)

**Figure 3.9.** Microscopy image of a bubble attached to a custom cantilever (top) and a bubble adhered to the glass surface (bottom, out of focus).

Once a bubble was affixed to the cantilever another suitable bubble was then located on the glass surface and the bubble radii were measured optically with the inverted microscope. The radii of the bubbles used within these experiments were in the range of 20 to 36 µm ± 2 µm. To determine the contact angle of both bubbles the contact area radii of both the cantilever and glass surface were measured and are shown schematically in Figure 3.10.

![Figure 3.10](image)

**Figure 3.10.** Schematic diagram of the important parameters to calculate the contact angle of a bubble attached to a surface.

Once the bubble and contact area radii have been measured the contact angle can be calculated via\textsuperscript{120}. 

45
\[ \sin(\theta_c) = \frac{r}{R} \]  

(3.3)

where \( r \) is the contact area radius, \( R \) is the bubble radius and \( \theta_c \) is the contact angle of the bubble.

Once the bubble and contact area radii have been measured the bubbles were aligned axisymmetrically via the use of the inverted microscope, and then refined based on the feedback of the maximum force achieved in a series of force curves taken between the two bubbles. Then direct force measurements were able to be undertaken for a bubble pair.

### 3.2.6 pH Adjustment of Solutions

The pH of the NaPSS solutions was 8.7 throughout this work to ensure the bubble interface was negatively charged. Prior to use the pH meter (Hanna Instruments, HI 255, Woonsocket, Rhode Island) was calibrated with a three point calibration at pH values of 4.01 ± 0.02, 7.0 ± 0.5 and 10 ± 0.02 (pH calibration buffer, ProSciTech, Townsville, QLD, Australia). The pH of the solution was measured and then if an adjustment was required a small amount of a concentrated sodium hydroxide solution was added. The solution was then thoroughly mixed and the pH meter left to stabilise to determine the value. Care was taken to ensure that the pH did not exceed the required value to avoid additional chemicals within the solution.

### 3.2.7 Surface Tension Measurements

Surface tension measurements were conducted via the pendant drop method with the use of a Dataphysics OCA20 tensiometer. In order to use a geometry relevant to the AFM measurements the desired solution was placed in a quartz cell in which an air bubble was generated with a glass syringe and a u-shaped needle. The tensiometer program takes an optical microscopy image of the bubble and fits the bubble interface to the mathematical equations, discussed below, to determine the surface tension. Bubbles were left to equilibrate until the measured surface tension was stable.
Figure 3.11. Schematic image of the experimental arrangement of the tensiometry measurements used in this thesis work. The bubble is formed in a u-shaped needle in the desired aqueous solution. The important mathematical parameters for the determination of the surface tension are also shown.

The mathematical description to determine the surface tension of a bubble with the use of the pendant drop method will be discussed here and the parameters required are shown in the schematic of Figure 3.11. If the bubble were spherical the two radii of curvature, \( R^*_1 \) and \( R^*_2 \), would be the same. In the case of the pendant drop method where the bubble is attached to a needle and elongated due to buoyancy forces, the description of the bubbles curvature must account for gravity and is no longer spherical, the radius of curvature for \( R^*_2 \) when it is taken from the same point on the bubble interface is related as \( R^*_2 = \frac{x}{\sin \phi} \).

If the point where the pressure difference is measured is taken from the apex (Point O in Figure 3.11) of the bubble, from symmetry of the system simplifies to Equation 3.4 below:

\[
\Delta P = \frac{2\sigma}{b} \tag{3.4}
\]

where \( \Delta P \) is the pressure difference between the inside and outside of the bubble, \( \sigma \) is the surface tension of the bubble and \( b \) is the radius of curvature at the apex of the bubble. If the pressure difference is determined at a point other than the apex, for
example point S, of the elongated bubble, the pressure change from the inside to the outside of the bubble equals:

$$\Delta P = \frac{2\sigma}{b} + \Delta \rho g z$$  \hspace{1cm} (3.5)$$

where $\Delta \rho$ is the density difference from the inside to the outside of the bubble, $g$ is the gravitational constant and $z$ is the change in height. By equating Equation 3.4 and 3.5 they form Equation 3.6 which was solved originally by Bashford and Adams$^{388}$. 

$$\sigma \left( \frac{1}{R_1} + \frac{sin\phi}{x} \right) = \frac{2\sigma}{b} + \Delta \rho g z$$  \hspace{1cm} (3.6)$$

Equation 3.6 above can be rearranged and the constant $\beta$ is the dimensionless Bond number to give Equation 3.7.

$$\sigma = \frac{\Delta \rho g b^2}{\beta}$$  \hspace{1cm} (3.7)$$

The sign of the Bond number is dependent on the orientation and the density differences of the fluid being measured. In the case of a bubble in an aqueous solution the Bond number is negative.

### 3.2.8 Polydisperse NaPSS Specific Measurements

#### 3.2.8.1 Sample Dialysis

For the measurements conducted with samples that were dialysed prior to use, NaPSS with a molar mass of 70,000 g/mol was used. A sample of 50,000 ppm was prepared and placed into a dialysis tube. The mass of the tube was weighed prior to dialysis. The tube was placed in a minimum of 5 L of Milli-Q water. This water was exchanged at one, two, three, five and eight hours, with the sample undergoing dialysis for 24 hours.

Once the sample had been dialysed the mass of the sample was determined to compare to the starting value. A 5 mL aliquot of the dialysed sample was pipetted into a petri dish and placed into an oven overnight with a temperature range of 40 to 50 °C to allow the water present to evaporate. Once the sample was dried the mass remaining was used to verify the concentration of the dialysed NaPSS. Dialysis tubes of 1 kDa and 14 kDa MMCO were used for these experiments.
3.2.8.2 *Gel Permeation Chromatography*

Gel permeation chromatography (GPC) was performed on a Shimadzu liquid chromatography system equipped with a Shimadzu RID-10 refractometer ($\lambda = 633$ nm). Three Waters Ultrahydrogel columns were used in series, with the first having a 250 Å porosity and a 6 µm diameter bead size. The subsequent two columns had a linear, 10 µm diameter bead size. The eluent was a 50 mM NaNO$_3$ solution operated at room temperature with a flow rate of 1 mL/min. The molar mass characteristics were determined using Astra software (Wyatt Technology Corp.) and a known refractive index increment, $dn/dc$, value of 0.198 mL/g for NaPSS in 50 mM NaCl$^{389}$ was used.

3.2.9 *Deformable Interface Force Curve Analysis*

The quantitative analysis of the AFM force measurements conducted between two bubbles is more complicated than the analogous analysis between two rigid interfaces due to the interfacial deformation of the bubbles. The surface deformation of the bubbles means that the absolute separation of the interfaces is not able to be measured experimentally via a direct force measurement. The model previously developed by Chan-Dagastine-White$^{133-135}$ accounts for the changes in interfacial deformation of a deformable and rigid interface. The derivation for the measurement between two deformable interfaces is the only form that has been presented in this thesis$^{120}$. This model assumes a separation between the interfaces to calculate a theoretical AFM force curve that is then compared to the experimental result to determine how the interfacial separation changes during the force measurement. The modified Young-Laplace equation that is used to relate the deformation of the bubble surfaces, bubble separation and the disjoining pressure is shown as Equation 3.8.

\[
\frac{\sigma}{2r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) = \frac{2\sigma}{R_0} - \Pi
\]  

(3.8)

where $r$ is the radial distance from the apex of the undeformed bubble, $h$ is the separation of the bubbles, $R_0 = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$ is the average bubble radii of the bubble pair and $\Pi$ is the disjoining pressure of a thin film separating to infinitely flat interfaces.
For the entire bubble geometry, the above equation is not able to be solved analytically when surface interactions and deformation are significant, and therefore the inner region of the bubble is solved numerically and the outer region solved analytically. As the bubble volume is constant the interfacial profile (for a discussion on the constant volume assumption at these pressures and why this is appropriate, see the work by Radke and co-workers\(^\text{390}\)) can be determined and for the inner region where the disjoining pressure is significant Equation 3.9 is used.

\[
\frac{d^2 h}{dt^2} = 2h_0R_0 \left( \frac{2}{R_0} - \frac{\Pi(h)}{\sigma} \right) - \frac{1}{t} \frac{dh}{dt}
\]  

(3.9)

where \(h_0\) is the initial central separation of the bubbles and \(t = \frac{r}{\sqrt{R_0h_0}}\) where it is the dimensionless radial variable.

Below as Equation 3.10 are the boundary conditions required to solve Equation 3.8.

\[
h(0) = h \quad \quad \quad \frac{dh(0)}{dt} = 0
\]  

(3.10)

The Derjaguin approximation is used to determine the total force and is shown as Equation 3.11.

\[
F = 2\pi\sigma G(h)
\]  

(3.11)

where \(F\) is the calculated force using the Derjaguin approximation and the interfacial profile of the deformed interfaces where \(G(h)\) is the integral defined in Equation 3.12.

\[
G = \frac{R_0h_0}{\sigma} \int_0^{\infty} t\Pi(h(t)) \, dt
\]  

(3.12)

The displacement of the AFM cantilever (\(\Delta X\)) during a measurement accounts for the geometry of the measurement and is described by Equation 3.13.

\[
\Delta X = h_0 + 2H(h_0) + \frac{F(h_0)}{2\pi\sigma} \left( \frac{1}{2} \ln \left( \frac{h_0}{4R_1} \right) + B(\theta_1) \right) + \frac{F(h_0)}{2\pi\sigma} \left( \frac{1}{2} \ln \left( \frac{h_0}{4R_2} \right) + B(\theta_2) \right)
\]  

(3.13)
where $H$ is the integral defined in Equation 3.14 and $B(\theta)$ is defined in Equation 3.15.

\[ H = \frac{R_0 h_0}{\sigma} \int_0^\infty t(ln(t))\Pi(h(t)).dt \]  \hspace{1cm} (3.14)

\[ B(\theta) = 1 + \frac{1}{2} \log\left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \]  \hspace{1cm} (3.15)

where $\theta$ is the contact angle of attachment of the immobilised bubble to the surface. The form of Equation 3.15 assumes a pinned contact line of the bubbles on the surface of the cantilever and substrate. This is the more realistic boundary condition for the three phase contact line. Alternatively, the contact line may slide, although unlikely on a glass surface, this form of the boundary condition can be found in the review by Chan and co-workers\(^{391}\).

To account for both depletion and structural forces separate descriptions were added to the existing modelling to account for each of these force types separately. In both cases a disjoining pressure ($\Pi(h(t))$) between two flat half spaces was calculated. In the depletion force case the disjoining pressure was determined from the appropriate theoretical colloidal force models based on polyelectrolyte solution scaling theory\(^{248}\) and for the structural force case the disjoining pressure is constructed from an empirical model. The resulting calculated AFM force curve can then be compared to AFM force measurement data to extract the separation between the drop or bubble interfaces as well as the relative importance of interfacial deformation and the different colloidal forces that may be present. This approach has previously been described and tested in detail\(^{48,211,213}\), and each force type will be discussed in more detail below.

3.2.9.1 Depletion Force Modelling

The disjoining pressure between the two half spaces was calculated from existing theoretical colloidal force models. The disjoining pressure is constructed as the negative of the gradient with respect to distance of the total potential energy between two flat half spaces, $V_{\text{TOT}}$:

\[ \Pi(h) = -\frac{\delta V_{\text{TOT}}}{\delta h} \]  \hspace{1cm} (3.16)
where in this instance, $V_{TOT}$, is defined as:

$$V_{TOT} = V_{EDL} + V_{DEP} + V_{vdW}$$  \hspace{1cm} (3.17)$$

where $V_{EDL}$ is the electrical double layer (EDL) potential energy, $V_{DEP}$ is the depletion potential energy and $V_{vdW}$ is the van der Waals potential energy. The EDL potential energy using the linear superposition approximation assumption has previously been well described$^{28,392}$ and has been used successfully to describe EDL forces between bubbles in this type of AFM measurement$^{120}$ and is given by:

$$V_{EDL} = \frac{64 k_B T n^0}{\kappa} \tanh \left( \frac{e \psi_{o1}}{4 k_B T} \right) \tanh \left( \frac{e \psi_{o2}}{4 k_B T} \right) e^{-\kappa h}$$  \hspace{1cm} (3.18)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $n^0$ is the bulk ion number density, $\kappa^{-1}$ is the debye length, $e$ is the charge on an electron, $\psi_{oi}$ is the surface charge of surface $z$ and $h$ is the separation. The van der Waals potential energy has the form:

$$V_{vdW} = -\frac{A(h)}{12\pi h^2}$$  \hspace{1cm} (3.19)$$

where $A(h)$ is the retarded Hamaker function calculated using Lifshitz theory$^{34}$ for the interaction of two air half spaces separated by water. The calculation approach and dielectric spectra for water are described in Dagastine et al.$^{37}$

The original depletion model proposed by Asakura and Oosawa has been used in a number of force measurements to describe direct force measurement methods between rigid interfaces$^{45,146,180,194,229}$ and by Gromer and co-workers on the force measured between two oil drops using AFM$^{25}$. The form for the depletion potential has a linear dependence with respect to separation:

$$V_{DEP} = \begin{cases} 
\Pi_{osm} (2\Delta - h) & \text{for } h < 2\Delta \\
0 & \text{for } h \geq 2\Delta 
\end{cases}$$  \hspace{1cm} (3.20)$$

where $\Pi_{osm}$ is the osmotic pressure and $\Delta$ is the depletion layer thickness. The osmotic pressure for a system with polyelectrolyte present is related to the depletion layer thickness where $\xi$ is the characteristic length of the polyelectrolyte in solution and is equal to twice the depletion layer thickness, $\Delta$ $^{250}$. It has been assumed that the number
of monomers or the ionisation state of the NaPSS does not change throughout the measurements and the osmotic pressure term in Equation 3.21 can be defined by:

$$\Pi_{\text{osm}} = \frac{C^2}{k_B T} \left( \frac{1}{4A^2C_S + AC} + \frac{1}{\xi^3} \right)$$  \hspace{1cm} (3.21)$$

where $C$ is the polyelectrolyte monomer concentration, $A$ is the number of monomers per charge and $C_S$ is any additional electrolyte concentration. An expression for the characteristic length of NaPSS with a molar mass of 77,000 g/mol in solution with varying concentration has been determined experimentally to be $\xi = 665C^{-0.45}$ by Biggs et al. This correlation has been selected as the molar mass is similar to the one used in this study and gives a good approximation of the characteristic length.

$$V_{\text{DEP}} = \begin{cases} B\Pi_{\text{osm}}(2\Delta - h) & \text{for } h < 2\Delta \\ 0 & \text{for } h \geq 2\Delta \end{cases}$$  \hspace{1cm} (3.22)$$

In Equation 3.22 the osmotic pressure term has been scaled by the parameter, $B$, defined as a partition coefficient. This coefficient accounts for the fraction of depletants, in this instance, the polyelectrolytes, that have not been excluded from the film between the surfaces. The partition coefficient above has been previously developed by Bevan and co-workers for a range of depletion force measurements for rigid systems with particles undergoing Brownian motion in the presence of surfactant or polymers. The effective osmotic pressure difference between the bulk solution and the depletion layers will decrease due to the remaining depletants.

### 3.2.9.2 Structural Force Modelling

The disjoining pressure between two flat air/water interfaces is constructed by fitting an empirical model to a direct force measurement between rigid interfaces (in this case hydrophilic silica) within the same solution conditions, in order to determine the required fitting parameters for an empirical model given by:

$$\frac{F}{R_p} = 2\pi a \exp \left( \frac{-h}{\varepsilon} \right) \cos \left( \frac{2\pi h}{\lambda} + \phi \right) + c$$  \hspace{1cm} (3.23)$$

where $F$ is the force, $R_p$ is the radius of the particle, $a$ is the amplitude of the oscillations, $h$ is the separation of the particle and flat surface, $\varepsilon$ the decay length of the
oscillations, $\lambda$ the characteristic length of the oscillation period, $\phi$ the phase shift factor and $c$ is an offset in the force.

At small separations, this disjoining pressure is expected to be inaccurate as it is obtained between rigid interfaces with surface chemistry that differs from an air/water interface. However, as shown previously, the force measurement between bubbles does not sample these separations due to deformation of the interfaces. Once the disjoining pressure has been constructed based on the data for the structural force between rigid surfaces, it is used as the input into the Chan-Dagastine-White model described above in Section 3.2.9.

3.3 Microfluidic Devices Methods

3.3.1 Materials

For the preparation of the microfluidic chips, SU-8 3025 and SU-8 developer were used as received from Microchem. Trichloro(1H,1H,2H,2H-perfluorooctyl) silane was sourced from Sigma Aldrich and 2-propanol was obtained from Ajax Finechem. Nitrogen and instrument air compressed gas was used as received from CoreGas. Both the base and curing agent of polydimethylsiloxane (PDMS) (Sylgard 184) were sourced from Dow Corning. All solutions were prepared with Milli-Q purified water with a resistivity of 18.2 M$\Omega$.cm at 25 °C. Poly(styrene sulfonic acid sodium salt) (NaPSS) with a molar mass of 77,000 g/mol and sodium dodecyl sulfate (>99.0%) were sourced from Sigma Aldrich and used as received. Glassware cleaning was conducted in the same manner as described above in Section 3.2.1.2.

3.3.2 Microfluidic Chip Preparation

The bubbles were generated with the use of a microfluidic chip and the manufacture of the chips was a multi-staged process as described in literature. These steps involved the design of the device, manufacture of the designs onto a mask, preparation of a silicon wafer to use as a template and preparing the chip itself.

3.3.2.1 Design of the microfluidic chip and preparation of the photo mask

The microfluidic devices were designed and then subsequently a photo mask was made with a direct writing instrument (Intelligent Micropatterning, SF100 XPRESS, St. Petersburg, Florida). The resultant photo mask is shown below as Figure 3.12. Due to
the complicated nature of operating this piece of equipment the photo masks used within this thesis work were produced at either the Melbourne Centre for Nanofabrication or the Minnesota Nano Center at the University of Minnesota.

Figure 3.12. Image of produced photo mask (chrome side down).

3.3.2.2 Wafer Preparation

A 4 inch silicon wafer was used as the substrate for preparation of the template. This wafer was spun at 500 rpm with an acceleration of 100 rpm/sec for 10 seconds followed by 3000 rpm with an acceleration of 300 rpm/sec for 30 seconds (Spin Coater Model WS-650MZ-23NPP, Laurell Technologies Corporation, North Wales, Pennsylvania) with approximately 5 mL of SU-8 3025. This resulted in an SU-8 3025 layer with a thickness of 35 µm, which was measured with a Stylus Profilometer (Ambios XP 200) and is shown in Figure 3.13. The wafer was then soft baked for 15 minutes at 95 °C.
Figure 3.13. Profilometer data showing the thickness of the SU-8 3025 film to be 35 µm.

The resultant wafer with the SU-8 3025 film was exposed to 180 mJ/cm² of UV light with the use of the prepared mask and an EVG 6200 Mask Aligner (EV Group, St. Florian am Inn, Austria). A post exposure bake of one minute at 65 °C followed by five minutes at 95 °C was performed. The cross linked SU-8 3025 film was developed with the use of SU-8 developer for 5 minutes. The wafer was then rinsed with SU-8 developer followed by 2-propanol and then dried with the use of nitrogen gas. The resultant wafer produced is shown as Figure 3.14.
3.3.2.3 Construction of Microfluidic Devices

The prepared wafer was then treated with trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane under vacuum for a minimum of one hour to render the surface hydrophobic. Once the surface was rendered hydrophobic, PDMS was mixed with the aid of a conditioning mixer (ARE-310, Thinky Mixer, Tokyo, Japan) in a 10:1 ratio of base and curing agent. The resultant mixture was slowly poured over the silicon wafer and then degassed under vacuum for a minimum of 1 hour. The wafer was then placed in an 80 °C oven for an hour to cure the PDMS.

Once the PDMS was cured it was allowed to cool, after which it was cut to the required size with holes punched for the tubing. The prepared glass slides were cleaned with 2-propanol and deionised water and were then placed in a plasma cleaner (Harrick Plasma, Ithaca, New York) with the PDMS samples for 45 seconds at a pressure of 300 mTorr. The glass slide and PDMS were brought together after being in the plasma cleaner to bond the two surfaces together. Once bonded, small pieces of tubing were placed inside the holes punched previously and liquid PDMS placed around the tubing. The chip was then placed in the oven for a further 20 minutes to cure the PDMS and help fuse the bonded surface as shown in Figure 3.15. Further tubing and syringe

Figure 3.14. Image of a wafer prepared with SU-8 3025 design following treatment with trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane.
connections were inserted and glued with two part epoxy glue, which was left to dry for at least 24 hours prior to use.

![Image of a microfluidic device]

**Figure 3.15.** Image of prepared microfluidic device prior to tubing and syringe connections being attached.

### 3.3.3 Experimental operation of the microfluidic devices

Once the microfluidic device had been manufactured it was ready to be used. Generally the devices had one liquid, one gas and one exit stream. The liquid was delivered by a syringe pump (NE-1000, New Era Pump Systems, Farmingdale, New York) with the use of a 500 µL glass syringe (Hamilton Company, Reno, Nevada). The outlet of the exit stream was placed in a collection beaker. The gas stream was delivered via a gas cylinder with an appropriate gas regulator. The output of this regulator was connected to a voltage driven low pressure regulator (ControlAir Inc., Type 550X CIA Miniature E/P Transducer, Amherst, New Hampshire). The input voltage was delivered to the low pressure regulator by a USB device (NI USB 6009, National Instruments, Austin, Texas) via the LabVIEW 2009 computer program (National Instruments, Austin, Texas). This is shown in the experimental schematic shown in Figure 3.16.
Figure 3.16. Schematic of experimental set up showing the arrangement of the gas and liquid input streams to the microfluidic device.

To observe the bubble generation, the microfluidic device was placed on an inverted optical microscope (XDS-2 Inverted Biological Microscope, Daintree Scientific, St. Helens, Tasmania, Australia). Images were taken with the use of a CCD camera (Flea3, Point Grey Research, Richmond, Canada) at 610 frames/second. A photograph of the experimental set up is shown below in Figure 3.17.

Figure 3.17. Photograph of the experimental set-up showing the microfluidic device, syringe pump, gas input, voltage generator, optical camera and low pressure regulator (gas cylinder not shown in picture).

As the low pressure regulator was controlled via a voltage input the regulator needed to be calibrated to determine the output pressure for a given voltage and the calibration for the region of use and was shown below in Figure 3.18.
Figure 3.18. The measured output pressure of the low pressure regulator verses the input voltage.

To begin operation the liquid flowrate was set to the value to be used during the experiment and left to allow liquid to fill the channels. Once this had occurred the gas pressure was slowly increased to determine the minimum pressure required for bubble generation to occur. Once steady state operation had been reached the streams were left to equilibrate for 15 minutes prior to measurements being taken. Images were then taken and when sufficient data had been generated the gas pressure was slowly increased. In between each separate gas pressure the device was allowed to reach equilibrium for 10 minutes. This process was continued until the pressure was sufficiently large that bubbles were no longer able to be generated.
Chapter 4 - Direct AFM force measurements between air bubbles in aqueous polyvinylpyrrolidone solutions

A brief discussion of measurements conducted with aqueous polyvinylpyrrolidone solutions and the reasons that depletion forces were unable to be measured is presented.
4.1 Introduction

Depletion interactions were first described by Asakura and Oosawa and occur when molecules within solution are excluded between two larger interacting colloids\textsuperscript{49}. This exclusion of molecules creates a solvent rich environment and subsequently creates an attractive interaction between the larger colloids. Depletion interactions or flocculation can be induced by molecules such as polymers\textsuperscript{393-395}, polyelectrolytes\textsuperscript{244,396}, surfactant micelles\textsuperscript{40,165,204,397-400}, or nanoparticles\textsuperscript{401-402}. Control of particle flocculation to remove impurities is vital in industrial processes including water treatment\textsuperscript{403} and pharmaceuticals production\textsuperscript{404}. A polymer of interest is polyvinylpyrrolidone (PVP) due to its wide range of uses, in areas such as pharmaceutical medications and adhesives\textsuperscript{405}.

