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Insoluble Lipids and Colloidal Particles
at the Oil-Water Interface

Joe Forth

Doctor of Philosophy
The University of Edinburgh
September 2015
Declaration

I declare that this thesis was composed by myself, that the work contained herein is my own except where explicitly stated otherwise in the text, and that this work has not been submitted for any other degree or professional qualification except as specified.

Parts of this work have been published in [1].

(Joe Forth, September 2015)
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Abstract

The films formed by tetradecylamine (TDA) at the water-dodecane interface in the presence of hydrogen phosphate ions have been studied. Between pH 5 and 8, tetradecylammonium cations bind to hydrogen phosphate anions to form needle-shaped crystallites of tetradecylammonium hydrogen phosphate (TAHP). Fourier Transform Infrared Spectroscopy (FTIR) shows that these films consist of two tetradecylammonium cations and one hydrogen phosphate anion. Light microscopy and Small Angle Neutron Scattering (SANS) results show that these crystallites self-assemble into films with a hierarchical structure. On the molecular level, the TAHP has lamellar order. On a mesoscopic level, these lamellae assemble into needle-shaped crystallites with a size on the order 0.1-100 µm. These crystallites assemble into interfacial films with a range of morphologies; below pH 7 they form continuous sheets, at pH 8 they form lace-like networks.

The films have both unusually high elastic shear moduli \(G'_s \approx 10\) N/m and a structure that can be directly imaged using light microscopy. Varying the structure of the films affects their rheology. The lace-like networks deform plastically when sheared, whilst the continuous sheets are highly brittle. The films are temperature-responsive: when the system is heated the film thins and its rheological moduli drop. The temperature response is caused by dissolution of the film into the bulk fluid phases.

The TAHP film also stabilises water-in-oil emulsions. The rheological properties of the film are directly