Studies investigating the depletion and structural interactions induced by the presence of PVP have used a variety of methods. The stability of silica nanoparticles in the presence of PVP solutions showed that bridging flocculation or depletion interactions were induced and were dependent on polymer concentration\textsuperscript{23}. Similar studies have also used titanium dioxide\textsuperscript{406,407} particles or polystyrene latices\textsuperscript{408} as the interacting colloids of interest. Rheological measurements of suspensions containing PVP have also allowed insight into the effects of the polymer and allow theoretical modelling of the depletion force\textsuperscript{409}. The depletion interaction has been shown to increase with both increasing polymer concentration\textsuperscript{179} and molar mass\textsuperscript{410}. Direct force measurements have been used to show that only a steric repulsion interaction was present with molecules of absorbed PVP on layers of graphite\textsuperscript{411}. However, this result could be due to the molecules being absorbed to a surface and not in bulk solution. Studies have also included the adsorption of PVP to an air/water interface\textsuperscript{412,413} and modelling the distribution of charged and uncharged polymer molecules between two approaching surfaces\textsuperscript{237}.

There are currently limited studies in the literature that measure the force of interaction between colliding colloids in aqueous solution of PVP or other uncharged polymers. Studies have been conducted with the use of the surface forces apparatus (SFA) to measure depletion interactions between lipid bilayers in aqueous solutions of poly(ethylene glycol)\textsuperscript{179,414,415}. The inclusion of the lipid bilayers in this system adds complex interactions between all the components.
The aim of this study was to use direct force measurements to study the depletion interactions present between colliding air bubbles in a simple system only containing PVP. The selection of bubbles as the interacting colloids is due to the ability for the air/water interface to deform. As will become clear later the deformation of an interface during a measurement leads to an increase in the interaction area and this subsequently leads to an increase in the sensitivity of the measurement\(^{210}\). The use of direct force measurement with deformable interfaces has been used to measure depletion and structural forces for surfactant micelles, nanoparticles, micro-emulsions and polyelectrolytes\(^{25,48,127,211,213}\) and allows the possibility of measuring depletion interactions induced by aqueous solutions of PVP which have not been previously measured.

### 4.2 Results and Discussion

Direct AFM force measurements were designed to investigate whether or not depletion and structural forces could be observed in the presence of an uncharged polymer. These measurements were conducted with a PVP molar mass of 29,000 g/mol and at a polymer concentration of 10,000 ppm.

![Graph](image.png)

**Figure 4.1.** Direct force measurements in an aqueous solution of PVP (molar mass of 29,000 g/mol) with a concentration of 10,000 ppm between two air bubbles and a
Chapter 4

collision velocity of 200 nm/s. The bubble radii of the bubbles used in these measurements were 40 and 26 with a normalised radius ($R_0$) of 43 µm. The approach phase has been drawn with filled circles and the retract phase with open circles.

A direct force measurement conducted between colliding air bubbles in the presence of an aqueous PVP solution with a concentration of 10,000 ppm is shown in Figure 4.1. The measurement exhibits a pure short range repulsive force and does not show any evidence of an attractive van der Waals force. This indicates that the PVP polymer has absorbed to the bubble interfaces, creating a repulsive force and not allowing the bubbles to coalesce during the collision. This result is typical for direct force measurements conducted when molecules, such as electrolytes or surfactants have absorbed to the air/water interface. Both the approach and retract phases of the direct force measurement exhibit minimal hysteresis between them, which is a typical result for this type of measurement. It has previously been shown that measurements conducted at a collision velocity of 200 nm/s do not exhibit a hysteresis between the phases, which is due to hydrodynamic effects.

A previous study observed changes in the silica nanoparticle stability upon the addition of PVP to the system. This was attributed to a depletion interaction between the silica surfaces that occurred when the polymer concentration was of a sufficient concentration to saturate the surface with PVP molecules. This work showed for PVP with a molar mass of 55,000 g/mol or 360,000 g/mol, the onset of a depletion interaction occurred at a concentration of approximately 1000 ppm. Another study measured the surface tension of an air/water interface exposed to various concentrations of PVP with a molar mass of 29,000 g/mol. This worked showed that above a PVP concentration of approximately 100 ppm the surface tension of the interface does not change from approximately 65 mN/m, demonstrating full adsorption of PVP to the interface. Yet, the direct force measurement of a 10,000 ppm PVP aqueous solution in Figure 4.1 does not measure a depletion or structural interaction. If a depletion force was present there would be an attractive jump-in present in the approach phase of the measurement. Structural interactions would be demonstrated through several oscillations in the force response. This measurement was conducted at a concentration where a depletion or structural interaction would be expected. The use of a deformable interface in a direct force measurement has previously been shown to have a higher sensitivity to the force imparted on it when
compared to a rigid interface measurement\textsuperscript{210}. From the results of Figure 4.1, it is clear that even with a heightened level of sensitivity in the measurements undertaken this increased sensitivity still does not allow a depletion interaction to be measured.

**Figure 4.2.** Direct force measurements in aqueous solutions of PVP between two air bubbles with a concentration of 10,000 ppm and a molar mass of 29,000 g/mol. The bubble radii of the bubbles used in these measurements were 40 and 26 with a normalised radius (R\textsubscript{0}) of 43 \(\mu\)m. The collision velocity was varied between 500 nm/s (green), 1 \(\mu\)m/s (purple), 2 \(\mu\)m/s (blue) and 4 \(\mu\)m/s (orange). The approach curve is drawn as filled points and the retract curve as the open points.

The direct force measurements shown in Figure 4.2 demonstrate the effect of varying the bubble collision speed in an aqueous solution of 10,000 ppm PVP. Unlike the previous measurement shown in Figure 4.1 the increased collision velocities of the interacting bubbles are now influenced by hydrodynamic fluid flow. As the collision speed of the bubbles increase, the magnitude of the forces measured also increase and a hysteresis between the approach and retract phases beings to develop. These observations are typical of measurements conducted at increased collision velocities and do not reveal any new features which may well be expected from the influence of the depletion forces. The effects of hydrodynamic fluid flow will not be discussed in further detail here as they are also presented in Chapter 5 and 6. Within these chapters
these measurements are able to be considered in greater detail and more fully developed.

Measurements were also conducted with the polymer concentrations of 20,000 and 50,000 ppm, but no evidence of a depletion force was measured. It has also been demonstrated previously that decreased polymer concentrations cannot induce depletion interactions\textsuperscript{23}. Increasing the concentration of PVP also increases the solution viscosity, which has previously been shown to increase the hydrodynamic interactions experienced during a measurement\textsuperscript{416}.

![Figure 4.3](image)

**Figure 4.3.** Variation of viscosity with varying concentration of water\textsuperscript{416} (red), PVP (29,000 g/mol)\textsuperscript{417} (purple) and PVP (360,000 g/mol)\textsuperscript{418} (green) solutions.

Figure 4.3 demonstrates the increase in solution viscosity with increasing PVP concentration and molar mass. An increase in concentration leads to an increased viscosity and thus a larger hydrodynamic fluid flow component. It has been shown in a previous study that even doubling the solution viscosity to that of water, approximately 0.0019 Pa.s, affects the ability to take direct force measurement between deformable interfaces without the influence of hydrodynamic drainage\textsuperscript{416}. Increasing the PVP
concentration to 50,000 ppm caused hydrodynamic drainage in the measurements to overwhelm the measurement of any potential depletion force. Measurements with a molar mass of 360,000 g/mol were also conducted at PVP concentrations of 1000 and 10,000 ppm, but the viscosities of these solutions were higher than those with the molar mass of 29,000 g/mol and once again the fluid hydrodynamics dominated the interactions between the bubble pair.

As well as the increased viscosity, the dispersity of the molar mass distribution could also be affecting the ability to measure a depletion or structural force. It has been shown previously that by mixing two monodisperse molar mass distributions in the same aqueous solution that the structural forces observed were smoothed\(^{47}\). The magnitude of the force oscillations were also decreased in these measurements. As the PVP used within this study had a polydisperse distribution the depletion or structural forces could have a lower magnitude then a monodisperse sample. Further studies presented later in this thesis address concept in more detail and will be discussed later.

Another reason that a depletion force might not be able to be measured with the method used is due to a lower osmotic pressure in the system when compared to a polyelectrolyte. Previous direct force measurements investigating depletion and structural forces have used polyelectrolytes such as sodium poly(styrene sulfonate) (NaPSS)\(^{45-47,191,192}\) and sodium poly(acrylate) (NaPAA)\(^{193}\). The osmotic pressure imparted by an uncharged polymer chain is on the order of a magnitude lower than that of a polyelectrolyte\(^{24,250}\). This is due to the polyelectrolyte having the added contribution from the dissociated counter ions in solution. The magnitude of the depletion interaction has then decreased in the case of uncharged polymer to the point it could be outside the range accessible by the method used.

The osmotic pressure of a polyelectrolyte can be described with Equation 4.1\(^{248}\).

\[
\frac{\Pi_{\text{osm}}}{k_B T} = \frac{C^2}{4A^2C_S + AC} + \frac{1}{\xi^2} \tag{4.1}
\]

where \(\Pi_{\text{osm}}\) is the osmotic pressure, \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(C\) is the polyelectrolyte monomer concentration, \(A\) is the number of monomers per charge, \(C_S\) is the additional electrolyte concentration and \(\xi\) is the...
characteristic length of the polyelectrolyte in solution. Thus in the case of no added electrolyte, \( C_S = 0 \), Equation 4.1 reduces to:

\[
\frac{\Pi_{osm}}{k_B T} = \frac{C}{A} + \frac{1}{\xi^3}
\]  

(4.2)

One can easily observe that the osmotic pressure is a function of the number density of counter ions, i.e. the number density of monomer divided by the number of monomers per charge, and the contribution based on the size of the polyelectrolyte.

From Equation 4.2 the osmotic pressure components of the counter ions in solution and the polymer contributions can be calculated. If the system of interest is assumed to be a 10,000 ppm NaPSS solution with a molar mass of 32,000 g/mol, the osmotic pressure component due to the counter ions is determined to be approximately 73% of the total osmotic pressure. For an uncharged polymer, Equation 4.2 reduces further, removing the counter ion number density, where the osmotic pressure of an uncharged polymer is significantly lower when compared to that of a polyelectrolyte of a comparable molar mass. By increasing the polymer concentration to increase the osmotic pressure of the depletion interaction, the solution viscosity and thus the effect of the hydrodynamic interactions also increases. In essence, based on the direct force measurement results, using the more force sensitive deformable bubble interfaces, the conditions are still not suitable for measuring depletion interactions. As a consequence, experiments were appropriately modified to increase the osmotic pressure sufficiently to measure depletion and structural force interactions by using a polyelectrolyte, NaPSS.
4.3 Summary and Conclusions

Previous measurements had indicated that a depletion force could be induced in solution in the presence of PVP. Direct force measurements were conducted between colliding bubbles in aqueous solutions of PVP in an attempt to measure a depletion interaction. It was not possible to measure a depletion force and we propose that there are several reasons why the force was unable to be measured.

It has previously been shown that direct force measurements are able to measure depletion and structural forces between interacting deformable interfaces\textsuperscript{25,48,127,211,213}. The osmotic pressure of a polyelectrolyte that governs these interactions has two important contributions, the dissociated counter ions and the polymer. The contribution due to the counter ions in solution on the osmotic pressure has been shown to be an order of magnitude larger than that of the polymer\textsuperscript{24,250}. Increasing the polymer concentration also increases the solution viscosity. An increase in solution viscosity also leads to an increase in the hydrodynamic interactions in the system and any potential depletion interaction is overwhelmed by this additional force component. The dispersity of the molar mass distribution could also be contributing to the inability to measure a depletion or structural force. The results of the present set of experiments provide useful guidance to the conditions that are needed to allow direct force measurements to be made in an aqueous polymer solution.
Chapter 5 - Direct AFM force measurements between air bubbles in aqueous polydisperse sodium poly(styrene sulfonate) solutions

The material in this chapter is drawn from the following publication:

5.1 Introduction

Polyelectrolytes have an important role in many industrial processes where emulsion and colloidal stability are required. Some areas that make use of polyelectrolyte effects, such as charge driven surface adsorption and lower viscosity when compared to uncharged polymers, are wastewater treatment\textsuperscript{419,420}, minerals processing\textsuperscript{421,422}, paints\textsuperscript{186,423}, model systems for foods\textsuperscript{25} and even biological applications such as protein crystallisation\textsuperscript{43}. The colloidal interactions that govern the stability of emulsions in the presence of polyelectrolytes have been shown to be a combination of depletion and structural forces when the polyelectrolyte is largely non-adsorbing on the colloidal material. In addition, there are also steric forces or polymer bridging in instances where the polyelectrolyte is adsorbed to the interface of the colloid.

There have been a number of studies where structural and depletion forces have been the focus of direct force measurements between rigid surfaces in the presence of non-adsorbing polyelectrolytes\textsuperscript{45-47,191}. Structural forces arise between approaching surfaces due to the ordering of smaller colloids such as micelles, polymers or nanoparticles that are present in the liquid between the surfaces. Depletion forces arise from an osmotic pressure difference due to an excluded volume effect when the surfaces are closer than the diameter of the smaller colloid. Since the first measurement of a structural force using the surface force apparatus\textsuperscript{143}, a range of methods have been used to study these forces in the presence of both charged and uncharged polyelectrolytes. One of the first examples using an AFM to measure a depletion force was completed by Milling and Biggs with poly(dimethyl siloxane)\textsuperscript{190}. Another commonly studied polymer is sodium poly(styrene sulfonate). Commonly, either AFM\textsuperscript{45-47,191} or total internal reflection microscopy (TIRM)\textsuperscript{176,177} and in one instance both types of measurements\textsuperscript{192}, are used. Thin film balance methods\textsuperscript{185,186,242} have been used as well, where one of the non-adsorbing surfaces is an air/water interface with a low coverage of surfactant. It is important to note that structural forces have also been observed with the use of AFM for a range of other systems, including nanoparticles\textsuperscript{43,201}, surfactant micelles\textsuperscript{40,204,205} and even microemulsions\textsuperscript{48}.

As discussed in Chapter 2, polyelectrolytes have concentration dependent spatial orientations in solution. The first transition, from the dilute to the semi-dilute regime, occurs at what is referred to as the overlap concentration, $c^*$, where the polyelectrolyte
no longer can be described in the form of discrete polymer chains in solution. In the
dilute regime (namely at concentrations below molecular overlap) the individual
polyelectrolyte molecules are coils which behave in a similar fashion to a space filling
lattice as individual chains, where their size and confirmation are defined by both the
charge on the polymer and the molar mass of the polyelectrolyte. Once the
concentration increases to the overlap concentration the polyelectrolyte coils become
densely packed$^{246}$. In the semi-dilute regime the coils can no longer have an
independent excluded volume and they start to form a network or three-dimensional
mesh in solution. The spacing between the polyelectrolytes in the dilute regime and the
network points in the semi-dilute regime are referred to as the characteristic length.
The concentration dependence of the characteristic length varies between the dilute and
semi-dilute regimes and this has previously been described with polyelectrolyte scaling
theory$^{250}$. Along with the characteristic length variations caused by changes to
concentration the solution viscosity also varies with concentration and polymer molar
mass$^{248,424}$.

Most previous direct force measurements have employed rigid interfaces to study
interaction forces. There are, however, several studies that have examined the
behaviour of structural and/or depletion forces in the presence of easily deformable
interfaces, such as bubbles and emulsion droplets. Previous studies using AFM have
shown that high concentration surfactant solutions, microemulsions or nanoparticles
induce structural forces between oil droplets$^{48,211,213}$. These studies can also be
extended by using polyelectrolytes as a model system to further the understanding of
food emulsions, such as study that used NaPSS to compare sugar beet pectin in an oil
emulsion$^{25}$. Structural forces between a silica particle and air bubbles in the presence
of nanoparticle/surfactant complexes have also been measured using direct force
measurements$^{127}$. Several advantages to using deformable interfaces when measuring
structural forces have been recognised. Coupling of the structural force with interface
deformation shows an interesting hysteresis between the collision and separation of
drops that has not been measured with rigid interfaces$^{21,26,27}$. There is also an increase
in the sensitivity to the forces experienced between the interacting droplets. This is due
to the deformation of their interfaces during collision when compared to colliding rigid
spheres, as deformation leads to an increase in the effective area of interaction$^{210}$.
These studies included a theoretical model$^{133-135}$ to account for interfacial deformation
and quantitatively decouple the effects of interfacial deformation from changes in oscillatory surface forces.

The purpose of the study presented in this chapter was to investigate the forces experienced between two deformable air bubbles in water in the presence of a polyelectrolyte, sodium poly(styrene sulfonate). Air bubbles have been selected due to their inherently clean and smooth surfaces and their sensitivity to applied forces. The parameters that have been focused on in this systematic study are NaPSS concentration, NaPSS molar mass and bubble collision velocity. The degree of molar mass dispersity of the samples has also been changed to further understand the effect of variation in the molar mass distribution on structural and depletion forces. The experimental parameters chosen cross the dilute/semi-dilute regimes of polymer packing in solution and allow the effects that these regimes have on the interactions between air bubbles to be studied. The study also has a specific relevance to the selection of effective reagents in industrial applications. Disperse molar mass chemicals, like the ones used in this work, are used almost exclusively instead of monodisperse size distribution polyelectrolytes due to the large cost differential between the two. Further knowledge and understanding of the interactions between deformable surfaces in the presence of disperse size distributions have the potential to benefit various processing industries.

5.2 Results and Discussion

Direct force measurements between air bubbles in aqueous solutions of NaPSS were conducted to study the changes in the interaction forces due to NaPSS concentration, bubble collision velocity and molar mass of the polyelectrolyte. The following measurements have all been conducted with polydisperse molar mass samples.

The molar mass dispersity ($D$) for each of the samples was measured with a gel permeation column (GPC) and the results are shown in Table 5.1. These data show that the molar masses of the samples are reasonably polydisperse ($D$ above 1.1) and the measured molar masses are similar to the specified value given by the supplier. It is expected that these polymers will also have batch variability from the supplier, thus to avoid this inherent variation the same chemical samples for each molar mass were used throughout the study. The overlap concentrations have also been calculated for these
polyelectrolytes for both the number and weight average molar masses and details of the calculation can be found in Appendix 10.1.

The surface tension of an air/water interface in the presence of NaPSS was independently measured with a tensiometer. These measurements are shown in Table 5.1 for all the molar masses studied in this work. These surface tension values indicate that NaPSS molecules adsorb to the air/water interface. Previous studies have characterised NaPSS as a non-adsorbing polyelectrolyte in the presence of silica/water interfaces\textsuperscript{45,176} due to electrostatic repulsion between the surface and the negative charges on the polyelectrolyte. Interestingly, at the pH of the solution in this study (approximately, pH 8) the air/water interface is expected to have a significant negative charge\textsuperscript{120}, yet there is a clear dependence of surface tension with increasing NaPSS concentration. The surface activity of NaPSS has been observed previously\textsuperscript{425-427} and is attributed to the interaction between the hydrophobic nature of the air/water interface and the hydrophobic backbone of the NaPSS. Neutron scattering results indicate that the adsorption of NaPSS is single layer in nature and lies flat relative to the air/water interface\textsuperscript{428,429}. The physical properties such as surface tension, molar mass dispersity and overlap concentration of the NaPSS samples lead to different influences on the interactions between colliding bubbles. These properties were probed in this study and the first experimental parameter that was investigated was the change in interaction between air bubbles with respect to varying the concentration of the polyelectrolyte in solution.
Table 5.1. Summary of the measured molar mass dispersity (D), molar masses, calculated overlap concentration and surface tensions (± 2 mN/m). The surface tension measurements were of air bubbles in aqueous NaPSS solutions at a temperature of 25 °C with varying concentration and molar mass.

<table>
<thead>
<tr>
<th>Supplier specified molar mass (g/mol)</th>
<th>Weight average molar mass (MW) (g/mol)</th>
<th>Number average molar mass (MN) (g/mol)</th>
<th>Mw/Mn dispersity (D)</th>
<th>Monomer number</th>
<th>Calculated overlap concentration (c*) (ppm)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Based on MN</td>
<td>Based on MW</td>
</tr>
<tr>
<td>7 × 10⁴</td>
<td>1.0 × 10⁵</td>
<td>6.7 × 10⁴</td>
<td>1.5</td>
<td>nₐᵥ = 338</td>
<td>2800</td>
<td>1900</td>
</tr>
<tr>
<td>2 × 10⁵</td>
<td>2.7 × 10⁵</td>
<td>2.0 × 10⁵</td>
<td>1.4</td>
<td>nₐᵥ = 965</td>
<td>1000</td>
<td>700</td>
</tr>
<tr>
<td>5 × 10⁵</td>
<td>6.7 × 10⁵</td>
<td>4.0 × 10⁵</td>
<td>1.7</td>
<td>nₐᵥ = 2413</td>
<td>500</td>
<td>300</td>
</tr>
</tbody>
</table>
5.2.1 Varying Concentration

Figure 5.1. Direct force measurements between two air bubbles in solutions of NaPSS with a molar mass of 70,000 g/mol and collision velocities between 250 and 500 nm/s. The concentrations of the various solutions (left to right) are 1000 ppm (red), 5000 ppm (blue), 10,000 ppm (purple) and 25,000 ppm (blue). The bubble radii for these measurements are in the range of 55 and 86 µm and were normalised by R₀. The R₀ values for each curve were 79 (1000 ppm), 56 (5000 ppm), 55 (10,000 ppm) and 73 (25,000 ppm) µm. The data for each of the concentrations has been offset for clarity. The approach curve is shown as filled points and the retract curve as the open points. Due to dissociation of sodium ions from the NaPSS in solution the calculated ionic strengths are 1.0 mM, 4.8 mM, 9.6 mM and 24.1 mM for 1000 ppm, 5000 ppm, 10,000 ppm, and 25,000 ppm concentrations. Inset. Experimental set up of direct force measurements between bubbles.

The concentration of the NaPSS in solution was systematically varied in order to study the effects on bubble interactions from a polyelectrolyte in solution with a disperse molar mass. The measurements on a NaPSS sample with a molar mass of 70,000 g/mol at concentrations of 1000 ppm, 5000 ppm, 10,000 ppm and 25,000 ppm are shown in Figure 5.1. These measurements were conducted at velocities between 250 and 500 nm/s as at these velocities the interaction between air bubbles in water are not expected to be influenced by hydrodynamic effects. At larger velocities the measured forces do show a systematic dependence on the collision velocity and this aspect will be discussed later in further detail. These measurements show that as the concentration of NaPSS in solution increases several different effects occur, noting that the overlap concentration (c*) for NaPSS based on a manufacturer specified M_W of 70,000 g/mol
was calculated to be approximately 2700 ppm. The selected concentrations start in the dilute regime, below $c^*$, where the spacing between polyelectrolyte chains is governed by the characteristic length, $\xi$, of the NaPSS in solution. This is defined by the radius of gyration of the polymer and scales with monomer concentration, $c$, according to $\xi \sim c^{-\frac{1}{3}}$. Above $c^*$, in the semi-dilute regime, $\xi$ is defined as the distance between cross links in a 3-dimensional network and scales with polymer concentration according to $\xi \sim c^{-\frac{1}{2}}$.

The attractive jump-in that is present in the approach curve is indicative of a depletion force and in stark contrast to the lack of a jump-in shown in the PVP measurements of Chapter 4. As already mentioned this force arises from an osmotic pressure difference due to the exclusion of the depletant (in this case NaPSS) from the thin film between the bubbles based on the size of the depletant. The magnitude of the attractive jump-in increases as the NaPSS concentration increases where this is consistent with polyelectrolyte scaling theory. The theory shows that the magnitude of the depletion force is not dependent on the number density of the polymer, but the number density of the counter ions associated with the NaPSS. As discussed in the Deformable Interface Force Curve Analysis method section in Chapter 3, the length scale of the depletion force is more closely related to the characteristic length, $\xi$, of the NaPSS.

Unlike direct force measurements previously conducted between rigid interfaces in the presence of monodisperse NaPSS$^{45,46}$ these polydisperse measurements do not show any evidence of further oscillations, indicative of further structuring of the polymer coils in solution. It appears that the polydisperse nature of the polymer obscures the structural forces between both rigid and deformable interfaces in both the dilute and semi-dilute regions. The work completed by Biggs$^{47}$ on the forces between rigid surfaces in the presence of binary mixtures of different molar masses of monodisperse NaPSS also observed a smoothing of the oscillations as a function of polymer mixing ratio at a constant polymer monomer concentration. In the dilute region the apparent force smoothing is due to the NaPSS molecules no longer being able to form a distinct ordered structure in solution that gives rise to oscillatory forces as observed with monodisperse systems. For the current study, this is also the case for the 1000 ppm concentration which is expected to be in the dilute regime.
It should be noted that in the Biggs’ study, the total monomer concentration was held constant where, in two instances, the lower molar mass NaPSS polymer concentration was below \( c^* \) and the higher molar mass polymer concentration was above \( c^* \). It was observed that the depletion length scale and osmotic pressure were a function of the concentration of the lower molar mass polyelectrolyte. It was suggested that the lower molar mass polymer partitioned into the depletion layer established by the larger molar mass polymer. When two polymers with larger molar masses were used with concentrations above \( c^* \), the osmotic pressure and depletion length were independent of concentration. This was attributed to the fact that both polymers were now in the semi-dilute region where the spacing is controlled by distance between inter-coil crosslinks and the structure is no longer dependent on the size of the polymer. This indicates that the variation in molar mass introduced through the use of a polydisperse sample should also not affect the length scale of the depletion force in the semi-dilute regime. Thus for the data in Figure 5.1 the observation of a lack of structural forces at 1000 ppm may be expected based on the mixing of a range of polymer sizes in the dilute concentration range. At higher concentrations the effect of polydispersity is more complicated as this system has a range of overlap concentrations for the different molar mass components making up the polymer distribution. The overlap concentration that was calculated based on \( M_W \) and \( M_N \) differed by 950 ppm for the sample with a supplier specified \( M_W \) of 70,000 g/mol. It is known from the dialysis of this sample, which is discussed in more detail later, that there are polymers with a molar mass as low as 1000 g/mol. This corresponds to an overlap concentration of 181,000 ppm. This means that even at 10,000 (or 25,000) ppm some fraction of the NaPSS is still below the overlap concentration for that monomer and this could be the reason for the lack of structural force observations between either the bubble or rigid interfaces at concentrations above \( c^* \).

The increase in the attractive force on separation between the bubbles with increasing concentration can be attributed to the attractive depletion force coupled with the mechanical instability of the cantilever, but the magnitude of the adhesion is also reflective of the deformation of the interface. The first remarkable feature to note is that even with this strong attractive force between the bubbles, the bubbles do not coalesce and are stable. Similar hysteresis effects have been observed between drops in the presence of structural forces\(^{48} \) or NaPSS from depletion interactions\(^{25} \) and come
about due to the presence of the depletant as well as the adsorption of surfactant or polymer to the drop interface, but this is the first observation of such effects for bubbles. Furthermore, it is also important to note that measurements conducted between air bubbles in aqueous solution without NaPSS present at pH 8 do not experience hysteresis between the approach and retract force profiles at velocities lower than 500 nm/s. This indicates that as a control measurement, the forces between the bubbles are expected to be an electrical double layer repulsion and an attractive force from van der Waals which have previously been measured using this AFM method\textsuperscript{120}. Therefore it would be expected at these velocities that the hysteresis originating from a hydrodynamic drainage force between the curves would be negligible.

The change of the slope of the curves at small separations is a consequence of bubbles with varying sizes. The gradient of this part of the force curve is dependent on the cantilever bubble diameter, contact angle and surface tension is given by the simple analytic relationship\textsuperscript{136}.

\[
\Delta X = \frac{F}{4\pi\sigma} \left[ \log \left( \frac{FR_0}{8\pi\sigma R_1^2} \right) + 2B(\theta_1) \right] + \frac{F}{4\pi\sigma} \left[ \log \left( \frac{FR_0}{8\pi\sigma R_2^2} \right) + 2B(\theta_2) \right] - \frac{F}{2\pi\sigma} \tag{5.1}
\]

where \(\Delta X\) is the separation, \(F\) is the interaction force, \(\sigma\) is the surface tension of the bubble, \(R_1\) and \(R_2\) are the bubble radii of the bubbles, \(R_0 = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)\) is the average bubble radii and assuming the contact lines of the two bubbles are pinned \(B(\theta_1)\) and \(B(\theta_2)\) is described by:

\[
B(\theta) = 1 + \frac{1}{2} \log \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \tag{5.2}
\]

where \(\theta_1\) and \(\theta_2\) are the contact angles of the bubbles with respect to the surface of attachment and NaPSS solutions. A schematic diagram showing the parameters used in this expression is provided as Figure 3.4 in Chapter 3 (Experimental Methods).
Figure 5.2. Approach phase direct force measurements (coloured points) and the high force formula result (black lines) between two air bubbles in solutions of NaPSS with a concentration of 10,000 ppm and a velocity of 1 µm/s were measured. The molar mass was varied to (left to right) 70,000 g/mol (red points and solid line), 200,000 g/mol (green points and dashed line) and 500,000 g/mol (purple points and dotted line). The bubble radii in these measurements varied between 54 and 58 µm.

An example of the agreement between this expression and these data for the approach force curves is shown as Figure 5.2. Due to the challenges of solution exchange in this system only one concentration and molar mass was studied for a single bubble pair. As the bubbles are generated ultrasonically in these experiments the bubble size can only be controlled within a limited range of sizes. This resulted in some variability of the gradient in Figure 5.1. In addition, surface tension can also affect the gradient as shown in Equation 5.1 where the surface tension of an air/water interface in the presence of NaPSS varies with concentration and molar mass as shown previously in Table 5.1.

In addition to qualitatively describing the effect of polymer concentration on the forces between interacting bubbles quantitative modelling was conducted. The modelling used a parameterised approach for the electrical double layer and depletion components as discussed in detail in the Experimental Methods Chapter. The original depletion model by Asakura and Oosawa\textsuperscript{19} describes a depletion layer adjacent to each surface that is an exclusion zone based on geometric arguments where the depletion layer thickness is typically half the characteristic length scale of the depletant (e.g., for a particle, the radius).
Yet, a number of studies have found for more complicated depletants, such as micelles, polymers and polydisperse systems, the depletion model can overestimate the magnitude or length scale of this force. This is due to some fraction of the depletant not being excluded from the film between the two larger interfaces. This is caused by configurational changes in solution, as is possible for polymers or with surfactant micelles due to variation in aggregation numbers or charge density. This is often accounted for semi-empirically as described below.

\[
V_{\text{DEP}} = \begin{cases} 
B\Pi_{\text{osm}}(2\Delta - h) & \text{for } h < 2\Delta \\
0 & \text{for } h \geq 2\Delta 
\end{cases}
\]  \hspace{1cm} (5.3)

where \( V_{\text{DEP}} \) is the depletion potential energy, \( \Pi_{\text{osm}} \) is the osmotic pressure, \( B \) is the partition coefficient, \( \Delta \) is the depletion layer thickness and \( h \) is the separation.

For monodisperse polyelectrolyte systems force measurement data were fitted to extract an osmotic pressure\(^{46} \) or in the case of uncharged polymers or surfactants systems a partition coefficient\(^{180} \), \( B \), was used to scale the osmotic pressure term in the depletion force. The partition coefficient is defined as the average number density of the NaPSS that remains in the thin film during the bubble collision\(^{180} \). The partition coefficient approach has been more readily applied to particle, surfactant and polymer systems with some theoretical basis for the magnitude of the coefficient\(^{228,428} \) where for example, the partition coefficient for a monodisperse polymer was quite low. In the case of this study, it is expected that the polydispersity of the sample will significantly impact the partitioning of the NaPSS within the film. It is also important to note that in the case of a polyelectrolyte as a depletant the molecule contains mostly solvent when compared to particle systems.

The typical approach for modelling the collision of deformable interfaces during a direct force measurement when using the Chan-Dagastine-White model\(^{133} \) is to calculate the disjoining pressure between two flat half spaces based on the appropriate theoretical colloidal force model. This calculated disjoining pressure is then used with the calculation of the AFM force curve, accounting for bubble deformation as described above, to compare to the direct force measurement. This links the experimental results to theory. In this case electrical double layer, van der Waals and depletion force components were used to calculate the disjoining pressure. As described above the van der Waals force was calculated based on the system and
experimental parameters including drop radius, contact angle and surface tension that were all measured independently. For the electrical double layer force, the ionic strength is set by the fraction of the polyelectrolyte monomers that dissociate, measured to be 20% for NaPSS\textsuperscript{248}. The surface potential of the bubble surfaces was set between -20 to -40 mV based on zeta potential measurements of NaPSS coated particles from the layer-by-layer method as these surfaces are expected to have similar orientation lying flat at the interface\textsuperscript{430,431}. The only unfixed parameter was the partition coefficient and a summary of the parameters used is shown in Appendix 10.3.

**Figure 5.3.** Direct force measurements between two air bubbles in solutions of NaPSS with a molar mass of 70,000 g/mol with the results from the analytical modelling overlaid. The concentrations of the various solutions (left to right) are 1000 ppm (red), 5000 ppm (green), 10,000 ppm (purple) and 25,000 ppm (blue). The data for each of the concentrations has been offset for clarity. The approach curve is shown as filled points and the retract curve as the open points.

Comparison between the experimental force curves and the calculated modelling, shown in Figure 5.3, was achieved using a partition coefficient of 0.2 for all concentrations. The jump-in on approach from the mechanical instability of the cantilever and the depletion interaction in the force data is captured quite well in the model force curve. The predicted jump-out of the modelling curve overestimates the depletion attraction on separation for several concentrations, but the model does not include the dynamics of the mechanical instability of the cantilever in any detail. These results also confirm that the hysteresis in the bubble measurements is due to deformation of the interfaces (i.e., flattening of the bubbles in the interaction region)
and this is not possible with rigid interfaces. The length scale of the depletion force is defined by the characteristic length of the NaPSS in solution and describes the approach force behaviour in this system well. It should be noted that these NaPSS concentrations span both the dilute and semi-dilute regimes and therefore there is a change in the mechanism controlling the characteristic length. The increase in the magnitude of the depletion jump-in and pull-off with increasing concentration indicates that the measured force is more sensitive to changes in the number of NaPSS molecules and their associated counter ions compared with the characteristic length. The modelling demonstrates a reasonable agreement with the experimental results and clearly demonstrates the trends with respect to concentration considering that the depletion component of the potential energy has previously not been able to be compared to data\textsuperscript{25}.

This agreement was made possible with the scaling of the calculated depletion energy by the partition coefficient that was used to incorporate the effects that polydispersity has on the measured interactions. In this system the partition coefficient allows the effects of polydispersity on the resultant osmotic pressure to be included. For measurements using a rigid interface with a NaPSS solution of a monodisperse molar mass several periods of oscillations occur, demonstrating that the NaPSS is ordering to a minimum of three measurable layers\textsuperscript{45}. From the bubble and rigid interface measurements of the polydisperse molar mass, it is shown that the NaPSS does not form discrete layers when compared to the monodisperse system. Therefore the difference between the monodisperse and polydisperse systems is attributable to the spread or dispersity of molecule sizes in solution. In the polydisperse case this minimum required separation distance for a molecule to remain in the thin film between the bubbles varies with regards to molecule size. The largest molecules are expelled first and set the depletion layer length and the smaller molecules remain in the thin film near the interface. Due to molecules remaining in the thin film and reducing the osmotic pressure, the partition coefficient allows for this and scales the depletion force.

As mentioned above, rigid interface AFM measurements were conducted with the polydisperse NaPSS system to allow comparison to be made between previously completed monodisperse measurements\textsuperscript{45-47,191}. Not only was there an absence of
structural forces, but no short range attractions were observed that could be attributed to an attractive depletion interaction prior to hard contact. This may be attributed to the polydisperse nature of the sample, the short range interactions in the silica system as well as any adsorption of the low molar mass NaPSS material. The observations from the rigid interfaces are consistent with the claim previously discussed that deformable interfaces are more sensitive to forces than rigid surface systems and in this case the depletion force of the polydisperse NaPSS would not be quantifiable without having deformable interfaces. Rigid interface measurements are shown in Appendix 10.4.

5.2.2 Varying Velocity

Variation of the collision velocity between bubbles allows the effects of thin film hydrodynamic drainage to be investigated. Previous studies\textsuperscript{56,119} of dynamic collisions between bubbles and bubble/flat plates have shown that with increased approach velocities the flow of fluid in the thin film between interacting surfaces can be explained by Reynolds lubrication theory coupled to the deformation of the interface. This has led to modification and expansion of the Chan-Dagastine-White model to allow quantitative analysis of bubble collisions at higher velocities. It has been shown that at increased collision velocities, bubbles that previously would experience coalescence at equilibrium speeds can become stable due to long ranged repulsive hydrodynamic drainage forces. By investigating bubble collisions in the presence of NaPSS at varying velocities we are able to probe the effect that thin film hydrodynamic drainage has on the observation of depletion forces in this system.
Figure 5.4. Direct force measurements between two air bubbles in aqueous solutions of NaPSS with a molar mass of 70,000 g/mol and a concentration of 25,000 ppm were measured. The bubble collision velocity was varied and measured at 1 µm /s (red), 2 µm /s (green), 5 µm /s (purple) and 10 µm /s (blue). The bubble radii in these measurements were 71 and 75 µm with an R₀ value of 73 µm. Inset. Zoom in on the force instability area of the force curves.

The results shown in Figure 5.4 highlight the effects of depletion forces and hydrodynamic drainage within this system. These measurements were conducted with a molar mass of 70,000 g/mol at a concentration of 25,000 ppm. These data show that as the velocity of the collision increases the magnitude of the forces experienced by the bubbles also increases, which is similar to the measurement shown of 10,000 ppm PVP in Chapter 4. This is due to the hydrodynamic drainage forces that occur during the film thinning/thickening process and can be seen in both the approach and retract phases of the curves. As discussed previously this is due to the speed of the collision being greater than the time scale of the flow of the fluid either into or out of the thin film between the interacting bubbles.

Also as the velocity of the bubble collision increases the apparent magnitude of the attractive depletion force in the approach curve decreases. Provided the fluid flow does not perturb the molecular orientation of the NaPSS (molecular structural changes are expected to occur on a much shorter time scale), the magnitude of the depletion force
does not decrease but its fractional contribution to the total force decreases relative to an increase in the hydrodynamic drainage force component. The increase in velocity means the amount of fluid able to be expelled from the film between surfaces decreases and that in turn increases the minimum film thickness. These effects contribute to the result that the depletion force component of the total interaction force decreases with larger velocities. In essence, the depletion interaction becomes overwhelmed by the larger hydrodynamic drainage effects at higher velocities in the system.

Previous AFM measurements of depletion and structural forces with aqueous solutions of NaPSS have all examined solutions of monodisperse NaPSS between rigid surfaces at velocities of 800 nm/s or lower \(^\text{47,192}\). It was reported that measurements conducted at higher velocities are no longer able to measure these forces and this is due to the influence of hydrodynamics \(^\text{192}\). It is worth noting that structural forces have been clearly observed at higher approach speeds and rigid surfaces using nanoparticles as depletants \(^\text{42}\), but these observations have not been made with polyelectrolyte systems where a much larger fraction of the depletant excluded volume is solvent compared to nanoparticles. The data from this study reveal that depletion forces are observable between colliding bubbles at velocities up to about 10 \(\mu\text{m/s}\). To further highlight the changes in the measured forces due to concentration and subsequently polyelectrolyte number density a measurement at a concentration 5000 ppm is shown in Figure 5.5.
Figure 5.5. Direct force measurements between two air bubbles in aqueous solutions of NaPSS with a molar mass of 70,000 g/mol and a concentration of 5000 ppm were measured. The bubble collision velocity was varied and measured at 1 µm/s (red), 2 µm/s (green) and 5 µm/s (purple). The bubble radii in these measurements were 40 and 54 µm with an R₀ value of 46 µm.

The data presented in Figure 5.5 depict measurements between air bubbles in a NaPSS solution with a concentration of 5000 ppm and a molar mass of 70,000 g/mol. The same trends regarding increasing velocity occur with respect to hydrodynamic drainage and depletion forces when compared to the concentration of 25,000 ppm. At the lower concentration of 5000 ppm any evidence of the attractive depletion force no longer exists at a bubble collision speed of 5 µm/s. This is similar to the measurements conducted at a concentration of 25,000 ppm where the depletion interaction is overcome by the hydrodynamic drainage effects within the system at higher velocities.

The difference in the velocity where the depletion interaction is no longer measured between the 5000 ppm and 25,000 ppm concentrations is due to the change in number density of polyelectrolyte molecules and the decrease in the osmotic pressure. As the number density decreases fewer molecules and counter ions are present to structure and contribute to the depletion interaction within the solution. A decrease in osmotic pressure also reduces the magnitude of the attractive depletion force and the fluid hydrodynamics now overwhelms the depletion interaction at a lower velocity.

These observations link to the effects shown with the concentration variation at the equilibrium velocities where the magnitude of the depletion interaction increased with larger concentrations or a similar number density of NaPSS. Unlike the previous rigid interface study on nanoparticles, a large fraction of the excluded volume of the polyelectrolyte is solvent, thus more detailed modelling of the dynamic behaviour would have to account for fluid flow around the polymer chains. This is a much more complicated analysis than the previous Reynolds lubrication modelling applied to AFM dynamic data provided. In the next section, we show changes in number density can also be achieved by varying the molar mass.

5.2.3 Varying Molar Mass

Effects on interaction forces associated with variation in the molar mass are not as straightforward as those that stem from changes in concentration and velocity.
Changing the molar mass for a set polyelectrolyte concentration varies the number density of polymer coils in solution. As discussed previously the magnitude of the depletion force is affected by the number density of the polyelectrolyte and therefore a direct comparison of molar masses at set concentrations is not possible. The number density of each solution and the overlap concentration for each molar mass has been calculated and is shown in Figure 5.6.

![Figure 5.6.](image)

**Figure 5.6.** The number density of the aqueous NaPSS solutions varying with regards to concentration with molar masses of 70,000 g/mol (red circles), 200,000 g/mol (green squares) and 500,000 g/mol (purple triangles). The overlap concentration based on the $M_W$ of the supplier specified molar masses are shown as 70,000 (red line), 200,000 (green dashed line) and 500,000 (purple dotted line).
Figure 5.7. Direct force measurements between two air bubbles in aqueous solutions of NaPSS with a concentration of 1000 ppm and a velocity of 100 nm/s were measured. The molar mass was varied (bottom to top) to 70,000 g/mol (red), 200,000 g/mol (green) and 500,000 g/mol (purple). The data has been offset with respect to the normalised force axis for clarity. The approach curve is shown as filled points and the retract curve as the open points. The bubble radii in these measurements varied between 46 and 72 µm and were normalised by $R_0$. The $R_0$ values for each curve were 63 (70,000 g/mol), 49 (200,000 g/mol) and 51 (500,000 g/mol) µm.

Figure 5.7 shows the force curves for 1000 ppm NaPSS concentration with varying molar masses. The depletion well in the above curves does not exhibit the jump-in behaviour that was measured at higher concentrations due to the mechanical instability of the cantilever. It is likely that the lack of a jump-in is due to the lower osmotic pressure at these concentrations and this does not impart a force gradient that is large enough to cause mechanical instability of the cantilever. As discussed earlier the variation in the gradient of the curves at low separations is due to the differences in the surface tensions and bubble sizes used in these measurements.

At a concentration of 1000 ppm the molar mass of 70,000 g/mol is in the dilute regime with the 200,000 and 500,000 g/mol molar mass samples in the semi-dilute regime. The size of the molecules in solution increase with larger molar masses, but this causes the overlap concentration of the system, and therefore the characteristic length, to
decrease. Rigid interface measurements conducted with NaPSS at larger concentrations and molar masses exhibit a depletion interaction, but do not show any further structuring. These force curves are shown in Appendix 10.4.

The changes that occur with respect to the characteristic length with variation in molar mass are not obvious in these curves. The difference in the characteristic length between the 70,000 g/mol and the 200,000 g/mol at a concentration of 1000 ppm is expected to be approximately 19 nm$^{45,46}$, thus one would expect a difference in the force behaviour. The 200,000 and 500,000 g/mol molar masses are both above $c^*$ and have roughly the same monomer concentration and therefore no large differences are expected in the force behaviour, and this is consistent with Figure 5.7. Bubble deformation also plays a role in masking the change in characteristic length in the measurements, but the main cause rests with the monomer concentration with the molar masses used.

![Figure 5.8](image.png)

**Figure 5.8.** Direct force measurements between two air bubbles in aqueous solutions of NaPSS with a concentration of 10,000 ppm and a velocity of 500 nm/s were measured. The molar mass was varied (left to right) to 70,000 g/mol (red), 200,000 g/mol (green) and 500,000 g/mol (purple). The data has been offset for clarity. The approach curve is shown as filled points and the retract curve as the open points. The bubble radii in these measurements varied between 39 and 58 µm and were normalised by $R_0$. The $R_0$ values for each curve were 55 (70,000 g/mol), 44 (200,000 g/mol) and 57 (500,000 g/mol) µm.

In Figure 5.8 the changes in the interaction between bubbles with various molar masses was examined in further detail at a concentration of 10,000 ppm and with a collision
velocity of 500 nm/s. Due to the increase in concentration from the 1000 ppm data the osmotic pressure has increased and that results in the attractive jump-in to be present in these data. Also, with the concentration increase all these measurements were conducted in the semi-dilute range where the depletion interaction length scale is not expected to be sensitive to molar mass but instead on the number of cross links in the network. Again, the magnitude of the depletion interaction would be expected to scale with monomer concentration, which is constant for these three curves. Thus, as expected, the force behaviour is largely similar for the approach curves, but there is a notable variation in the attractive jump-out that occurs for the 70,000 to 200,000 g/mol molar masses. This may be reflective of changes in the partitioning of the lower molar mass NaPSS in the thin film in the interaction volume thereby mediating the osmotic pressure of the depletion force for different molar masses where polydispersity and fraction of lower molar mass material varies. Further force curves of the 10,000 ppm NaPSS concentration for each molar mass are included in the Appendix 10.5.

5.2.4 Variation in the Size Distribution of Molecules

To investigate further the effects of molar mass dispersity on the interactions between bubbles a sample of the NaPSS with a molar mass of 70,000 g/mol was dialysed to obtain a less polydisperse polymer. This molar mass was selected as it has the highest $c^*$ based on the $M_W$ molar mass as specified by the manufacturer. The samples were dialysed with a molar mass cut off (MMCO) of 1 kDa and 14 kDa following the procedure previously described. These samples were fractionated during the dialysis and this in turn reduced the dispersity of the polyelectrolyte size distribution. For the 1 kDa and the 14 kDa MMCO 42% and 57% of the starting material was removed respectively from each sample. This indicates that a large fraction of the sample is low molar mass material and contributes greatly to the molar mass dispersity of the sample. The concentration of NaPSS for these measurements was 1000 ppm and was selected as this was below the overlap concentration for this molar mass.
Figure 5.9. a) Direct force measurements between two air bubbles in aqueous solutions of NaPSS with a concentration of 1000 ppm, collision velocities between 200 and 500 nm/s and molar mass 70,000 g/mol. The data has been offset for clarity. The approach curve is shown as filled points and the retract curve as the open points. The bubble radii for these measurements are in the range of 51 and 65 µm. The data (left to right) are for the non-dialysed sample (red), dialysed with a 1 kDa MMCO (purple) and dialysed with a 14 kDa MMCO (green). Right. Schematic of NaPSS molecules ordering in solution between two bubble interfaces in the dilute regime. b) Sample prior to dialysis. c) After sample has undergone dialysis and has a decreased molar mass dispersity.

The force curves presented in Figure 5.9 show the effect of sample dialysis and changing the molar mass dispersity (Ð) of the samples. These measurements show that as the molar mass dispersity of the samples decreases the magnitude of the attractive interaction increases. Along with an increase in force magnitude another oscillation at larger separations becomes clearly visible. These observations show that polydispersity of the PVP samples in Chapter 4, could also influence the inability to measure depletion or structural forces in that system. Similar trends with regards to polyelectrolyte concentration and collision velocity hold for the dialysed samples. Rigid interface direct force measurements were also conducted with these samples and show oscillatory behaviour that is not present in the polydisperse sample. These measurements are included in Appendix 10.4. As the molar mass dispersity of a solution decreases the ability of the molecules to pack in an ordered fashion increases and this is shown as a schematic diagram in Figure 5.9. Due to this ordering or increase in the packing density, the ordering of coil layers become more distinct and when the bubbles collide, this increase in solution structuring is able to be measured.
It should be noted that the dialysis of the NaPSS would result in the removal of excess counter ions from solution. A previous study has shown that an increase in background electrolyte concentration screens the interaction between the NaPSS molecules and decreases the magnitude of the structural and depletion force components and at sufficiently large electrolyte concentrations these forces are no longer measured\textsuperscript{45}. It was also shown in that study that the polyelectrolyte screening length that affects the period of the oscillations was weakly dependent on electrolyte concentration. The period of the oscillations between the two dialysed samples varies and this is more noticeable with the measurements conducted with rigid interfaces (shown in Appendix 10.4), as the oscillation period is masked by deformation with the bubble interface. The change in oscillation period shows that the size distribution of the molecules involved in the interaction has varied. This indicates that the change in counter ion concentration was not the reason for the increased solution structure measured after dialysis of the samples.

The appearance of force oscillations with the use of the dialysed sample shows that depletion and structural interactions are able to be controlled via the size distribution of the depletant in solution. Further analysis of these data could describe the effect of deformation on minima spacing, however we recognise that completing this analysis with a monodisperse sample is a better approach and to this end will be dealt with in a subsequent chapter. These measurements provide useful insight into the role that molar mass dispersity has on the interaction forces.
5.3 Summary and Conclusions

Depletion forces have been shown to dominate interactions between colliding air bubbles in aqueous solutions of polydisperse NaPSS. By probing the effects of polyelectrolyte concentration, collision velocity and molar mass, we have demonstrated how such interactions can be controlled. The attractive force well due to the depletion force increases in magnitude with an increase in the number density of polyelectrolyte molecules and hence counter ions in solution. This has been further supported by analytical modelling presented in this study, which shows that the effects due to concentration variations can be accounted for using a simple scaling theory. At pseudo-equilibrium bubble approach velocities of less than 500 nm/s the depletion force could be measured, but this force was overwhelmed by hydrodynamic fluid flow in the film between the bubbles at higher interaction velocities. A decrease in the dispersity of the molar mass distribution leads to an increase in solution structure that was measured. The increase in structure is due to the polymer coils forming discrete layers in the dilute concentration regime and shows that the structure of the solution can be changed by manipulating the degree of molar mass dispersity of the sample.

This study has extended our understanding of the forces between colloids in aqueous solutions of polyelectrolytes and demonstrated that molar mass dispersity plays an important role in the measured interactions. As polydisperse systems are more commonly used in industrial processing settings knowledge of the effects and an ability to influence these interactions in systems that contain complex fluids with polyelectrolytes is important. Significantly, by controlling dispersity of the molar mass, the interactions between deformable bubbles can be tailored to facilitate system design for control of rheology and processing behaviour.
Chapter 6 - Direct AFM force measurements between air bubbles in aqueous monodisperse sodium poly(styrene sulfonate) solutions

The material in this chapter is drawn from the following publication:

6.1 Introduction

Structural and depletion forces have been the focus of many studies due to their relevance to a host of complex fluid systems, from the interior of cells to dairy processing. Structural forces arise in a fluid when nanoscale material additives such as nanoparticles, micelles or polymers are trapped between interacting large colloids such as particles, bubbles, droplets or surfaces. Closely-related depletion forces are the result of an osmotic pressure difference between the thin film and the bulk solution created when the separation between the larger colloids decreases sufficiently such as to exclude the nanomaterial.

As stated in the previous chapter, some of the earliest studies of structural forces focused on the ordering of solvent molecules using the surface forces apparatus (SFA)\(^ {143}\), first with a liquid crystal and then an organic solvent\(^ {44}\). Subsequent to this, structural forces have been studied for a number of colloidal additives using a range of methods including the SFA, atomic force microscope (AFM)\(^ {45-47,191,193,194,204,205}\), total internal reflection microscopy (TIRM)\(^ {176,177,180,192}\) and the thin film balance\(^ {182-184,242,433}\). The advancement of methods for both the measurement and the subsequent analysis of the interaction forces between microbubbles and microdroplets using AFM have provided a ‘front seat view’ of the behaviour for a range of solution additives and structuring colloids of relevance to the physical properties of foams and emulsions\(^ {54,115-117,119,133,136,210,390}\). This has included observations of structural forces between emulsion droplets in the presence of spherical micelles, micro-emulsions, nanoparticles\(^ {48,211}\), polyelectrolytes and naturally derived food polymers\(^ {25}\) and even rod shaped micelles\(^ {213}\). Due to the deformation of the interface, AFM measurements using microbubbles and microdroplets provide an improved sensitivity to structural forces experienced during measurements when compared to rigid interfaces\(^ {210}\). The deformation and structural forces also couple in such a way that a hysteresis exists between the approach and retract phase which suggests secondary flocculation pathways may be present for deformable systems that are not accessible with rigid interfaces\(^ {211}\).

Variation in the size and structure of the solution additives leads to changes in the length scale and magnitude of the structural force oscillations as shown for additives such as nanoparticles\(^ {12,202,212}\), surfactant micelles\(^ {40,204}\) and synthetically or naturally...
derived polyelectrolytes\textsuperscript{25}. These forces can also be influenced by the shape of the colloid in the system, with interesting studies using non-spherical colloids showing that there may be more than one important length scale in the system\textsuperscript{232,434}.

In Chapter 5, the interactions between air bubbles in the presence of a polydisperse sample of sodium poly(styrene sulfonate) (NaPSS) were discussed\textsuperscript{435}. In that chapter, purely attractive depletion forces, rather than oscillatory structural forces were measured between the colliding bubbles using AFM as a function of polyelectrolyte concentration, collision velocity between bubbles and the molar mass of the polyelectrolyte. The absence of any type of oscillatory forces was attributed to the polydispersity of the polyelectrolyte. This was further supported by the observations that dialysis of the NaPSS sample reduced the polydispersity with a concomitant appearance of oscillatory forces. Due to experimental challenges such as batch variation, the ability to explore these effects with dialysed samples remains problematic. The use of a more refined system, such as a monodisperse molar mass distribution, allows a more fundamental point of view to be taken when compared to that of the industry relevant, polydisperse molar mass distribution. The majority of previous rigid interface measurements\textsuperscript{45-47,191} and the one measurement between oil droplets\textsuperscript{25} have focused on monodisperse samples, and thus to fully understand how these data can be interpreted and extended to deformable colloids this chapter has examined the interactions between air bubbles in the presence of monodisperse NaPSS samples. The role of molar mass dispersity has also been studied by creating well controlled polydisperse or bimodal distributions through mixing monodisperse samples of different molar masses.
6.2 Results and Discussion

Direct force measurements conducted between two air bubbles in aqueous solutions of monodisperse NaPSS as a function of the polyelectrolyte concentration, collision velocity of the bubbles and molar mass of the NaPSS are presented here. In addition, we have also measured the effect of creating bidisperse NaPSS samples to model polydisperse systems in a controlled fashion.

6.2.1 The Effects of Varying Polyelectrolyte Concentration

![Figure 6.1](image)

**Figure 6.1.** Direct force measurements in aqueous solutions of NaPSS (molar mass of 77,000 g/mol) between two air bubbles and collision velocities between 200 and 500 nm/s. The concentrations of the solutions vary from left to right and are 300, 500, 1000 and 2500 ppm. The bubble radii used in these measurements varied between 38 and 78 µm. The approach phase has been drawn in blue and the retract phase in pink. The data has been offset on the \( \Delta X \) axis for clarity.

Direct force measurements were conducted between air bubbles in the presence of aqueous NaPSS solutions with varying polyelectrolyte concentration are shown in Figure 6.1. The NaPSS used in these measurements had a molar mass of 77,000 g/mol and the collision velocities varied between 250 and 500 nm/s, where hydrodynamic film drainage effects are not expected to influence these measurements\(^{56}\). The overlap concentration, \( c^* \), between the dilute and semi-dilute concentration regimes of the
NaPSS solutions was calculated to be approximately 2500 ppm by mass (all ppm concentrations within this work are determined by mass). Therefore the concentrations of 300, 500 and 1000 ppm are below $c^*$. The concentration of 2500 ppm was selected in order to examine if any different interactions occur near the change in concentration regimes. In the dilute concentration regime, below the overlap concentration, the polyelectrolytes behave as a space-filling lattice such that the radius of gyration of the individual chains describes to the characteristic length of the structural force. As the concentration of the polyelectrolyte increases, the polymer chains can no longer occupy their own space in solution and begin to form an overlapping network with the surrounding NaPSS molecules.

For the measurements conducted in the dilute concentration regime there were several clear oscillations that were indicative of structural forces. These oscillations, as indicated earlier, come about due to an osmotic pressure mismatch with the bulk when a layer of the ordered molecules are expelled from the thin film between the colliding bubbles into the bulk solution. Upon expulsion of a layer of molecules, the remaining molecules in the thin film reorder and then a subsequent layer of molecules are expelled. This generates another osmotic pressure mismatch and another oscillation in the force profile. As the solution concentration increases, it was also seen that the characteristic length of the oscillation, as expected, decreased. This observation can be described by polyelectrolyte scaling theory and is largely due to the increase in ionic strength, which screens the charge repulsion on the polyelectrolyte chains as well as inter-chain repulsion.

The extent of hysteresis between the approach and retract phases of the force curves increases as the concentration increases and is not attributed to hydrodynamic drainage effects. The hysteresis shown in Figure 6.1 is attributed to the bubbles deforming in the oscillatory structural force field coupled with mechanical instability of the cantilever. The physical rationale for this ‘force well’ has been described in detail previously. As the polymer concentration increases, the magnitude of the force that accompanies the expulsion of a layer from the film between the bubbles also increases. It is interesting to note that at concentrations in the dilute regime, oscillations in the direct force measurement are also exhibited in the retract phase.
As the concentration increases, the clear periodic nature to the oscillatory force behaviour that is observed at 300 ppm becomes more irregular, in stark contrast to extensive rigid interface measurements in the literature\textsuperscript{45,46,191} and those shown in Appendix 10.6 of this thesis. This effect comes about due to deformation of the bubble interfaces, as demonstrated later with modelling of the AFM force curves and in previous AFM studies between droplets\textsuperscript{25,48,211,213} and bubbles\textsuperscript{435}. At the approximate polyelectrolyte overlap concentration of 2500 ppm, there are several distinct changes in the force profiles. There is a notably larger force barrier between the bubbles than at other concentrations during the approach phase. The jump-in denotes the expulsion of another layer of polyelectrolyte closer to the bubble interface, which is most likely at a smaller separation than achieved in the force curves of lower concentrations and this will be discussed in further detail later. The oscillations that were also present in the retract phase of the force curves in the dilute concentration regime are now a single pull-off. This is indicative of a more ordered structure in solution leading to a larger attractive force causing the jump-out from the mechanical cantilever instability as the polyelectrolyte network begins to form at $c^\ast$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Direct force measurements in aqueous solutions of NaPSS (molar mass of 77,000 g/mol) between two air bubbles at collision velocities between 200 and 500 nm/s. The concentrations of the solutions vary from left to right and are 2500 (repeated from Figure 6.1), 5000, and 10,000 ppm. The bubble radii used in these measurements vary between 43 and 80 $\mu$m. The approach phase has been drawn in blue and the}
\end{figure}
retract phase in pink. The data has been offset on the $\Delta X$ axis for clarity. **Inset.** The attractive maximum values with varying NaPSS concentration from the retract phase of the direct force measurements.

Direct force measurements conducted for concentrations above the polyelectrolyte overlap concentration are shown in Figure 6.2. The data for the 2500 ppm concentration have been repeated from Figure 6.1 to facilitate comparison between the data at the overlap concentration and in the semi-dilute concentration regime. The molar mass of these aqueous NaPSS solutions is the same as the dilute concentration regime measurements at 77,000 g/mol. The velocities between 200 and 500 nm/s were selected to avoid the effects from hydrodynamic drainage on the measurements. As the concentration of the polyelectrolytes in solution continues to increase above the overlap concentration, the solution structure enters the semi-dilute concentration regime. In this regime the molecules are no longer able to occupy their own discrete space in solution and start to form a network. As the solution concentration increases further the number of network points or crosslinks increases and the characteristic length, in this case the distance between crosslinks, decreases.

As the concentration of NaPSS is increased from 5000 to 10,000 ppm the number of measurable oscillations begins to decrease. At a concentration of 10,000 ppm the large jump-in that is present in the approach phase is no longer measured. This is most likely due to an increase in the number of crosslinks that strengthens the polyelectrolyte network. Due to the increased strength of the polyelectrolyte mesh and the deformation of their interfaces, the bubbles reach a point where the pressure in the film from the structural force between them is commensurate with the Laplace pressure of the bubbles. Once the Laplace pressures are equal the separation no longer decreases axially and with increasing force the deformation grows radial which causes the two interfaces to begin to flatten.

The behaviour of the attractive maximum force of the retract phase increases until the highest value of approximately 0.03 mN/m is reached with a concentration of 2500 ppm ($c^*$), with a further increase in NaPSS concentration, the values begin to decrease. We attribute this maximum value in the attractive force to the differences in the spatial orientation of the polyelectrolyte coils between the dilute and semi-dilute concentration regimes. In the dilute concentration regime, the structural forces (based on
measurements with rigid interfaces\(^{45-47,176}\) increase in number of observable oscillations and force amplitude with increasing concentration. The force measurements between bubbles sample these increasing forces with concentration, sampling an increasing number of layers of NaPSS molecules, leading to more observable oscillations or jump-in events. The increase in the maximum attractive force during the retract phase of the interaction between the bubbles arises from sampling an increasingly larger amplitude in the oscillations in the structural forces with change in polyelectrolyte concentration. In the semi-dilute concentration regime, the magnitude of the structural forces continue to increase, but as mentioned above, the polyelectrolyte mesh increases in strength such that the bubbles flatten as opposed to expelling ‘layers’ of NaPSS. This can be described more accurately in the region where the separation between the bubbles only samples the outer oscillations in the structural force disjoining pressures. Thus, the separation between the bubbles now corresponds to oscillations in the structural force at larger separations, which have a lower magnitude. As the concentration increases, this leads to a decrease in the maximum attractive force sampled by the bubbles in the semi-dilute concentration regime. To access the inner layers of the structural force an increase in the Laplace pressure would be required. This could occur by the use of bubbles with smaller diameters and experimentally this is difficult to achieve as the bubbles need to be of sufficient size to attach to the gold disc of the cantilever. A more quantitative explanation of this description is presented in the discussion of Figure 6.3 below.
6.2.2 The Effects of Changing the Force Applied to the Bubbles

![Image of force measurements and bubble interactions]

**Figure 6.3.** Left. Direct force measurements between two air bubbles in aqueous solutions of NaPSS (molar mass of 77,000 g/mol) with a concentration of 2500 ppm. The applied force was varied with the high force (green) and low force (red) having a bubble pair with radii of 43 and 78 µm with a normalised radius ($R_0$) of 56 µm and collision velocities between 150 and 250 nm/s. The intermediate force (purple) has a bubble pair with radii of 49 and 68 µm with a normalised radius ($R_0$) of 57 µm and a collision velocity of 500 nm/s. The approach curve was drawn as filled points and the retract curve as the open points. **Inset.** The modelling result depicting the interface of the bubble and the film thickness at different stages of the collision where the dotted lines indicate the predicted jump-in lengths due to the NaPSS characteristic length and a) the low force film profile b) the intermediate force profile just prior to the retract phase and c) the high force film profile. **Right.** A stylised diagram of the NaPSS molecules in the thin film at the various points as indicated in the data.

In Figure 6.3 direct force measurements between air bubbles in an aqueous NaPSS solution with a concentration of 2500 ppm are shown. In these measurements, the applied force was varied at approximately the polymer overlap concentration ($c^*$) and the measurements were conducted at collision velocities where the effect of fluid hydrodynamics would have been negligible. The applied forces have been named low (red curve), intermediate (purple curve) and high (green curve) within this section. It can be seen that as the applied force increases (red to green curve), another force oscillation can be measured and this corresponds to the bubble traversing another mesh point in the network (marked on Figure 6.3 as points a through c). The measurement
conducted with the highest force, the green curve, pushes through this mesh point and the bubbles once again deform in the solution. The lowest force applied in these measurements, the red curve, does not reach, point \( b \), and is retracted below the force value, at point \( a \), and this attractive jump-in is not measured. With the intermediate force measurement, the purple curve, the highest force experienced by the bubbles was set to be equal to the force required to expel the last layer of polyelectrolyte molecules in the high force measurement, the force at point \( b \). In the purple curve, at this point, \( b \), the attractive jump-in then occurs once the bubbles are pulled away from each other by the AFM. Note, all data in the other figures was acquired at forces applied sufficiently high to ensure that no further structural force oscillations were able to be measured.

There is also a noticeable change in the magnitude of the pull-off force experienced during the retract phase when the extra jump-in is measured for the green and purple curves. This clearly shows that structural forces play a role in both the approach and separation of deformable colloids, and shows that the hysteresis in this case is clearly due to solution structure, not hydrodynamic flow effects. The magnitude of the attractive force maximum is dependent on how many polyelectrolyte layers or oscillations in the structural force are sampled at the closest approach of the two bubbles. Note that the small difference in the depth of the pull-off force between the purple and green force curves is due to different bubble pairs being used for these measurements. The overall magnitude of the force curve is expected to change proportionally with bubble radius as the force scales with interaction area between the bubbles that is a function of bubble radius\(^{133,435}\).

From the quantitative modelling used in this work, the film thickness profiles between the bubbles can be determined and this is shown as an inset in Figure 6.3. The thin film thickness varies depending on the force applied to the bubbles during the direct force measurements. The dotted lines indicate where the bubbles jump through a layer of NaPSS in the approach phase of the collision. In the low force measurement (a) the bubbles transition through a layer of polyelectrolyte molecules and then due to the settings in the measurement the AFM pulls apart the bubbles prior to reaching the next layer of polyelectrolyte molecules. In the intermediate force measurement (b) the bubbles deform slightly on the next layer of polyelectrolyte molecules in solution. If the bubbles push through that layer, as in the high force measurement (c), then they are
able to deform on the thin film remaining between the bubbles. As explained earlier, when the pressure in the film approaches the Laplace pressure of the bubbles, the bubbles cease to move closer together, but instead deform radially causing the interaction force to increase as a direct consequence of the growth in their interaction area.

6.2.3 Deformable Interface Modelling

The modelling of the thin film profiles was based on predicted AFM force curves, shown in Figure 6.4 for the complete concentration range studied and were constructed with the methods previously described\textsuperscript{48,211,213} and shown in the Deformable Interface Force Curve Analysis section in Chapter 3. The modelling undertaken consists of using an empirical structural force model to determine the disjoining pressure between two flat interfaces based on the measurement of force curves taken between two rigid interfaces where the NaPSS is non-absorbing (\textit{i.e.}, using borosilicate-glass interfaces) for the same conditions as the force curves acquired between bubbles. This empirical model is then used in conjunction with the Chan-Dagastine-White (CDW) model to describe the force curves between colliding bubbles and accounts for the interplay between interfacial deformation and the oscillation of the structural forces. The parameters used for the modelling are shown in Appendix 10.7. As mentioned in the Experimental Methods Chapter, the surface tension (shown in Appendix 10.8) was measured independently as well. Consistent with the work in Chapter 5 and literature\textsuperscript{425-427,435}, the NaPSS is slightly surface active and is expected to adsorb at the interface in parallel configuration\textsuperscript{428,429}, increasing the charge on the bubbles. As the separations sampled by the bubbles in the AFM force measurement do not expel the final layer of NaPSS in the film, it does not sample these short-range effects and therefore they are not captured in the disjoining pressure construction using the empirical structural force model.
Figure 6.4. The results from the modelling overlaid on the direct force measurements conducted between two air bubbles in the presence of aqueous NaPSS solutions with varying concentration. The modelling results are shown as red lines for the approach phase and black dashed lines for the retract phase. The concentrations of solutions (left to right) are 300 (a), 500 (b), 1000 (c), 2500 (c*) (d), 5000 (e) and 10,000 (f) ppm. The approach phase has been drawn in blue and the retract phase in pink. The data has been offset on the $\Delta X$ axis for clarity.

By direct comparison of model predictions and experimental data (Figure 6.4) it is clear that the theory presented accurately describes interactions between deformable interfaces. The hysteresis between the two phases of the force curves have been shown, via the model, to be due to the bubble interface deformation. The predicted force oscillations and jump-in of the deformable interface force curves have been well described. The modelling predicts that for concentrations below $c^*$ the attractive maximum in the retract phase is larger than the one measured experimentally. The difference in the predicted pull-out forces can be attributed to variation in the mechanical instability in the cantilever during the jump-out process or a larger contribution from the underlying electrical double layer force not captured in the empirical structural force model, which is longer range at lower concentrations. For example, the calculated Debye length of these solutions due to the dissociated sodium ions from the NaPSS decreases from approximately 19 nm at a concentration of 300 ppm to 3 nm at a concentration of 10,000 ppm. It is also interesting to note that the modelling predicts observations that were made experimentally, where at concentrations below $c^*$ oscillations occur in both the approach and retract phases, and at concentrations above $c^*$ oscillations only occur in the approach phase. The
modelling also predicts the strength of the crosslinked network leads to a decrease in the minima as the disjoining pressure resulting from the strength the polyelectrolyte mesh strength exceeds the Laplace pressure of the bubbles. This causes the bubbles to deform and so not expel more layers, in contrast to the opposite trend observed between rigid interfaces.

In the previous study conducted by Gromer and co-workers they compared the interactions between two oil droplets in aqueous solutions of either NaPSS or sugar beet pectin. They selected a molar mass of 32,900 g/mol for the NaPSS, as this is a similar size of the sugar beet pectin molecules. The direct force measurements, conducted in the dilute concentration regime, with either the NaPSS or sugar beet pectin had at least one and in some cases two observable force oscillations. There was no measureable hysteresis between the approach and retract phases of the droplets in these measurements. When the concentration was increased, though still remaining in the dilute regime, the NaPSS measurements have an oscillation and hysteresis similar to what was observed in our system as the concentration and structure increased. It is also interesting to note that when the work conducted by Gromer and co-workers increased the concentration into the semi-dilute regime the oscillations in the retract phase were no longer measureable and this was observed in this current study. They provide a qualitative description of the CDW model using an EDL and depletion model but do not qualitatively compare their data to the model or account for structural forces. Their study provides the first observations with NaPSS in any deformable droplet or bubble system and is consistent with the more detailed and quantitative analysis provided here for bubbles.

6.2.4 Polyelectrolyte Scaling Theory

A scaling relationship of the chain size as a function of concentration was determined for this system and is shown in Figure 6.5. This was constructed by calculating the change between the attractive force maxima with measurements conducted with silica rigid interfaces (measurements shown in Appendix 10.6). This has been demonstrated previously and for these measurements in the dilute concentration regime the distance scales as $450c^{-0.34}$ and the semi-dilute concentration regime scales as $1648c^{-0.53}$. These values are in accordance with the expected values from polyelectrolyte scaling theory.
Figure 6.5. The change in the attractive force maxima positions of the closest polyelectrolyte layers between two interacting silica surfaces. The measurements in the dilute concentration regime are shown as red circles and the semi-dilute concentration regime are shown as blue squares. The scaling relationship (shown as a dotted line) of the aqueous NaPSS solutions in this work are as $450c^{-0.34}$ for the dilute regime and $1648c^{-0.53}$ for the semi-dilute regime.

Attempts to create a scaling relationship with the use of the bubble measurements was made, however due to the irregular spacing between the force oscillations this was not possible. The irregular spacing was caused by the deformation of the bubble interfaces which obscures the scaling relationship, though the interactions were still governed by the characteristic length of the polyelectrolyte in solution and follow scaling theory behaviour. A further attempt at determining a scaling relationship was attempted with the use of the $\lambda$ (characteristic length of the oscillation period) values determined during the modelling from the rigid interface measurements, but these values do not meet the expected relationship for chain size from polyelectrolyte theory. This is due to the presence of the $\varepsilon$ value, which relates to the decay length of the oscillations, obscuring the ability to accurately determine the characteristic length of the polyelectrolyte solution via this method. A polyelectrolyte scaling relationship could not be established with the characteristic length of oscillation determined via the empirical model. This shows that the use of this model is limited due to the effect of
interface deformation when comparing rigid and deformable interface measurement. Further detailed description of the oscillations and linking the observations back to theory would be difficult.

6.2.5 The Effects of Varying the Bubble Interaction Velocity

Variation of the bubble collision velocity allows observation of the effects of hydrodynamic drainage and fluid flow on the observed structural forces to be examined. Comparison of AFM measurements between colliding droplets or bubbles, in a range of different solution conditions, to modelling that accounts for both interfacial deformation and the presence of surface forces and hydrodynamic film drainage behaviour using Reynolds lubrication theory, has been completed previously\textsuperscript{55-57}. It was shown that hydrodynamic drainage forces can affect and stabilising interactions that would result in coalescence at equilibrium speeds between bubbles and a bubble and a flat plate\textsuperscript{54,56,119,391,416}. The stabilisation of the interacting bubbles is due to long-range repulsive hydrodynamic drainage forces.

\textbf{Figure 6.6.} Direct force measurements in aqueous solutions of NaPSS between two air bubbles with a polyelectrolyte concentration of 300 ppm and a molar mass of 77,000 g/mol. The bubble radii of the bubbles used in these measurements were 52 and 56 µm with a normalised radius (R₀) of 54 µm. The collision velocity was varied between 1 µm/s (green), 2 µm/s (purple), 5 µm/s (blue) and 10 µm/s (orange). The approach
curves are drawn as filled points and the retract curves as open points. **Inset.** Enlargement of the small separation region where the structural forces are of particular interest.

The measurements shown in Figure 6.6 demonstrate the effect of variation in the collision speed of air bubbles in an aqueous solution of 300 ppm NaPSS, which is in the dilute concentration regime. From these measurements it can be seen that as the velocity of the collision increases the effect of fluid flow (hydrodynamic drainage) becomes more pronounced and the amplitude of oscillations of the structural forces decrease. The structural forces between the bubbles are still present, but they become obscured by the additive effect of the hydrodynamic drainage and this is a similar observation that was made in the polydisperse NaPSS system shown in Chapter 5. The definition of the oscillations in the retract section of the curve also progressively disappears and this indicates that the structural forces can be overwhelmed by fluid flow in the system.

Previous studies, including experimental measurements and modelling, on the interaction between drops and bubbles in the presence of electrical double layer and van der Waals forces have shown that the pressure between the deformable interfaces arising from surface forces can be added to the pressure arising from hydrodynamic drainage between the deformable interfaces to give the total pressure in the thin film between the drop or bubble pair. This approach has not yet been quantitatively extended to bubbles or drops in the presence of structural forces. For rigid interfaces in the presence of nanoparticles, studies by Walz and co-workers\(^{42}\) have shown that the structural or depletion forces and the force that arises from hydrodynamic drainage are largely additive in nature. For the case of bubbles in the presence of NaPSS, this may not be the case, as the NaPSS molecules are associated with a large portion of solvent (in this case water) where hydrodynamic flow through the polyelectrolyte molecules and network during the direct force measurements may be possible. This can be supported by the observations that droplet collisions at velocities of 10 \(\mu\text{m/s}\) in the presence of \(\beta\)-lactoglobulin (a protein molecule) exhibited increased relaxation times when compared to SDS\(^{58}\). This result was attributed to a slower film drainage through the protein molecules compared to that a surfactant coated interface. To quantitatively model these data using the existing Reynold’s lubrication model established previously\(^{54}\) would require equilibrium surface forces descriptions for the structural
forces between bubbles with a higher degree of accuracy than the empirical models employed for the modelling presented in Figure 6.3 and Figure 6.4. Thus, we limit our discussion of Figure 6.6 and Figure 6.7 to qualitative comments. Variations in the concentration of the NaPSS aqueous solutions with different collision velocities were also measured to further explore these effects.

![Graph](image)

**Figure 6.7.** Direct force measurements in aqueous solutions of NaPSS between two air bubbles with a polyelectrolyte concentration of 2500 ppm and a molar mass of 77,000 g/mol. The bubble radii of the bubbles used in these measurements were 78 and 43 µm with a normalised radius ($R_0$) of 61 µm. The collision velocity was varied between 400 nm/s (red), 1 µm/s (green), 2 µm/s (purple) and 5 µm/s (blue). The approach curve is drawn as filled points and the retract curve as the open points. **Inset.** Enlargement of the small separation region where the structural forces are of particular interest.

The measurements shown in Figure 6.7 were completed in an aqueous NaPSS solution of concentration 2500 ppm with varying collision velocities and the measurements conducted with a high force trigger. As the collision speed increases, the oscillations at large separations are the first features to no longer be measureable and it can be seen that by a velocity of 2 µm/s there are minimal changes in the force profile at these higher forces, and smaller separations can be measured due to structuring of the polyelectrolyte molecules. Due to the additive effect of the structural force and
hydrodynamic drainage, the force at which the jump-in or kink is observed to expel this layer of molecules, increases at larger velocities. This is similar to the measurements conducted at a concentration of 300 ppm, though the structural forces are overwhelmed by the drainage fluid flows at lower velocities in the 2500 ppm case. Similar observations were made by Gromer and co-workers where the structural force component was overwhelmed by hydrodynamic drainage\textsuperscript{25}. Further increases in concentration continue to show the same trends with respect to bubble collision velocity.

6.2.6 The Effects of Varying Molar Mass and Variation in the Size Distribution of Molecules
Motivated by our earlier study using a polydisperse molar mass NaPSS with an M\textsubscript{W} molar mass of 70,000 g/mol, we examined the behaviour of aqueous solutions containing a mixture of two monodisperse NaPSS samples on the interactions between bubbles. We used binary mixtures of 6800 g/mol and 77,000 g/mol molar mass materials at a 50:50 mixing ratio by weight. The total NaPSS concentrations of 1000 and 5000 ppm were used in this section. The calculated overlap concentration of the 6800 g/mol molar mass is approximately 27,500 ppm based on the M\textsubscript{W} molar mass compared to approximately 2500 ppm for the larger molar mass sample. Thus for the lower concentration of 1000 ppm, both molar masses are in the dilute concentration regime and for the 5000 ppm the larger molar mass is in the semi-dilute concentration regime.
Figure 6.8. Direct force measurements conducted between two air bubbles in the presence of a 1000 ppm NaPSS aqueous solution with collision velocities between 300 and 500 nm/s. The concentrations of the solution were kept constant and the polyelectrolyte molar mass was varied (left to right) 6800 g/mol, a 50/50 split of 6800 and 77,000 g/mol and then 77,000 g/mol. The radii of the bubbles used in these measurements varied between 43 and 77 µm. The approach phase has been drawn in blue and the retract phase in pink. The data has been offset on the ΔX axis for clarity.

As shown in Figure 6.8 for the total NaPSS concentration of 1000 ppm of the mixed sample the different molecules sizes reduce the ability of the system to form well-ordered layers. The data shown for the 77,000 g/mol system has been repeated from Figure 6.1 for ease of comparison. The measurement of the 6800 g/mol molar mass when compared to that of the 77,000 g/mol shows a decrease in the number and magnitude of the force oscillations. It is interesting to note that, whereas the number density for the molar mass of 6800 g/mol is approximately 10 times higher than for the molar mass of 77,000 g/mol, most of the structure in the mixed system is lost where only a small number of larger molecules are required to disrupt the structure of the polyelectrolyte.

In the binary measurement, the lack of well-defined order and molecule layering means that the number of force oscillations decreases as seen in this measurement. There is one clear attractive well, that has a similar appearance to the depletion interactions we have previously measured with polydisperse molar mass samples and this is indicative
of a decrease in the solution structure as the two disparate sized NaPSS molecules, both in the dilute concentration range, pack in the thin film, leading to the loss of force structure. In the previous chapter with polydisperse NaPSS samples, a similar lack of force oscillation below the overlap concentration due to poor ordering in the solution was measured⁴³⁵. These observations are also consistent with a binary mixture study of NaPSS using AFM force measurements between rigid interfaces reported by Biggs⁴⁷.

![Graph](image)

**Figure 6.9.** Direct force measurements conducted between two air bubbles in the presence of a 5000 ppm NaPSS aqueous solution with collision velocities between 100 and 300 nm/s. The concentrations of the solution were kept constant and the polyelectrolyte molar mass was varied (left to right) 6800 g/mol, a 50/50 split of 6800 and 77,000 g/mol and then 77,000 g/mol. The radii of the bubbles used in these measurements varied between 58 and 74 µm. The approach phase has been drawn in blue and the retract phase in pink. The data has been offset on the ΔX axis for clarity.

The data presented in Figure 6.9 is of the aqueous NaPSS solution with a concentration of 5000 ppm and varying molar masses. First, an increase in NaPSS concentration with a molar mass of 6800 g/mol shows a commensurate increase in the number of measureable force oscillations. This is due to an increase in the number density of polymer chains and associated counter ions in solution and this is also the reason that the amplitude of the force oscillations has increased.

On comparison of the measurements conducted in a NaPSS aqueous solution with one molar mass present and that of the binary mixture it can be seen that the changes are
similar in appearance to the 1000 ppm measurements. In Biggs’ study of the binary mixtures with the rigid interfaces, it was shown that when at least one of the molar masses was above \( c^* \), the characteristic length or spacing was dependent on the spacing between network points\(^{47}\). The deformation of the bubble interface causes difficulty in extracting the characteristic length to compare changes quantitatively between these systems. The only observation we make is that there is a loss of solution structure with the binary mixture when compared to the 77,000 g/mol molar mass. Furthermore, in our earlier polydisperse NaPSS work, modelling of the observed depletion forces when above the polyelectrolyte overlap concentration, based on the \( M_W \) molar mass, suggested that the lower molar mass NaPSS partitioned into the depletion zone that is set by the length scale of the larger molar mass material. As the current measurement is only a mixture of two molar masses and not a distribution of sizes, more solution structure persists in the mixture, but one would expect that the lower molar mass materials are more likely to partition into the excluded volume regions that correlate with the large molar mass NaPSS. The decrease in solution structuring is also demonstrated by both of the attractive maximum values in the retract phase of the binary measurements decreasing when compared to the pure molar mass measurements. This is also consistent with the rigid mixture work for NaPSS\(^{47}\).

6.2.7 Comparison of Binary and Dialysis Measurements

The measurements of both the binary measurements presented in this chapter and the dialysis measurements in Chapter 5 show the effect of varying the molar mass distribution of NaPSS on the force profiles and are highlighted below in Figure 6.10.
Figure 6.10. A sample of the measurements conducted within this study highlighting the effect of molar mass dispersity on the resultant force response between colliding air bubbles. All these measurements shown here are conducted at a NaPSS concentration of 1000 ppm and at collision velocities below 500 nm/s. All of the above results have previous been shown throughout this chapter and Chapter 5. The molar mass dispersity of each measurement are a) binary measurement (red) b) monodisperse (blue) c) polydisperse (purple) and d) dialysed with the 14 kDa MMCO (green).

The binary measurement (a) shows a loss of solution structure when compared to the monodisperse measurements (b), and the presence of a pure depletion force, which is similar to the measurements conducted with the polydisperse samples (c). When the polydisperse samples underwent dialysis (d) and the lower molar mass molecules were removed from the sample, the force curves demonstrated that the solution was more structured. These measurements demonstrate that by altering the molar mass dispersity of the sample the force types present can be manipulated. As shown from the dispersity values (D) for the samples in Chapter 5, a small deviation from a value for the
monodisperse case (D<1.1) results in large changes to the force types that were measured and characterised in this study.

As discussed in Chapter 5, dialysis of the polydisperse NaPSS samples leads to a removal of excess counter ions from solution and thus varies the overall counter ion concentration. In the binary measurements, when the polyelectrolyte concentration is the same regardless of the molar mass mixture used, the free sodium ion concentration remains constant as the same number of NaPSS monomers was present in solution. If the concentration of counter ions present was the sole reason for the structural forces to return in the dialysis measurements, a loss of solution structure would not have been determined by the binary measurements.
6.3 **Summary and Conclusions**

Structural forces between deformable air bubbles in the presence of aqueous monodisperse NaPSS solutions have been directly measured. These interactions are influenced by NaPSS concentration, collision velocity and variations of polymer molar mass. Distinct differences were seen in the interactions between bubbles in the dilute and semi-dilute polymer concentration regimes: in the dilute regime, more numerous and clearly defined oscillations were observed, whereas in the semi-dilute regime these oscillations are lower in amplitude and number. In both concentration regimes, the spacing between the force oscillations was consistent with polyelectrolyte scaling theory. These measurements are well described by quantitative, analytical modelling and link the observations made between both rigid and deformable interfaces.

As the collision velocity of the bubbles is increased fluid hydrodynamics begins to overwhelm and obscure the structural forces regardless of polyelectrolyte concentration. When the molar mass was decreased from 77,000 to 6800 g/mol, the spacing between oscillations decreased, as expected. In a binary mixture of these two molar masses, the polyelectrolyte molecules were unable to form a well-defined structure and the number and amplitude of the force oscillations decreased, indicating that molar mass and dispersity can be used as precise control parameters for fine-tuning force behaviour in soft colloidal systems.

In conjunction with the work described in the previous chapter, work presented in this chapter showed that the dispersity of the polyelectrolyte significantly alters the ability of the molecules to order in solution and in doing so affects the interactions between both deformable and rigid interfaces. Due to their deformation, bubbles are more sensitive to solution structure than rigid interfaces, indicating new opportunities for designing control and functionality in complex fluids. Significantly, the relationship between additive size, concentration and crucially molar mass dispersity has been fully explored for the first time, providing a road-map for formulating soft colloidal materials with desired properties. These observations are significant for applications such as paints and food emulsions, where the final product quality or the ability to control the processing conditions depend almost exclusively on interactions between the dispersed colloids.
Chapter 7 - Formation of an air bubble within a microfluidic device

This chapter focuses on the fabrication of microfluidic devices which generate bubbles with a diameter of less than 100 micrometres, without the presence of a surfactant or similar surface stabilising molecule.
7.1 Introduction

The use of microfluidics has rapidly expanded and provides a platform for fundamental studies into various aspects of emulsions and foams due to the ability to reproducibly create well-defined droplets and bubbles. A further understanding of the underlying fundamental behaviour of emulsions and foams in areas such as food products\cite{36}, targeted drug delivery\cite{258}, ultrasound contrast agents\cite{332} could lead to improvements in these areas. In addition, microfluidic generated droplets and bubbles can be vehicles for chemical reactions and diagnostic tests that are difficult or expensive to complete on a macroscopic scale. Due to the size and control of the fluid handling in these devices, issues in scaling-up the technology to allow use in an industrial setting have been encountered. Studies are currently ongoing to investigate these issues\cite{284,375}. Even though this downside exists, microfluidic devices offer the advantage of being able to finely tune the size and produce monodisperse bubbles and droplets. This can be achieved through variation of the flowrates, solute type and concentrations of the solutions used as well as the type of the device design. As the devices are generated from computer drawn designs they are only limited by ones imagination, but typically design types are t-junction (crossflow)\cite{289,300,302,308,309}, flow focusing\cite{318,330,334,353} and co-flow\cite{340}. Success has also been bought about with devices that incorporate fine glass capillaries such as capillary microfluidic devices\cite{346-349}, capillary t-junction devices\cite{355,357,358} and the combination of both by incorporating a capillary in a microfluidic device\cite{359,360}.

The different types of designs offer both advantages and disadvantages to the user. T-junctions, flow focusing and co-flow devices allow different sized emulsions to be generated by varying the flowrate ratio of the dispersed and continuous phases\cite{294}. It has previously been shown that typically used syringe pumps have difficulty in maintaining a constant flowrate\cite{362} and create oscillations due to the piston drive mechanism\cite{361}. This effect becomes exacerbated with the use of a compressible fluid, such as gas. These design types also require a surface stabilising component such as a surfactant, alcohol or lipid to allow the generation of stable bubbles\cite{318,338}.

The present study demonstrates a design in which bubbles with a diameter of approximately 100 µm can be generated without the use of an interface stabiliser. This bubble diameter was selected, as it is similar to size of the bubbles used in the direct
force measurements conducted in the previous chapters. The design type used to achieve this is a block-and-break style that has been previously shown to be fluid flowrate and property independent for droplet generation\textsuperscript{345}. To adapt this design approach to generate air bubbles several small, yet critical, design changes were required. These changes were due to the interaction and wetting between the air and PDMS surface and sharp channel edges often encountered in microfluidic devices. The devices have also been characterised in the presence of sodium dodecyl sulfate (SDS) and sodium poly(styrene sulfonate) (NaPSS). The staged addition of SDS and NaPSS was demonstrated via the use of additional channels downstream of the block-and-break generation zone. This method also offered the ability to further investigate the air/water interface when flowing through a confined channel. This is the first work to demonstrate generation of air bubbles with flowrate independent bubble sizes without a surface stabiliser using a microfluidic device.

7.2 Results and Discussion

Two different microfluidic design types were utilised within this work, flow focusing and block-and-break. Flow focusing has previously been shown to produce monodisperse droplets or bubbles\textsuperscript{318} whereas block-and-break has been used to generate droplets\textsuperscript{345}.

7.2.1 Flow Focusing Design

The flow focusing design for bubble generation consists of two liquid streams that intersect a gas stream at a t-junction. The centre of the gas stream was opposite an orifice in which the resultant bubble stream passed through and into the outlet channel. A schematic diagram of this design and optical microscopy image of the bubble generation point is shown as Figure 7.1.
Figure 7.1. Left. Schematic diagram of a flow focusing microfluidic device. The liquid phase is shown in blue, the gas phase is white and the channel walls are grey. $W_g$ is the gas phase width, $W_L$ is the liquid phase width, $W_{or}$ is the orifice width, $L$ is the length of the orifice and $W_{out}$ is the outlet width. Right. Optical image of the flow focusing point within a microfluidic device with dimensions of $W_L = 250 \, \mu m$; $W_g = 200 \, \mu m$; $W_{or} = 30 \, \mu m$; $W_{out} = 500 \, \mu m$ (complete channel width not shown); $L_{or} = 50 \mu m$; $h$ (depth of channels) = 75 $\mu m$.

The microfluidic devices were produced following the procedure discussed in Chapter 3, Experimental Methods. Bubbles were able to be produced in the presence of liquid that contained sodium dodecyl sulfate (SDS). Due to the flow focusing design the resultant bubble sizes varied with the flowrates of the gas ($Q_g$) and liquid ($Q_L$) streams and optical microscopy images are shown as Figure 7.2.

Figure 7.2. Bubble generation with a device that contained a liquid phase of 0.5 M SDS and a gas phase of atmospheric air. Device dimensions were $W_L = 250 \, \mu m$; $W_g = 200 \, \mu m$; $W_{or} = 60 \, \mu m$; $W_{out} = 500 \, \mu m$ ; $L_{or} = 50 \mu m$; $h = \sim 75 \, \mu m$. The liquid and gas phase volumetric flowrates were Left. $Q_L = 10 \, mL/h$, $Q_g = 0.4 \, mL/h$; Middle. $Q_L = 15 \, mL/h$, $Q_g = 0.2 \, mL/h$; Right. $Q_L = 20 \, mL/h$, $Q_g = 0.2 \, mL/h$.

The bubbles that were produced in these devices were relatively monodisperse for fixed liquid and gas flowrates. The results in Table 7.1 show the liquid and gas flowrate, the flowrate ratio and the diameter of the bubbles produced. This shows that as the ratio of liquid to gas increases the bubble diameter decreases, which is consistent with literature reports$^{353}$. 

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Table 7.1. Fluid flowrates, flowrate ratio and bubble diameter of bubbles generated in a microfluidic device with dimensions $W_l = 250 \, \mu m$; $W_g = 200 \, \mu m$; $W_{or} = 60 \, \mu m$; $W_{out} = 500 \, \mu m$; $L_{or} = 50 \, \mu m$; $h \approx 75 \, \mu m$.

<table>
<thead>
<tr>
<th>$Q_L$ (mL/h)</th>
<th>$Q_g$ (mL/h)</th>
<th>$Q_L/Q_g$</th>
<th>Bubble diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.4</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>15</td>
<td>0.2</td>
<td>75</td>
<td>57</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>100</td>
<td>59</td>
</tr>
</tbody>
</table>

Bubbles could be generated in pure water but coalesced after formation. This was due to the design, because when the bubbles were formed through the orifice and exit into the outlet channel the fluid velocity in the channel decreases dramatically, due to the channel expansion. Due to the decrease in fluid velocity the formed bubbles come in close proximity to each other. Variation in the degree of the channel expansion could be included in an attempt to increase the distance between the individual bubbles. For flow focusing devices to generate bubbles the design requires a constriction and subsequent expansion. The changes in channel dimensions would cause the bubbles to be generated in close proximity and therefore design changes in this position of the device could lead to bubbles not being generated. Without the presence of a surface active agent, such as SDS, the bubbles coalesce\(^{318}\). As the aim of this project was to form air bubbles in water without additives in a microfluidic chip, the flow focusing design was deemed not suitable and no further investigation was undertaken.
7.2.2 Block-and-Break Design

Previous work\textsuperscript{345} has shown that block-and-break designs for microfluidic chips were able to produce monodispersed water-in-oil emulsions. This design allowed the size of the emulsion droplets generated to be flowrate independent, which was either difficult or not achievable in other flow arrangements commonly used in microfluidics. The aim of this work was to use the block-and-break design to generate bubbles in pure water.

![Block-and-Break Design Diagrams](image)

**Figure 7.3.** Schematic diagrams and optical images of the modified block-and-break design where the production of air bubbles is controlled via a pressure balance and hence, the size of the generated bubble is flowrate independent. The original design was based on that in the literature\textsuperscript{345} and the modifications shown here allow air bubbles to be generated in the block-and-break microfluidic devices. The scale bar in both images represents 100 \( \mu \text{m} \).  

- **a)** and **b)**: The dimensions of this design were varied with the following values being used, \( L = 150, 200 \ \mu \text{m} \), \( w = 35, 50 \ \mu \text{m} \), \( w_g = 15, 17 \ \mu \text{m} \), \( w_b = 70, 100 \ \mu \text{m} \) and height (h) (into page) = 35 \( \mu \text{m} \).  

- **c)** and **d)**: A design with a variation in the outlet channel width (w) and the dimensions of this design are, \( L = 200 \ \mu \text{m} \), \( w = 40 \ \mu \text{m} \), \( w_g = 17 \ \mu \text{m} \), \( w_b = 100 \ \mu \text{m} \) and h = 35 \( \mu \text{m} \).

The designs of the microfluidic devices in this work were calculated with the aid of the design guidelines for block-and-break devices\textsuperscript{345}. Schematic diagrams and optical images of the devices are shown in Figure 7.3. The block-and-break designs were a modified version of a t-junction, where a bypass channel allowed the continuous phase to be passed around the dispersed phase. In this arrangement the dispersed phase filled a set volume before being pinched off at the exit of the bypass channel. The length (L) of the channel from the dispersed phase inlet to the exit of the bypass channel, which
dictates the size of the bubble, was varied between 150 to 200 µm. The width of the inlet channel \(w_g\) for the gas phase was either 15 or 17 µm and the width of the bypass channel \(w_b\) was 70 or 100 µm. The width \(w\) of the outlet channel either remained constant, or in one design decreased at the end of the block-and-break mechanism. For the designs where the channel remained constant the selected values were 35 or 50 µm, and it was 40 µm for the design with the decrease in width. The height \(h\) of all the channels was 35 µm as measured with the use of a profilometer (as shown in Chapter 3, Experimental Methods). The critical design modifications for bubble generation in pure water are discussed in the next section.

This work employed the block-and-break design in order to generate bubbles with a diameter of less than 100 µm without the presence of surfactant or similar interface stabilising additive. In a block-and-break design, the size of the bubbles was dictated by the area bounded by the gas inlet and bypass channel inlet and outlet. Based on \(L\) dimensions of 150 and 200 µm and a channel height of 35 µm, the block-and-break volume correlated to spherical bubble diameters of 71 and 87 µm. The work explored the performance of the block-and-break design for bubble generation along with further optimisation for improved bubble generation. A part of the study also focused on solutions of SDS and NaPSS as the continuous fluid and the effects of these solution additives had on bubble formation. The final part of this work demonstrated the different strategies that have the potential to be implemented in future studies to further explore various aspects of interfacial science.

### 7.2.2.1 Preliminary block-and-break microfluidic design

The preliminary designs for the block-and-break devices were based on literature reports\(^{345}\). The arrangement of the block-and-break design was the same as previously presented, but scaled to allow bubbles with a diameter of less than 100 µm to be generated. The design rules provided in the original work by van Steijn and co-workers\(^{345}\) were used.
Figure 7.4. Optical images of bubble generation in the block-and-break design based on literature information\textsuperscript{345}. The sequence of the images is left to right, top to bottom. The dimensions of the device used were L, w, w\textsubscript{g}, w\textsubscript{b} = 150, 35, 15, 70 µm a) The continuous phase was pure water. The water flowrate was 200 µL/h and the gas pressure was 6 kPa. b) The continuous phase was an aqueous solution of 4 mM SDS. The continuous phase flowrate was 200 µL/h and the gas pressure was 23 kPa.

The optical images in Figure 7.4 show the operation with both pure water (a) and an aqueous solution of 4 mM SDS (b). In pure water, this design did not result in single bubbles but a continuous stream of air. The image of t\textsubscript{0} showed the gas began to enter the block-and-break generation zone and in subsequent images (t\textsubscript{1} onwards) the gas phase completely filled the main channel, without individual bubbles being formed. This occurred regardless of the gas pressure or liquid flowrate used with the microfluidic device. If the gas pressure was reduced the gas phase was unable to enter into the generation zone and once it had entered this area a continuous stream of air was formed. With the use of the 4 mM SDS aqueous solution, bubbles were generated in the device when gas pressures between 15 and 41 kPa were used. Notably, this pressure was larger than the operating gas pressure of 6 kPa that was used with pure water. The images in Figure 7.4 b), from t\textsubscript{0} to t\textsubscript{s}, showed the formation and then pinch off of the bubble. It should be noted that the break-off mechanism present in this device was considerably different to that presented in the original block-and-break microfluidic device\textsuperscript{345}.

This break-off mechanism effectively created a different style of a t-junction generation design. Except in this case, the continuous phase (liquid phase in the present study) was at 90° to the dispersed phase instead of flowing in a straight channel with the dispersed phase being introduced perpendicularly. In a traditional t-junction, the drop break-off mechanism can be in a dripping or squeezing regime. These regimes are
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a balance of the viscous shear stress, surface tension and available area for the continuous phase to flow in the channel\textsuperscript{339}. The transition between the two phases has been shown to occur at a capillary number of approximately $10^{-2}$, where the capillary number was dependent on the fluid flowrates, geometry, surface tension and solution viscosity. Within the squeezing regime (low capillary number) the viscous shear stress dominates and the dispersed phase was able to bridge the microfluidic channel. This caused the continuous phase to flow in a small area of the channel. The bridging of the dispersed phase created a pressure difference in the continuous phase upstream of where the dispersed phase formed and when the continuous phase pressure increased sufficiently, the bubble or droplet broke off\textsuperscript{289,440}. When the t-junction was operating in the dripping regime, the dispersed phase was unable to bridge the microfluidic channel and occupied a smaller portion of the channel width\textsuperscript{298}. The bubbles or droplets formed were typically smaller and were generated further downstream than those in the squeezing regime\textsuperscript{440}. Due to the pressure driven break-off in the squeezing regime, the droplet or bubble size was influenced more by the channel geometry and was less sensitive to continuous phase flowrate over a larger operating range. The 90$^\circ$ junction that has been placed in our design means that bubbles are formed in a squeezing flow regime as the dispersed phase filled the channel prior to the break-off point.

This design was a similar geometry to work previously presented by Tan and co-workers where they used an orientation they referred to as a cross-junction\textsuperscript{441}. It is a similar arrangement to a standard t-junction, except the continuous phase enters the junction perpendicular to the main channel instead of the dispersed phase. They showed that when a low dispersed phase flowrate was used, an emulsion was able to be formed. When the flowrate was increased the emulsion was no longer able to be formed, in a similar way as shown in t$_1$ and t$_2$ of Figure 7.4 a). A subsequent study showed that the change in orientation from a traditional crossflow t-junction to that of a cross-junction arrangement, the slug size of the dispersed phase changed. This observation indicated that the size of the generated emulsion or foam was dependent on the break-off mechanism\textsuperscript{442}. This also demonstrated that the break-off mechanism varied between the two styles, which was due to the angle at which the continuous phase intersected with the dispersed phase. This showed that the angle of the intersection point was important to the eventual formed bubble or emulsion droplet\textsuperscript{443}.
The break up mechanism of a bubble with a similar arrangement to the present work has been studied by Wang and co-workers. They observed two phases of the break-off mechanism, namely the squeezing and pinch off stages. The squeezing stage was characterised by a formation and then thinning of a neck, which was demonstrated in images t2 to t3 in Figure 7.4 b). The rate of change or thinning rate of the neck thickness decreased and then remained constant with time during the squeezing phase. When the bubble formation process reached the pinch off stage the thinning rate increased and the bubble was broken off as shown in t4 of Figure 7.4 b). This break-off mechanism has currently been further studied with theoretical modelling which determined the important parameters involved are the channel dimensions, surface tension, flowrates and densities of the dispersed and continuous phases.

The formation of bubbles in the 4 mM SDS system was due to a change in the surface chemistry and wetting properties of SDS when compared to those of water. The surfactant molecules lowered the equilibrium surface tension of the air/water interface to 46 mN/m, which was measured with the use of tensiometry. The decreased surface tension caused a change in the wettability of the PDMS channel walls when compared to a system of pure water. Xu and co-workers have also shown that the slug size of a generated emulsion in a crossflow t-junction arrangement was varied in the presence of a surfactant for the same flow conditions. They proposed that the addition of surfactant influenced both the shape of the interface and the wetting properties of the system, which could be the reason that bubbles were able to be formed in the 4 mM SDS aqueous solution in the current study. To overcome this problem when operating in the absence of surfactant it was found the position of the junction above the gas inlet channel was vital. The width of the outlet channel was also decreased to observe any possible changes in the bubble formation process.
Figure 7.5. Details of the alignment of the junction point with the gas inlet. **Left.** The junction point is aligned with the left hand side of the gas inlet channel. **Middle.** Junction point aligned to the centre of the channel. **Right.** Junction point aligned to the right hand side of the channel.

The various positions of the junction above the gas inlet channel that were tested are shown in Figure 7.5. In the original design the junction point was aligned with the left hand side of the gas inlet channel and the gas stream pinned on the right hand side of the liquid exit point at the end of the bypass channel. This example is shown by the red arrow in Figure 7.5. When no other dimensions in the design were changed, except the junction point was aligned with the centre or right hand side of the gas inlet channel, as demarked by the blue arrows in Figure 7.5, the gas no longer pinned at the exit of the bypass channel. This allowed bubbles to be formed in pure water.

Figure 7.6. Optical images of the bubble generation process with the modified device design in a continuous phase of pure water. The device dimensions were $L, w, w_g, w_b = 200, 40, 17, 100 \, \mu m$. The water flowrate was $300 \, \mu L/h$ and the gas pressure was $11 \, kPa$.

The bubble generation within a block-and-break design in a solution of pure water are shown in Figure 7.6. These images showed that air bubbles without a surfactant or other interface stabilising chemical were able to be generated in a microfluidic device fabricated in PDMS, though the break-off mechanism was similar to that shown in Figure 7.4. By moving the junction point to the right meant that the channel widening
into the generation zone was longer in length. This allowed the gas phase to enter the channel between the generation zone and the liquid bypass channel and instead pin at the beginning of the channel as opposed to the junction point.

We speculate that the change in the pinning location of the air/water interface played a role in bubbles being able to be generated in pure water. Pressure changes due to water droplet formation and break-off has previously been shown to change in a t-junction device\textsuperscript{289,440}. When a bubble was formed and subsequently broke off a pressure oscillation was created within the channel. Due to the compressibility of the gas phase and the presence of two air/water interfaces exposed to different pressures linked by the bypass channel, this field is propagated through the device. The pinning of the interface in this manner possibly fixes the location of the air/water interface at the entrance to the bypass channel. The pinned interface causes the bubble to become less compliant to pressure oscillations and other forces experienced within the microfluidic device, which allows bubble formation in pure water.

The different break-off pattern to that demonstrated previously with droplets was due to the differing surface properties of oil and air when interacting with PDMS. As PDMS is hydrophobic in nature, when the liquid phase was water the channels would not be wetted fully by the liquid phase. This meant that the gas phase was more likely to pin to the surface leading to the variation in the break-off mechanism. Due to the cost and time constraints with techniques which involve etching or milling of microfluidic channels\textsuperscript{343}, the use of PDMS was preferable with respect to minimising the fabrication time of the devices. Even though this break-off pattern was different to that of the oil/water system previously studied, the current design was used for the remainder of the study. It will be subsequently shown in this chapter that the generated bubble diameter remained the same with respect to variations of the operating gas pressure with a continuous phase of pure water.

The decrease in the outlet channel width was introduced to investigate whether this would change the bubble break-off mechanism. The bubble break-off mechanism shown in Figure 7.4 was for the outlet channel width that remained the same and Figure 7.6 was the channel with a decreased channel width. The break-off mechanism remained the same and these were the variations in the block-and-break design that were investigated in this study.
7.2.2.2 Varying the geometry of the microfluidic device

Several differing geometries were fabricated and used through this study to investigate the effect of varying the geometry of the devices on the resultant generated bubbles. The designs tested in this section all had the junction point above the gas inlet in a suitable location to ensure that bubbles in pure water could be generated. Two designs were similar to the work previously reported in the literature\textsuperscript{345} where the width of the outlet channel did not change and one where the was a narrowing of the channel near the block-and-break generation zone. This was to investigate whether changes in the operation and bubble size occurred across these two different designs.

![Figure 7.7](image)

**Figure 7.7.** The length of bubbles generated with the use of two different block-and-break designs with respect to changes in the gas pressure. The geometries of the devices shown were $L, w, w_g, w_b = 150, 35, 15, 70 \mu$m (orange diamonds) and $L, w, w_g, w_b = 200, 50, 17, 100 \mu$m (green circles) and the liquid flowrate remained constant for each design at 200 and 350 $\mu$L/h, respectively. The error bars indicate one standard deviation from the value indicated by the data point. **Inset.** The $L/W$ ratio of bubbles generated with the use of two different block-and-break designs with respect to changes in the gas pressure. **Top right.** A schematic diagram of the block-and-break design used (green circles), which had a constant outlet channel width and an $L/W$
A schematic diagram of the block-and-break design used (orange diamonds), which has a constant outlet channel width and an L/W ratio of 4.3.

Variations of the block-and-break geometry and the resultant lengths and L/W ratio of the bubbles with respect to changes to the operating gas pressure with a constant liquid flowrate are shown in Figure 7.7. The geometries presented in this section were those with a constant outlet channel width and the data showed that the bubble L/W ratio produced did not fit with that expected from the block-and-break design. This showed that the change in break-off mechanism caused the size of the generated bubble not to be geometry driven, as was the case in the block-and-break design conducted previously\footnote{345} with a liquid/liquid system.

The microfluidic device with an L/W ratio of 4.3 has smaller channel dimensions which allowed for a smaller diameter free bubble to be formed. In this case a free bubble would be described as a bubble that was within solution with a spherical interface. For a smaller free bubble to be formed a decreased volume of the channels was required. The channel dimensions of the device must be decreased as all of the devices in this section were produced with the same channel height (35 µm). A decrease in the channel dimensions means that a lower liquid flowrate was used to maintain the pressure balance required for the block-and-break generation zone during operation of the device.

With both of the block-and-break geometries used in this study the operating gas pressure was slowly increased until bubbles were able to be generated. Optical images of the generated bubbles were then taken and the gas pressure increased slowly until bubbles were no longer formed. In both of these designs the maximum operating gas pressure was at least double of the minimum gas pressure used. Over this pressure range the resultant bubble size remained relatively constant. Previous studies which used either a crossflow or cross-junction t-junction designs have shown the size of the bubbles or droplets produced were flowrate dependent\footnote{289-292,439,442,443}, unlike those generated in this study. There are two flow regimes of importance within a t-junction, squeezing and dripping regimes. Within a t-junction device the size of the bubbles produced remained constant when in the squeezing flow regime and with increased flowrate of the dispersed phase the bubble size was elongated\footnote{289}. This transition has been shown to occur when the capillary number was approximately below $10^{-2}$\footnote{289,440}.
When the capillary number was calculated based on the geometries and flowrates used in this study the capillary number would remain under $10^{-2}$ and therefore in the squeezing regime. Even though the size was not as expected from the geometry of the microfluidic device, the relatively constant bubble size with variation of the gas pressure has the potential to have many useful applications in other microfluidic studies. The next design change focused on a decreased outlet channel width to observe any change in the size of the generated bubbles.

![Figure 7.8](image)

**Figure 7.8.** The length of bubbles generated with the use of one block-and-break geometry with respect to changes in the gas pressure. The geometry of the device shown was $L, w, w_{\text{g}}, w_{b} = 200, 40, 17, 100 \mu\text{m}$ (L/W of 5), which was the design with the decreased outlet channel width. The liquid flowrate of the two data sets were 300 (red squares) or 350 $\mu\text{L}/\text{h}$ (blue triangles). The error bars indicate one standard deviation from the value shown by the data point.

The data shown in Figure 7.8 was the generated bubble size from a block-and-break device with a decreased outlet channel width and two different operating liquid flowrates. This design was similar to that presented in Figure 7.7 with the L/W ratio of 4, except for a decreased outlet channel width. In a similar fashion to the previous design the gas pressure was varied whilst the liquid flowrate remained constant. This
showed that the decreased outlet channel width allowed that bubbles to be generated at a smaller size when compared to a standard outlet channel. The decreased channel outlet width changes the flow patterns of the liquid stream as it comes through the bypass channel. The decrease in the channel width means that the liquid and gas phase were both getting squeezed at the same point in the device. This mechanism allowed the bubbles to be formed at a smaller bubble size.

The gas pressures used for this device design were lower when compared to those shown in Figure 7.7. This would be due to a higher pressure at the point in the device where the bypass channel joins the outlet channel, due to the decrease in channel width. The higher pressure increased the rate at which the pressure builds up in the gas phase and the bubbles were broken off more frequently, resulting in smaller bubbles and a decreased operating gas pressure.

Liquid flowrates of 300 µL/h and 350 µL/h were used with the device and these results demonstrate approximately constant generated bubble size with respect to the liquid flowrate. The change in liquid flowrate results in a variation of the pressure drop experienced by the liquid through the bypass channel and this leads to a change of the gas pressure required. In the original design of the devices the liquid flowrate was fixed to maintain the same pressure drop in the bypass channel and this was the reason that the liquid flowrates were maintained at one value for the remainder of the study. The block-and-break device was dependent on a pressure balance set-up by the gas pressure and liquid flowrate this indicates that the liquid flowrate would not be able to be varied greatly and the same size bubbles were still generated.

The error bars in both Figure 7.7 and Figure 7.8 represent one standard deviation of the data points shown. These errors were larger than those shown by van Steijn and co-workers and a number of possible factors could have been the cause. These factors could be artefacts of using a syringe pump for the liquid stream or a pressure field that is set-up by the compression of the gas phase during the formation and subsequent break-off of the bubbles. It would be expected that the changes in pressure throughout the block-and-break device would be present in a system with droplets, but in that case the two fluids are immiscible liquids instead of a gas and liquid phase used in this study. This observation was not unexpected with the use of a gas phase, due to the inherent compressibility of the phase. Any pressure fluctuations through the device
would also affect the gas within the bubbles, compressing and decompressing them as the pressure fields propagated. These pressure fields also have the potential to vary the pressure balance required for bubble formation and therefore small changes in bubble size are not unexpected. As discussed previously the change in the break-off mechanism also played a role in the increased error of the bubble size. The reader is directed to Appendix 10.10 for histograms of the measured bubble size with respect to gas pressure changes.

7.2.2.3 Effect of various solution additives

To investigate the effect the surface active molecules have on the generation of bubbles in the block-and-break design SDS and NaPSS solutions were used as the liquid stream. SDS was selected as it is a common surfactant and NaPSS as it was of relevance to the AFM work described in earlier chapters, and both absorb to the air/water interface on different time scales. The design used in this part of the study was the device that had a decreased outlet channel width, which was the same design used for the data presented in Figure 7.8. The design was the same regardless of the solution additive and had the following dimensions, \( L, w, w_g, w_b = 200, 40, 17, 100 \, \mu m \).

![Figure 7.9](image_url)

**Figure 7.9.** The length of bubbles generated in different solution additives with respect to changes in the gas pressure and liquid flowrate ratio. The data presented was for
solutions of 1000 ppm NaPSS (purple diamonds), 10,000 ppm NaPSS (orange squares) and 4 mM SDS (black circles). The liquid flowrates remain constant at 300 µL/h for the 1000 ppm and 10,000 ppm NaPSS, and 100 µL/h for the 4 mM SDS measurements. The error bars indicate one standard deviation from the value indicated by the data point. Inset. The length of the generated bubbles with respect to varying operating gas pressure. These data points represent the same aqueous solutions presented in the main figure.

The length of the generated bubbles in aqueous solutions of 1000 ppm NaPSS, 10,000 ppm NaPSS and 4 mM SDS are shown in Figure 7.9 with either a varying gas pressure or the ratio of gas pressure and liquid flowrate. Even though the microfluidic design was the same for each of the conditions presented here, the liquid flowrate of the 4 mM SDS aqueous solution varied to that of the NaPSS aqueous solutions. A change in the liquid flowrate caused a change in the gas pressure required to balance the pressure required for the block-and-break device to generate bubbles. Therefore, to allow a comparison of the different aqueous solutions we used a ratio of the gas pressure and liquid flowrate. This is a typical approach in microfluidic studies. In this case, the two phases were supplied differently (gas regulator and a syringe pump) to the microfluidic device and the ratio did not result in a dimensionless number. We used this method as comparing the different systems was easier with a gas pressure and liquid flowrate ratio than observations in the trends of the operating gas pressure. This also means that scaling relationships presented in the literature with respect to capillary numbers or expected bubble sizes were difficult to apply as the gas flowrate were unknown.

The bubble lengths that were generated in the NaPSS and SDS aqueous solutions shown in Figure 7.9 have a similar value to those for pure water shown in Figure 7.8. Even though the bubble lengths did not vary greatly regardless of the molecules present in solution, these data highlight that gas pressure at which bubbles in pure water were able to be generated was lower than those of NaPSS aqueous solutions. This will be discussed in more detail later. However, this observation did indicate that the surface active species affect the bubble generation. Xu and co-workers have previously demonstrated that the addition of surfactant to a t-junction device operating with oil and water phases affect the ability of droplets to be generated\textsuperscript{360}. They also showed that with an oil continuous system, water droplets were not able to be formed unless Tween surfactant was present or the surfactant Span was present in an oil continuous system. They proposed that this was due to changes in the wetting
properties of the solutions and PDMS channel walls\textsuperscript{360}. This study also demonstrated droplet size was dependent on the surfactant concentration below the critical micelle concentration (CMC), due to the varying surface tension. These observations do not agree with the data presented in Figure 7.9. The variation in the observations between the previous study and the present one is potentially due to the change in break-off mechanism employed with the block-and-break geometry as discussed previously.

Different aqueous solutions in this study required operating gas pressure. The largest gas pressure and liquid flowrate ratio value for pure water was 0.12 kPa.h/µL, which was calculated from the data presented in Figure 7.8. For the measurements conducted with 4 mM SDS and 1000 ppm NaPSS the maximum values for the gas pressure and liquid flowrate ratio increased to 0.31 and 0.20 kPa.h/µL, respectively. There was an increase in the bubble length value for the 4 mM SDS solution when the gas pressure and liquid flowrate ratio reached above a value of approximately 0.2 kPa.h/µL. This was potentially due to the decrease in surface tension of the air/water interface and changes in the channel wettability in the presence of SDS. This was similar to the observations of Xu and co-workers\textsuperscript{360}. It is interesting to note that the gas pressure and liquid flowrate ratio for the 10,000 ppm NaPSS solution remained at a similar value to that of pure water. This is an interesting observation as a decrease in surface tension of the air/water interface would cause a lowering of the pressure in the main channel (where the bubble forms) and an increase in solution viscosity causes an increase in pressure drop across the bypass channel. The changes in the solution properties such as surface tension and viscosity across the NaPSS and SDS aqueous solutions varied the gas pressure in which bubbles could be generated on the microfluidic device, as the geometry remained the same.
Figure 7.10. The average advancing or receding dynamic wetting angle with respect to the varying gas pressure and liquid flowrate ratio. The data presented was for all of the experimental conditions previously shown in this chapter. The geometries and flowrates ($v_l$) of the devices conducted with the use of water as the liquid stream were $L, w, w_g, w_b, v_l = 200, 50, 17, 100 \, \mu\text{m}, 350 \, \mu\text{L/h}$ (green circles), $L, w, w_g, w_b, v_l = 200, 40, 17, 100 \, \mu\text{m}, 300 \, \mu\text{L/h}$ (red squares), $L, w, w_g, w_b, v_l = 200, 40, 17, 100 \, \mu\text{m}, 350 \, \mu\text{L/h}$ (blue triangles). The data for the various additives all had a microfluidic device design of $L, w, w_g, w_b = 200, 40, 17, 100 \, \mu\text{m}$ and are shown as 1000 ppm NaPSS (purple diamonds), 10,000 ppm NaPSS (orange squares) and 4 mM SDS (black circles). The liquid flowrates remained constant at 300 $\mu\text{L/h}$ for the 1000 ppm and 10,000 ppm NaPSS, and 100 $\mu\text{L/h}$ for the 4 mM SDS measurements. The dynamic contact angle of the original design which worked in the presence of 4 mM SDS solution and not pure water (grey squares) had a liquid flowrate of 300 $\mu\text{L/h}$. **Left.** Dynamic advancing wetting angle. **Right.** Dynamic receding wetting angle. **Inset.** A schematic diagram showing the location of the dynamic wetting angles measured as a bubble moved down the channel in the direction of the red arrow.

The solution additives also played a role in varying the dynamic wetting angle (DWA) of the formed bubbles along the main channel as shown in Figure 7.10. This was not an equilibrium contact angle or an advancing or receding contact angle. An equilibrium contact angle can be described by a force balance conducted at the three-phase contact line of a solid-liquid-gas interface. The advancing contact angle is determined by the moving three-phase contact line when for example, a drop moves down an inclined plane. In this measurement, the air/water/PDMS contact line at the front of the bubble when it flows down the channel. The forces on the three-phase contact line also include hydrodynamic pressure from the motion the fluid flow moving the bubble. This can
affect the air/water meniscus and the force balance at the three-phase contact line. Even though the angle of the air/water meniscus with the channel can be extracted this may not directly correlate to the equilibrium wetting properties of the channel.

These measurements showed that the dynamic advancing wetting angle (DAWA) of the 4 mM SDS bubbles in both the original (grey squares) and modified (black circles) designs have a similar value of approximately 40°. The 10,000 ppm NaPSS measurements had an increased DAWA, approximately 60°, when compared to those of 4 mM SDS. The bubbles formed in solutions of water and 1000 ppm NaPSS had approximately the same DAWA of 70°. These results indicate the difference in the rate of molecule absorption to the air/water interface and this has been discussed in more detail later. It should be noted that changes in the fluid flow within the bubble and the thin film due to the Gibbs Marangoni effect would be minimal as the concentration and velocity of the bubbles through the microfluidic channels is relatively small. If large fluid flow were present it could be expected that the bubbles within the channels would split and there is no evidence of this occurring throughout the measurements.

The measurements of the dynamic receding contact angle (DRWA) had a similar value of approximately 110° regardless of the operating gas pressure or molecules present in solution. This indicates that, as observed for the DAWA, the velocity of the bubbles down the channel does not affect the DRWA. The observation of the DRWA showing no variation regardless of the aqueous solutions used is interesting and different from that of the DAWA. This is most probably due to the wetting/dewetting of the channel that occurs as a bubble travels down the channel, as well as the effect of the pressure field due to the compression of the gas phase. In the case of the DAWA the air phase follows the liquid phase and therefore de-wets the channel as it moves. Conversely, the measurement of the DRWA occurs during the wetting phase of this process. The observation of the DRWA having similar values was not surprising considering that the measurement was taken during a dynamic process, occurs whilst the pressure within the channel was oscillating and the bubble was confined in a channel.

The DWA was determined as the bubbles moved down the main channel after formation in the block-and-break device. The observations were made possible with the use of an image processing program and this has been described in Appendix 10.9. The average DWA presented was taken within the midsection of the channel, as the
pressure changes at the beginning and end of the channel varied the measured DWA value. This was due to the pressure gradient that occurred during the bubble formation process. Also, within some microfluidic devices, an expansion at the end of the channel caused pressure and flowrate changes. The error bars shown in Figure 7.10 represent one standard deviation of the DWA determined from the midsection of the channel. Due to the dynamic nature of the measurements and that the channel has three PDMS walls and one glass wall, the actual error of these values was estimated to be a minimum of ±10°. Whilst it was difficult to determine the DWA with high accuracy in the microfluidic devices, it allows general trends with respect to the concentration and type of solution additives to be discussed.

The equilibrium surface tension of the 4 mM SDS solution measured with the use of tensiometry was 46 mN/m and indicates the absorption of SDS molecules to the air/water interface. The observation of a decreased DAWA demonstrates that SDS molecules were absorbing to the interface and therefore there was a decrease in surface tension. It should be noted that due to the dynamic nature of the bubbles in a microfluidic channel the equilibrium surface tension might not be reached in this situation. A decreased surface tension increases the wetting of the channels, which leads to the decrease of the contact angle of the bubbles with the channel and this was observed with the decrease in the DAWA. Due to the increased wetting and reduced DAWA, the curvature of the advancing edge of the bubbles in the channel increased and allowed bubbles to be generated at higher gas pressures and liquid flowrate ratios than without SDS present. The viscosity of the 4 mM SDS solution remains relatively unchanged to that of pure water and therefore, did not lead to noticeable changes in the fluid flow and bubble generation.

For solutions of NaPSS the surface tension also decreased with increased concentration in the same manner as SDS, but the solution viscosity was also affected. The equilibrium surface tension of the NaPSS was measured to be 62 and 44 mN/m for the 1000 ppm and 10,000 ppm solutions, respectively. The time scale of adsorption of NaPSS to an air/water interface has been shown to be on the order of minutes. The longer absorption time of the NaPSS molecules to the air/water interface when compared to those of SDS was consistent with the DAWA observations. This slower time of absorption of NaPSS molecules to the air/water interface also decreases the
modification of the channel wetting which was observed with SDS. A smaller increase in the channel wettability would occur and this was consistent with the observations of the DAWA. When the NaPSS concentration was decreased to 1000 ppm, there were fewer molecules in solution to adsorb to the air/water interface and therefore this leads to a decrease in the change to the channel wettability observed. Due to this adsorption time frame the bubbles generated in NaPSS solutions are potentially affected more by the viscosity change of the solution, rather than surface tension.

The viscosity of polyelectrolyte solutions increases with concentration in the well-defined relationship of $\eta - \eta_s \sim c^{\frac{1}{2}}$ for polyelectrolyte concentrations above the overlap concentration (in this case approximately 2400 ppm)$^{248,424}$ (where $\eta - \eta_s \sim c^{\frac{1}{2}}$ is the specific viscosity). For concentrations below the overlap concentration the viscosity scales with the relationship of $\eta - \eta_s \sim c^{\frac{2}{5}}$. From the literature, the specific viscosity of the 1000 ppm and 10,000 ppm NaPSS solutions were approximately 0.8 and 1.5, respectively$^{191}$. The pressure drop across the bypass channel of the device increases with increasing solution viscosity as described by the block-and-break design equations$^{345}$. If this was the primary driving factor to the gas operating pressure, the 10,000 ppm NaPSS aqueous solution should have had a larger gas pressure when compared to that of 1000 ppm NaPSS or pure water. The measurement conducted with a concentration of 1000 ppm NaPSS was able to continue operation at higher gas pressure than the measurements conducted in water. The measurements conducted at a NaPSS concentration of 10,000 ppm were only able to operate up to gas pressures similar to those of water. This indicates that changes in the wetting behaviour and the equilibrium surface tension led to the effects observed with the dynamic wetting behaviour as opposed to the solution viscosity. A decrease in the surface tension also leads to a decrease of the required gas pressure and this could also be a contributing factor in the decreased operating pressure with the 10,000 ppm NaPSS aqueous solution. These observations indicate that the operating gas pressure was dependent on the device geometry, surface tension and solution viscosity.
7.2.2.4  *Staged amphiphilic addition for interface dynamic studies*

In this section an additional channel was added downstream of the bubble generation zone. The purpose was to investigate whether the additional channel would affect the bubble generation and whether changes to the bubble interface could be detected. This section was not designed to provide insight into the adsorption of molecules to the interface, but rather a proof of concept that could be used in subsequent studies.

**Figure 7.11.** Optical images of the two side channel designs used for this study with the block-and-break generation design. The block-and-break dimensions were L, w, \( w_g, w_b = 150, 35, 15, 70 \) µm. **Left.** The midline of the intersection zone was level with the top of the main channel (Design 1). **Right.** The midline of the intersection zone was level with the midline of the main channel (Design 2).

In Figure 7.11 there are shown two different designs for the intersection point of the additional side and main channels. In both designs the 50 µm (the same as the main channel width) side channel enters 500 µm downstream of the generation zone. At the intersection point of the two channels the width of the channel is 100 µm to allow an area where the two streams intersect before moving down the main channel to the exit of the microfluidic device. Due to the flowrates being in the laminar flow regime, complete mixing of the liquids does not occur in this area. Mixing of the fluids will continue to occur down the channel. In the first design, now referred to as Design 1, the midline of this zone was the top of the main channel. In the second design (Design 2) the midline was aligned with the centre of the main channel. Both zone designs had a tapering of the channel back to a width of the main channel of 50 µm.

In these measurements aqueous solutions of either SDS or NaPSS were added to the experiment via the side channel and the bubbles were always generated in water. Care in the selection of the concentration and flowrate of the solutions was required, as these affect the resultant solution concentration. Variation of the side channel flowrate allows the possibility of several concentrations to be studied subsequently and under the same experimental conditions.
Figure 7.12. Optical images of a bubble being generated in water and then exposed to a 16 mM SDS solution through the side channel in Design 1. A change of the bubble interface was observed as the SDS molecules adsorb to the interface. The water flowrate was 300 µL/hr, the gas pressure was 19 kPa and the SDS flowrate was 300 µL/hr (results in an 8 mM SDS solution after mixing).

The sequence of optical images shown in Figure 7.12 shows a bubble being generated and then subsequently exposed to a solution containing SDS molecules before leaving down the main channel of Design 1. There would be changes in the pressure profile of the microfluidic device with the introduction of the side channel and these experiments show that bubbles were still able to be generated with this change. The images show that the bubbles were generated in the usual manner and then enter the intersection zone, where the presence of SDS molecules change the interface during adsorption. The change in the colour of the interface after the SDS was introduced was due to the change in the wetting behaviour of the system as discussed previously. With this design a small bubble was always broken off the main bubble during the channel confinement from the intersection zone to the main channel.
Figure 7.13. Optical images of a bubble being generated in water and then exposed to a 16 mM SDS solution through the side channel in Design 2. A change of the bubble interface was observed as the SDS molecules adsorb to the interface. The water flowrate was 300 µL/hr, the gas pressure was 19 kPa and the SDS flowrate was 150 µL/hr (results in a 5.3 mM SDS solution after mixing).

Shown in Figure 7.13 is a sequence of optical microscopy images demonstrating the generation of a bubble and exposure to SDS in Design 2. In this case the first generated bubble remains trapped in the intersection zone and requires another bubble to coalesce with it prior to moving down the main channel. If larger bubbles were not required in the study a possible solution would be to have two side channels entering the intersection zone. The additional side channel could be located at the bottom of the intersection zone to ensure the flow from both the top and bottom of the created bubble occurred in the intersection zone. In a similar fashion to Design 1, this design clearly shows that the SDS molecules adsorb to the bubble interface in the intersection zone and show channel wetting behaviour characteristic of SDS. Unlike Design 1, there was
no evidence of the bubble breaking up upon leaving the intersection zone into the main channel. This is potentially due to the shape change of the intersection zone or the reduced angle of entry into the main channel when compared to Design 1.

**Figure 7.14. Top.** Optical images of a bubble being generated in water and then exposed to a 10,000 ppm NaPSS solution through the side channel in Design 1. The water flowrate was 300 µL/hr, the gas pressure was 23 kPa and the NaPSS flowrate was 100 µL/hr (results in a 2500 ppm NaPSS solution after mixing). **Bottom left.** Optical image of the intersection zone with water in the side channel. **Bottom right.** Optical image of the intersection zone with the side channel containing NaPSS solution.
Experiments with Design 1 were also conducted with the addition of NaPSS solutions as shown in Figure 7.14. These experiments supported the measurements conducted above in that the solutions containing NaPSS do not affect the air/water interface in the same manner as SDS molecules. This was due to either the equilibrium absorbed amounts being less or that the dynamics of the adsorption being slower than the time scale of the bubble-water contact at this point in the channel. This was shown by the limited changing of the air/water interface in these images. It should be noted the evidence of the NaPSS molecules influencing the interface can be demonstrated when the bubble was in the intersection zone and not confined in the main channel. The image on the bottom left in Figure 7.14 was of a bubble in the intersection zone in the presence of water and on the right the side channel had a NaPSS solution. The bubble in NaPSS has a rounded advancing and receding interface, whereas the bubble in pure water was pinning to all surfaces of the PDMS channels and moving in slug flow. Once the bubble in an aqueous solution of NaPSS was confined in the main channel the differences become less noticeable.

The studies presented in this section are just some of the design changes that could be made to the microfluidic device design to investigate varying aspects of interfacial science. They demonstrate the flexibility in designing a suitable experimental design dependent on the measurement of interest. Due to the advantage of adding the desired solution into the experiment after the bubble has been generated, solutions that prove difficult to generate bubbles could still be studied with the use of side channels. Fabricating various side channels in parallel has the potential to allow the surface properties of the one bubble to be changed several times, thus building stepwise experimental complexity.

The channel designs are not limited to those shown in this thesis but further possibilities are that a longer or more tortuous path is included in the design to allow time for surface active molecules to adsorb to the interface. Various larger areas can be included to allow stability studies of foams to occur. Two bubble generating areas could be included on the same device and the bubbles bought together to study bubble coalescence events. Microfluidic devices offer a method in which bubbles can be generated and then the study of interest conducted all the same device without the concern of contamination of the interface after bubble generation.
7.3 Summary and Conclusions

Air bubbles without the presence of a surface stabiliser were generated in a microfluidic device. Bubbles in solutions of pure water have previously been generated in various microfluidic device designs such as traditional t-junctions, but the size has not been shown to be flowrate independent. We used a block-and-break design that has previously shown that with an oil and water system, droplets were formed with a flowrate independent sizing. The break-off mechanism of the design with the use of a gas phase did not behave in the same way when compared to an oil/water system. The break-off mechanism led to the bubbles being broken off in the exit channel of the device, which was effectively a modified t-junction. The orientation of intersection between the air and liquid phases was similar to a cross-junction\textsuperscript{441}, where the devices in this work always operate in the squeezing regime of a t-junction. Bubbles were able to be generated in aqueous solutions of SDS with a microfluidic device design based on the original block-and-break design\textsuperscript{345}, but to be able to use pure water, further design modifications were required to control the pinning of the air/water interface.

With the modified design the influence of the 4 mM SDS, 1000 ppm and 10,000 ppm NaPSS aqueous solutions on the generated bubble size were also studied. It was found that the bubble size remained independent of the gas pressure used. The DAWA was found to be dependent on the surface tension of the air/water interface and the dynamics of the molecules within solution. It was found that the 4 mM SDS aqueous solutions decreased the DAWA to approximately 40° and the 10,000 ppm NaPSS decreased it to 60°. The time scale of the NaPSS molecules to move to the air/water interface was slower\textsuperscript{447} than those of SDS which led to a change in the DAWA, even though these molecules have a similar equilibrium surface tension. The DAWA of the 1,000 ppm NaPSS and pure water solutions were similar at approximately 70° and this was also due to the dynamics of the NaPSS molecules within solution.

Staged addition of the different aqueous solutions were also shown to be possible in this study. A side channel was also introduced after the generation zone, where various aqueous solutions of SDS or NaPSS were introduced. The addition of the side channels did not affect the bubble generation within the block-and-break device. This process has the possibility to allow molecules of interest to be used for various studies regardless of whether the bubbles were able to be generated in that particular solution.
Additional side channels in parallel on a single microfluidic device have the potential to allow stepwise complexity to be built up within an experiment allowing each individual step to be investigated separately to understand the contribution to the final result. The ability to generate a bubble and conduct the required study within the same device avoids contamination of the interface and improves the ease in which these types of measurements can be completed.

Further work has the potential to be undertaken to further examine the changes in the break-off mechanism. Whilst we speculate on the reasons for flowrate independence of the generated bubble size, further studies, both experimental and theoretical modelling, have the potential to provide more detailed explanations and results. Changes to the fabrication material could also be examined to investigate the variation in the bubble break-off mechanism further.
This chapter summarises the material presented in this thesis and highlights the important outcomes.
This thesis reports on two main areas of interest with the overarching objective of studying bubble interactions during collisions and interface effects at different timescales in the presence of water soluble polymers. Direct force measurements in aqueous solutions of PVP and NaPSS have been completed in a study that investigates the role of polyelectrolyte concentration, collision velocity and molar mass dispersity on the interactions between air bubbles. The fabrication and use of microfluidic devices studied the time scale dependent adsorption of surface active molecules to newly generated interfaces.

Collisions between air bubbles in the presence of NaPSS were quantitatively recorded with the use of direct force measurements. Due to the deformation of the bubble interface, they provided a more sensitive condition to the measurement of forces in the system when compared to interactions between colliding rigid interfaces. It has been shown previously that monodisperse NaPSS causes the molecules to structure within solution so that depletion and structural forces are able to be measured between rigid interface systems. The study in this thesis work included both monodisperse molar masses and also polydisperse systems. It has been found that due to structuring effects the dispersity in molar mass of the molecules is important in the force response of the system.

The measurements conducted in the polydisperse systems demonstrated that a depletion force was present. This is the first time this force type has been measured between an interacting bubble pair. When the polyelectrolyte concentration was increased in the polydisperse measurements the force response of both the attractive jump-in (approach phase) and attractive maximum (retract phase) increased. It should be noted that even at pseudo-equilibrium bubble approach velocities hysteresis between the approach and retract phases was measured. As the concentration was increased the number density of NaPSS molecules and the ionic strength of the system increased. Both of these factors caused the osmotic pressure of the interaction to increase and thus led to an increased force response. These interactions were able to be modelled with the use of polyelectrolyte scaling theory, an analytical description of a depletion force and the Chan-Dagastine-White model. It was shown that reasonable agreement between theory and experimental results could be obtained, indicating that the hysteresis between the approach and retract phases of the interaction was due to bubble interface deformation.
When the concentration of the monodisperse NaPSS was increased a different force response was measured compared to that of the polydisperse system. In the dilute polyelectrolyte concentration regime (below $c^*$) the force response increased with increasing concentration. Measurements conducted with a NaPSS concentration of 300 ppm demonstrated a force-separation profile without hysteresis between the two phases of the measurement. The maximum force response between the bubbles was reached at the overlap concentration and in the semi-dilute concentration regime the measured force magnitudes and number of oscillations decreased, which has not been observed with the use of rigid interfaces. In the semi-dilute concentration regime the NaPSS molecules started to cross link and form a three-dimensional mesh in solution. This mesh meant that the bubbles were no longer able to displace as many cross linking points when compared to a rigid interface measurement. Once the pressure exerted by the thin film between the interacting bubble surfaces is equal to the Laplace pressure of the bubble, the interfaces deform radially and flatten instead of approaching each other further. Empirical modelling showed that the measurements conducted with rigid and deformable interfaces were able to be described with polyelectrolyte scaling theory.

The effect of the NaPSS structuring on the number of force oscillations and the magnitude of the attractive maximum force was determined by varying the force applied to the bubble pair during the approach phase of the force-separation measurement. When the bubble interfaces approached sufficiently close to each other all the possible molecule layers were expelled from the intervening thin film. The force applied to the bubbles during a direct force measurement was varied and the effect of the structural force on the attractive maximum could be studied. It revealed that the magnitude of the attractive force maximum is dependent on the number of layers of molecules that were expelled from the intervening thin film.

The velocity of the bubble collision and the molar mass of the NaPSS molecules affects the fluid hydrodynamics of the system. It was shown with both the monodisperse and polydisperse molar masses that an increase in collision velocity led to a large hydrodynamic fluid flow that overwhelmed the depletion and structural forces during these interactions. The hydrodynamic fluid flow can also be increased in a system by an increase in solution viscosity. An increase in the molar mass of the NaPSS molecule leads to an increase of solution viscosity which in turn increases the effect of hydrodynamic fluid flows and thus overwhelms the forces.
The increased effect of fluid hydrodynamics due to the increased viscosity of the PVP aqueous solutions played a role in the inability to measure depletion forces in this polymer system. It has also been demonstrated that a major component of the osmotic pressure that polyelectrolyte impart within these interactions is due to the counter ion dissociation and not the polymer chain. The dispersity of the molar mass distribution has the additional effect of lowering the ability to measure a depletion force in this system. With these factors combined depletion interactions in aqueous solutions of PVP were not observed, even though previous studies in the literature demonstrate that a depletion force should be present\textsuperscript{23}.

The role of molar mass dispersity on the measured force type was studied by dialysis of the polydisperse samples and by creating a bidisperse mixture with two different monodisperse molar masses. The dialysis of the polydisperse sample resulted in observing structural forces and the bidisperse mixture resulted in showing a depletion force. This indicates that the ability of the molecules to order is the most crucial aspect of whether a depletion or structural force can be measured. These measurements were also conducted with a rigid interface and those measurements demonstrated the same result.

Fluid and bubble flow through a microfluidic channel was investigated as well to complement the work that has been completed with the use of the AFM. Bubbles with a diameter of less than 100 micrometres (approximately the size used in the AFM measurements) were generated with flowrate independence in a block-and-break microfluidic device without the presence of a surfactant for the first time. The block-and-break design was first used to generate droplets\textsuperscript{345} and the difference in the surface properties of the two systems, meant that the break-off mechanism with an air/water system when compared to an oil/water system was different. The bubbles broke off down the exit channel of the device, though they still demonstrated flowrate independent sizing. The change in the break-off mechanism means the device has a similar orientation to that of a modified t-junction design. Due to the change in surface properties design changes were required to the original design to ensure bubbles in pure water were able to be generated even with the change in break-off mechanism.

Bubbles in aqueous solutions of NaPSS and SDS were also generated to demonstrate the ability of the devices to be used in various conditions. The use of these solutions
also allowed the study of the adsorption of NaPSS and SDS molecules to the air/water interface. It was shown that SDS had a short timescale for interaction with the freshly generated air/water interface when compared to the NaPSS. Due to the faster timescale of interaction the SDS was able to influence the interface and reduce the dynamic advancing wetting angle between the bubble and the channel wall.

The 10,000 ppm NaPSS concentration showed a decrease of the dynamic advancing wetting angle (DAWA) when compared to those measured when bubbles were formed in pure water, but not to the same value of the 4 mM SDS system. When the NaPSS concentration was reduced to 1000 ppm the DAWA was similar to those measured with pure water, even though the equilibrium surface tension values of both of the solutions was different. These measurements highlight the variations of the air/water interface and the interaction between the microfluidic channel walls in the presence of NaPSS and SDS aqueous solutions.

This study also included a microfluidic device design that had an additional liquid channel downstream of the bubble generation zone to allow staged amphiphilic addition. This additional channel allows bubbles to be generated in water and the molecule of interest to be added afterwards. In this work a solution of SDS was added after generation and showed that the bubble interface changed with adsorption of the molecules. This was also completed with NaPSS but further design changes would be required to investigate the timescales of the adsorption. These measurements show that the additional stream does not adversely affect the generation of the bubbles and various design changes would be possible downstream to study bubble dynamics, the timescale of adsorption of molecules to air/water interfaces and even the possibility of coalescence studies. Fabrication of the microfluidic devices from other materials such as glass, could allow bubbles to be generated in a block-and-break design with the traditional break-off pattern. The use of a microfluidic device for generation and then completing the study of interest offers the advantage of decreasing the possibility of contamination of the air/water interface reducing the need for additional equipment to complete desired measurements.
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Chapter 10 - Appendices
10.1 Overlap Concentration Calculation

The overlap concentrations have been calculated using the Equation 10.1\textsuperscript{248}.

\[ c^\ast \approx \frac{N}{L^3} \]  
\noindent \textit{(10.1)}

Where \( c^\ast \) is the overlap concentration, \( N \) is the degree of polymerisation and \( L \) is shown as Equation 10.2.

\[ L \approx Nb \left( \frac{u}{A^2} \right)^{\frac{2}{3}} \tau \]  
\noindent \textit{(10.2)}

Where \( b \) is the monomer length, \( u \) is the ratio of Bjerrum length on monomer length, \( A \) is the average number of monomers between charges and \( \tau \) is the reduced temperature.

The only parameter that changed in these calculations was the degree of polymerisation (\( N \)) as the other values have previously been determined\textsuperscript{248} and are shown in Table 10.1.

\textbf{Table 10.1.} Summary of values used for the calculation of \( c^\ast \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b )</td>
<td>3 Å</td>
</tr>
<tr>
<td>( u )</td>
<td>2</td>
</tr>
<tr>
<td>( A )</td>
<td>5</td>
</tr>
<tr>
<td>( \tau )</td>
<td>1</td>
</tr>
</tbody>
</table>
10.2 Cantilever Production

The production of custom cantilevers was required for direct force measurements between bubbles. As discussed in Chapter 3 these cantilevers have a gold disc located at the end to aid bubble attachment. This process was conducted via several steps and involved photolithography, gold evaporation, reactive ion etch (RIE) and hydrofluoric acid etch. Due to the shape of cantilevers silicon on insulator (SOI) 4 inch wafers were used (Semiconductor Wafer Inc, Hsinchu, Taiwan). The specifications of the wafer and a flowchart for the process are shown in Figure 10.1.

![Diagram showing the specifications of the wafer layers and a flowchart of the processes used for cantilever production. The gold discs for bubbles attachment were evaporated onto the SOI wafer in Stage 1. Stage 2 involved defining and subsequent etching of the cantilever shape. Stage 3 involved a deep RIE step to allow...](image-url)
the cantilever chip to be formed. Step 4 was the hydrofluoric acid etch to remove the exposed buried oxide layer.

10.2.1 Applying the Gold Discs (Stage 1)
This step evaporates the gold discs required for bubble attachment onto the cantilevers. On the polished device layer surface AZ 2070nLOF photoresist (Microchem) was spun at 3000 rpm for 30 seconds. The resultant wafer underwent a soft bake (SB) at 110 °C for 90 seconds, was exposed to 100 mJ/cm² of UV light and then underwent a post exposure bake (PEB) at 100 °C for 90 seconds. The photoresist was developed with AZ 726 developer for 90 seconds with a resultant film thickness of 3.5 µm. The prepared wafer had 7 nm of chrome followed by 40 nm of gold (Nanochrome II Electron Beam and Thermal Evaporation System, Intlvac Thin Film, Niagara Falls, New York) evaporated onto the surface. After the gold coating had been applied the wafer was placed in a bath of acetone and cleaned in an ultrasound cleaner for 3 minutes. The wafer was then rinsed with acetone, 2-propanol and then dried with nitrogen gas.

10.2.2 Defining the Cantilever Shape (Stage 2)
To define the cantilever shape AZ 9260 photoresist (Microchem) was spun at 2400 rpm for 60 seconds, then underwent a soft bake at 110 °C for 2:45 minutes, was exposed to 600 mJ/cm² of UV light. This photoresist was then developed with AZ400 developer (Microchem) in a 1:4 ratio with water. The resultant film thickness was approximately 5 µm. The silicon in the device layer (2 µm thickness) was then etched with a Bosch etch process (Plasmalab100 Inductively Coupled Plasma Reactive Ion Etching (ICP-RIE), Oxford Instruments, Abingdon, United Kingdom) until the buried oxide layer was reached to define the cantilever shape. The photoresist was then cleaned in a bath of acetone, which was place in the ultrasound cleaner for 3 minutes, then rinsed with acetone followed by 2-propanol and subsequently dried with nitrogen gas.

10.2.3 Etching the Cantilever Chip (Stage 3)
To etch the cantilever chip the wafer was then turned over and the photoresist and subsequent etching step was undertaken from the bulk silicon side of the wafer. Before applying the photoresist on the bulk silicon side a protective layer of photoresist was applied to the device layer to cover the cantilevers. On the device layer side AZ4562
photoresist (Microchem) was spun at 2000 rpm for 60 seconds and resulted in a layer approximately 9 µm thick. The soft bake was conducted at 110 °C for 5 minutes followed by at 140 °C for 10 minutes.

Once the cantilevers were protected the wafer was turned over and on the bulk silicon side AZ 40XT photoresist (Microchem) was spun at 50 rpm for 10 seconds, 200 rpm for 20 seconds, 500 rpm for 10 seconds and then 1000 rpm for 60 seconds. The photoresist was then soft baked at 126 °C for 5 minutes and then subsequently exposed with 400 mJ/cm² of UV light. The PEB was completed at 105 °C for 5 minutes and then developed in AZ 726 MIF (Microchem) for 4 minutes. Edge bead removal was then completed to ensure that the wafer did not stick in the Bosch etch instrument. To ensure the solvent had been driven out of the photoresist coating, the wafer was placed in the vacuum oven at 90 °C overnight.

The wafer then underwent the Bosch etch process and to protect the photoresist, 600 cycles were completed without a carrier wafer. The entire etch had not been completed after these cycles. To ensure that cantilevers did not dislodge into the instrument, a carrier wafer was placed underneath and secured with small amount of fomblin oil. Approximately 690 to 715 Bosch etch cycles were required in total until the buried oxide layer was exposed and the wafer at this stage is shown in Figure 10.2.

![Figure 10.2](image)

**Figure 10.2.** Left. The wafer after completing the Bosch etch processing on the bulk silicon side. The buried oxide layer and photoresist is still visible. **Right.** After the bulk silicon oxide layer has been removed the cantilever and buried oxide layer can be observed.
To remove the photoresist approximately 50 cycles with oxygen gas were conducted in the Plasmalab 100 ICP-RIE. After these cycles to remove the bulk of the photoresist the wafer was cleaned with piranha solution for approximately 5 minutes or until no photoresist remained.

10.2.4 Cantilever Release (Stage 4)

To remove the buried oxide layer the wafer was placed in a solution of 2% hydrofluoric acid for approximately 30 minutes. This resultant wafer was placed onto dicing tape to ensure that the cantilevers did not fall out of the wafer and to aid placing them into a gel box for storage.
10.3 Parameters used for depletion force modelling

The parameters used for the deformable interface modelling shown in Figure 5.3 of Chapter 5.

Table 10.2. Parameters used in the depletion modelling in Chapter 5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1000 ppm</th>
<th>5000 ppm</th>
<th>10,000 ppm</th>
<th>25,000 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension (±2 mN/m)</td>
<td>70</td>
<td>66</td>
<td>61</td>
<td>55</td>
</tr>
<tr>
<td>Contact angle drop 1 (°) (±5 °)</td>
<td>114</td>
<td>113</td>
<td>160</td>
<td>139</td>
</tr>
<tr>
<td>Contact angle drop 2 (°) (±5 °)</td>
<td>135</td>
<td>130</td>
<td>116</td>
<td>127</td>
</tr>
<tr>
<td>Radius 1 (±2 µm)</td>
<td>84</td>
<td>53</td>
<td>45</td>
<td>53</td>
</tr>
<tr>
<td>Radius 2 (±2 µm)</td>
<td>62</td>
<td>50</td>
<td>35</td>
<td>51</td>
</tr>
<tr>
<td>Depletion length (ξ) (nm)¹</td>
<td>30</td>
<td>14</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>Partition Coefficient (-)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

¹ Calculated with the relationship of $\xi = 665C^{-0.45}$ (Biggs, S. et al. *Langmuir* 2000, 16, 9242.)
10.4 Rigid Interface for Polydisperse NaPSS

In this section a series of data will be presented of the rigid interface measurements that were conducted in conjunction with this study. The data shown in Figure 10.3, Figure 10.4 and Figure 10.5 show the direct force measurements conducted with polydisperse NaPSS samples. These measurements were conducted at the concentrations of 1000, 5000, 10,000 and 25,000 ppm and the molar masses of 70,000, 200,000 and 500,000 g/mol. Rigid interface measurements conducted with NaPSS at larger concentrations and molar masses exhibit a depletion interaction, but do not show any further structuring. As discussed in Chapter 4, interface deformation of the bubble increases the sensitivity of the force measuring technique. The forces in interaction in the polydisperse NaPSS samples are of a magnitude that they are able to be measured with a deformable interface and not a rigid interface.

![Figure 10.3](image)

**Figure 10.3.** Direct force measurements between a silica sphere of radius of 2.5 µm and a flat silica surface in solutions of NaPSS with a molar mass of 70,000 g/mol and velocities between 80 and 250 nm/s were measured. The concentrations of the various solutions (bottom to top) are 1000 ppm (red), 5,000 ppm (green), 10,000 ppm (purple) and 25,000 ppm (blue). The data has been offset for clarity and the approach curve is shown as filled points and the retract curve as the open points. The retract curve has only been shown for one concentration for clarity and for the other concentrations the retract curve lays over the approach curve in a similar fashion.
Figure 10.4. Direct force measurements between a silica sphere of radius of 12 µm and a flat silica surface in solutions of NaPSS with a molar mass of 200,000 g/mol and velocities between 20 and 50 nm/s were measured. The concentrations of the various solutions (bottom to top) are 1000 ppm (red), 5,000 ppm (green), 10,000 ppm (purple) and 25,000 ppm (blue). The data has been offset for clarity and the approach curve is shown as filled points and the retract curve as the open points. The retract curve has only been shown for one concentration for clarity and for the other concentrations the retract curve lays over the approach curve in a similar fashion. Inset. Increased detail of the depletion interaction area of the force curves.
Figure 10.5. Direct force measurements between a silica sphere of radius of 12 µm and a flat silica surface in solutions of NaPSS with a molar mass of 500,000 g/mol and velocities between 25 and 50 nm/s were measured. The concentrations of the various solutions (bottom to top) are 1000 ppm (red), 5,000 ppm (green), 10,000 ppm (purple) and 25,000 ppm (blue). The data has been offset for clarity and the approach curve is shown as filled points and the retract curve as the open points. The retract curve has only been shown for one concentration for clarity and for the other concentrations the retract curve lays over the approach curve in a similar fashion. Inset. Increased detail of the depletion interaction area of the force curves.

The data shown below in Figure 10.6 are of direct force measurements conducted with a rigid interface with the two different dialysed samples used in this thesis study. These two measurements were conducted at a NaPSS concentration of 1000 ppm and had a MMCO of 1 kDa or 14 kDa. These measurements have observable oscillations in the force profile. As discussed in Chapter 4 decreasing the molar mass dispersity with the use of solution dialysis allows the molecules in solution to more readily structure. This increase in solution structure leads to an oscillatory force profile that is similar in nature to that measured with monodisperse dispersity.
Figure 10.6. Direct force measurements between a silica sphere of radius of 2.5 µm and a flat silica surface in solutions of dialysed NaPSS with a starting molar mass of 70,000 g/mol and concentration of 1000 ppm with a velocity between 50 and 100 nm/s were measured. The data has been offset for clarity and the approach curve is shown as filled points and the retract curve as the open points. The data are for the dialysed with a 1 kDa MMCO (red) and dialysed with a 14 kDa MMCO (purple).
10.5 Varying Molar Mass of Polydisperse NaPSS

The same trends were seen with regards to varying the velocity across the different molar masses for the polydisperse NaPSS measurements and are shown below as Figure 10.7, Figure 10.8 and Figure 10.9. The depletion interaction becomes overwhelmed by the hydrodynamic drainage forces at higher velocities in all cases at a similar velocity of approximately 4 to 5 µm/s. The main discussion of these results is presented in the Chapter 5.

![Figure 10.7](image)

**Figure 10.7.** Direct force measurements between two air bubbles in solutions of NaPSS with a molar mass of 70,000 g/mol and a concentration of 10,000 ppm were measured. The bubble collision velocity was varied and measured at 1 µm/s (red), 2 µm/s (green), 3 µm/s (purple), 4 µm/s (light blue), 5 µm/s (pink), 7.6 µm/s (dark blue) and 10 µm/s (orange). The bubble radii in these measurements were 55 and 54 µm. **Inset.** Increased detail of the depletion interaction area of the force curves.
Direct force measurements between two air bubbles in solutions of NaPSS with a molar mass of 200,000 g/mol and a concentration of 10,000 ppm were measured. The bubble collision velocity was varied and measured at 1 $\mu$m/s (red), 2 $\mu$m/s (green), 3 $\mu$m/s (purple), 4 $\mu$m/s (light blue), 5 $\mu$m/s (pink), 7.5 $\mu$m/s (dark blue) and 10 $\mu$m/s (orange). The bubble radii in these measurements were 56 and 54 $\mu$m.

**Inset.** Increased detail of the depletion interaction area of the force curves.
Figure 10.9. Direct force measurements between two air bubbles in solutions of NaPSS with a molar mass of 500,000 g/mol and a concentration of 10,000 ppm were measured. The bubble collision velocity was varied and measured at 1 µm/s (red), 2 µm/s (green), 3 µm/s (purple), 4 µm/s (light blue), 5 µm/s (pink), 7.5 µm/s (dark blue) and 10 µm/s (orange). The bubble radii in these measurements were 58 and 55 µm. Inset. Increased detail of the depletion interaction area of the force curves.
10.6 Rigid Interface Measurements for Monodisperse NaPSS

Direct force measurements were conducted in varying concentrations of NaPSS with a molar mass of 77,000 g/mol between rigid interfaces are shown below in Figure 10.10. These measurements were conducted to allow the structural force modelling in Chapter 5 to be completed. These measurements also allowed the effect of polyelectrolyte concentration on characteristic length of the molecules within to be compared with the use of polyelectrolyte scaling theory. Measurements with similar NaPSS concentrations with a molar mass of 77,000 g/mol have been shown previously in the literature and therefore further interpretation of the results will not be shown here\textsuperscript{45-47,191}.

![Figure 10.10](image)

**Figure 10.10.** Direct force measurements between a silica sphere of radius of 2.5 μm and a flat silica surface in solutions of NaPSS with a molar mass of 77,000 g/mol and velocities between 100 and 200 nm/s were measured. The concentrations of the various solutions (bottom to top) are 300 ppm (red), 500 ppm (green), 1000 ppm (purple), 2500 ppm (blue), 5000 ppm (orange) and 10,000 ppm (grey). The data has been offset for clarity and the approach curve is shown as filled points and the retract curve as the open points.
10.7 Parameters used for structural force modelling

The parameter used for the deformable interface modelling shown in Figure 6.4 of Chapter 6.

**Table 10.3.** Parameters used in the structural force modelling in Chapter 6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>300 ppm</th>
<th>500 ppm</th>
<th>1000 ppm</th>
<th>2500 ppm</th>
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<td>Surface tension (±2 mN/m)</td>
<td>65</td>
<td>65</td>
<td>62</td>
<td>60</td>
<td>51</td>
<td>46</td>
</tr>
<tr>
<td>Contact angle drop 1 (°) (±5 °)</td>
<td>140</td>
<td>151</td>
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<td>157</td>
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<td>Contact angle drop 2 (°) (±5 °)</td>
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<td>Radius 2 (±2 µm)</td>
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<td>80</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>(2.52 \times 10^{-5})</td>
<td>(2.82 \times 10^{-5})</td>
<td>(2.32 \times 10^{-5})</td>
<td>(2.97 \times 10^{-5})</td>
<td>(1.77 \times 10^{-5})</td>
<td>(6.20 \times 10^{-6})</td>
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<tr>
<td>( \varepsilon )</td>
<td>(1.65 \times 10^{-8})</td>
<td>(1.65 \times 10^{-8})</td>
<td>(1.75 \times 10^{-8})</td>
<td>(9.05 \times 10^{-9})</td>
<td>(1.21 \times 10^{-8})</td>
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<tr>
<td>( \lambda )</td>
<td>(8.81 \times 10^{-8})</td>
<td>(4.09 \times 10^{-8})</td>
<td>(2.97 \times 10^{-8})</td>
<td>(1.97 \times 10^{-8})</td>
<td>(1.84 \times 10^{-8})</td>
<td>(1.40 \times 10^{-8})</td>
</tr>
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<td>( \phi )</td>
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<td>1</td>
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</table>


10.8 Surface Tension Measurements

Shown below in Table 10.4 are the surface tensions of various aqueous solutions that were conducted for this thesis study. These measurements were conducted with the method discussed in Chapter 3, Experimental Methods.

Table 10.4. Surface tension measurements that were conducted on various aqueous solution.

<table>
<thead>
<tr>
<th>System</th>
<th>Surface tension (±2 mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mM SDS</td>
<td>46</td>
</tr>
<tr>
<td>16 mM SDS</td>
<td>36</td>
</tr>
<tr>
<td>300 ppm NaPSS (77,000 g/mol)</td>
<td>66</td>
</tr>
<tr>
<td>500 ppm NaPSS (77,000 g/mol)</td>
<td>63</td>
</tr>
<tr>
<td>1000 ppm NaPSS (77,000 g/mol)</td>
<td>62</td>
</tr>
<tr>
<td>2500 ppm NaPSS (77,000 g/mol)</td>
<td>58</td>
</tr>
<tr>
<td>5000 ppm NaPSS (77,000 g/mol)</td>
<td>54</td>
</tr>
<tr>
<td>10000 ppm NaPSS (77,000 g/mol)</td>
<td>44</td>
</tr>
<tr>
<td>1000 ppm NaPSS (6,800 g/mol)</td>
<td>70</td>
</tr>
<tr>
<td>5000 ppm NaPSS (6,800 g/mol)</td>
<td>70</td>
</tr>
<tr>
<td>1000 ppm NaPSS (binary mixture)</td>
<td>61</td>
</tr>
<tr>
<td>5000 ppm NaPSS (binary mixture)</td>
<td>57</td>
</tr>
</tbody>
</table>
10.9 Automated Image Processing

During the course of a microfluidic experiment a large number of images (in this thesis study approximately 750,000 images) are taken and therefore it was not feasible to manually sort and then subsequently size each of the individual bubbles formed by the devices. To optimise the bubble characterisation, the images were processed and then subsequently the data extracted via the use of custom Matlab code. The Matlab code will not be provided here, but a detailed outline of the processing steps and reasoning will be discussed.

10.9.1 Preliminary Feature Extraction

The aim of the preliminary feature extraction step is to extract the bubble features of interest to allow calculation of the bubble length, width and the wetting angles of the advancing and receding air/water interfaces. The images were first cropped so the area of interest was the main focus. In this work, all bubble sizing was conducted downstream of the block-and-break generation zone and within the straight section of the outlet channel. The cropping reduces the image size for the computer to process, thus reducing the processing time.
Figure 10.11. A series of images that depict the image processing involved in the preliminary feature extraction. **a)** An image taken during the microfluidic experiments. The dotted line shows the area of the image that is cropped and where the image processing is conducted. **b)** The resultant subtracted image where the background has been removed from the experimental image. The colours in this image have been inversed for easier viewing. The bubble located in the box is highlighted in the next images. **c)** Gamma corrected image for the body of the bubble. **d)** The body after thresholding. **e)** The bubble body after image noise reduction. **f)** Gamma corrected image of the cusps of the bubbles. **g)** The cusps after thresholding. **h)** The cusps after image noise reduction. **i)** The extracted body and cusp features of the bubbles as determined during the automated image processing. The features that were located within the cropped frame have been extracted and not the features outside of this area. The centroids of the bubble body or cusps are shown as yellow crosses.

The series of images outlining the various image processing steps are shown in Figure 10.11. An image taken during the experiment is subtracted from a background image and results in a greyscale image where the features of a bubble are highlighted. The pixels of an image in a greyscale are assigned a number between 0 and 255. In this case of the subtracted image, a greyscale number of zero (black) would indicate that the two pixels were the same in both images. If a large number was returned, this indicates a feature that has changed between the two images and this typically indicates the present of bubble. If all the resultant pixels in the subtracted image were close to
zero, this indicated that a bubble was not present and the image was discarded. If the numbers were significantly different, this indicated the presence of a bubble and further processing was applied. The subtracted images shown in Figure 10.11 have been inversed, i.e., black pixels have been changed to white pixels, to improve the ease of viewing the images.

The image then undergoes two image processing steps, gamma correction and image thresholding. The gamma correction lightens or darkens the image, depending on the values selected. In this case values were selected to enhance the bubble features in the subtracted image. The thresholding step turns the image into a binary image and was conducted with the Otsu method. In this step a determined value for a greyscale value was selected and values larger then were assigned the maximum value and the values below the thresholding value were assigned the minimum value. This results in an image that only has either white or black pixels, or in binary form it was allocated either a zero or one.

Once the gamma correction and image thresholding have been completed the image undergoes a process to remove any noise from other parts of the images. Typically noise in an image will be one or two isolated pixels, though it can be from defects in the channel walls as shown in Figure 10.11 e) and i). The program scans the pixels remaining and removed pixels that were not surrounded by another eight pixels. This ensured that the noise pixels were removed and the pixels that make up the bubbles were maintained.

The gamma correction and image thresholding were conducted with two different values to highlight both the air/water interfaces (referred to as cusps) and the air in the bubble (referred to as the body). Once the cusps and bubble bodies were identified the centroids of their location were calculated and used in the subsequent steps.
10.9.2 Feature Pairing

**Figure 10.12.** A schematic of the reasoning behind the body and cusp pairing after the features have been extracted from the images. Each line identifies a step taken in the pairing and eventual exclusion of features. The bodies are shown in red, the cusps shown in blue and the features not available in the next step shown in grey. The green box around a body and two cusps indicate the items that have been paired to form a bubble entity.

Above the air/water interfaces and the bubble body have been identified and now the program begins to pair these two features together. All the cusps and bodies are numbered from left to right across an image as shown in schematic of Figure 10.12. The program locates the coordinates of the first bubble body and locates cusp points to the left and the right. In the example above, Body 1 (B₁) has no cusps to the left and six to the right. As a body needs a cusp to the left and right of it, this body is excluded as an incomplete bubble and not involved in any of the subsequent processing steps. The program then observes B₂ and there are two cusps (C₁ and C₂) to the left and four to the right (C₃ through to C₆).

To ensure the correct cusp was associated with B₂, the program determines the distance between the centroid each of the bodies and cusps separately. It will only pair cusps, with a body when this distance from the each of two cusps was approximately equidistant. In this case the distance from B₂ to C₂, is similar to B₂ to C₃ so these items are paired together and not paired with the other four cusps. The two paired cusps and body of the bubble are now referred to as a bubble entity. Once these items have been paired the program continues onto the next bubble body, B₃ would be paired with C₄ and C₅. This process continues until all possible items for pairing occurs. In this case
B₁, C₁, B₄ and B₆ are remaining after all the possible pairs are matched and therefore these objects are analysed no further. The data of the pixel locations for all paired features within an entity is stored for use to calculate the bubble size and wetting angles.

### 10.9.3 Geometry Assignment

![Diagram](image)

**Figure 10.13.** The calculation of the bubble geometry is broken into three main steps.  
**a)** The paired bubble body and cusps with the determined centroid positions and pixels used for each bubble entity.  
**b)** The cropped image of a bubble cusp where a Gaussian distribution was fit to the grayscale values in lateral slices. The maximum values were determined, which indicate the location of the air/water interface.  
**c)** The shape and location of the air/water interface was determined by fitting the maximum values of the Gaussian distributions using the Taubin algorithm. The width of the bubbles is calculated as the mean separation value between the upper and lower cusp/channel wall intersection points (shown as red squares). The length of the bubble is determined from the intersection of the channel midpoint (dashed black line) and the bubbles cusps (shown as red crosses).

These next steps were used to allow the geometry of the bubble to be determined and the relevant sizing information to be gained. We now returned to the subtracted images prior to the gamma correction and image thresholding. With the use of the stored location of the bubble cusp pixels in each image, the program crops the image of each cusp that was formed an entity as shown in Figure 10.13. This image was then sliced perpendicular to the y-axis and a Gaussian distribution was fit to the greyscale values of each slice of the image. From the Gaussian distribution the maximum value in each of the slices was found. These maximum values allow an arc to represents the air/water interface.
interface to be formed. The Taubin circle fitting algorithm\textsuperscript{449} was then fit to the arcs and allows the two air/water interface to be described mathematically by a circle. The program then determines where each of the cusps finished along the circle and a straight line to drawn between them to determine the geometry of the bubble. As a geometric shape has now been extracted from the images the length, width and contact angles the bubbles made with the PDMS channel walls were able to be calculated.

10.9.4 Entity Tracking and Counting

Due to the number of images taken during the experiment, the same bubble can be observed multiple times in sequential images. The computer program needs to determine which observations are of the same bubble entity to ensure they were only counted once. For this, a dead-reckoning approach was used. This is the method used by GPS units use to predict the location of the unit between each signal received from the satellite. From sequential images the velocity of the bubbles down the channel can be determined. For each experimental condition the velocity remains relatively constant and therefore a prediction of the location of the bubble in the next image was able to be determined. If the location of the bubble in a sequential image was similar to the predicted location, the observations of the bubble were linked to be that of the same entity. This process continues down the channel until the bubble entity leaves the right hand side of the image frame. Depending on the experimental conditions and size of the cropped image a single bubble entity can be observed once or multiple times. In the case of multiple observations the bubble length used was the mean value of all the observations.
10.10 Histograms of the Length of the Bubbles Formed within a Block-and-Break Microfluidic Device Design

**Figure 10.14.** The histogram data shows the length of the bubbles formed within a block-and-break design with variations of gas pressure. The geometry of the device shown is $L, w, w_g, w_b = 200, 40, 17, 100 \, \mu m$, which is the design with the decreased outlet channel width. The liquid flowrate was held constant in these measurements at 300 $\mu$L/h. The gas pressures are a) 15 kPa, b) 19 kPa, c) 23 kPa, d) 27 kPa, e) 31 kPa and f) 35 kPa.

The histograms above in Figure 10.14 show the variation in the length of the bubbles generated in a microfluidic device with the geometry of $L, w, w_g, w_b = 200, 40, 17, 100 \, \mu m$. This is the geometry in which there was a decrease in the outlet channel width.
These data show that for this design the length stayed relatively consistent across the gas pressures investigated. There is some variation in the size of the bubbles formed and we propose that this is due to the change in break-off mechanism and pressure variations that are set-up down the microfluidic channel. These pressure fluctuations are difficult to minimise due to the bubble formation method and the inherent compressibility of the gas phase. Further discussion of the change in break-off mechanism and pressure fluctuations are presented in Chapter 7.
Author/s:
Browne, Christine Isabel

Title:
Depletion and structural force interactions of bubbles in aqueous polyelectrolyte solutions

Date:
2016

Persistent Link:
http://hdl.handle.net/11343/113942

File Description:
Depletion and Structural Force Interactions of Bubbles in Aqueous Polyelectrolyte Solutions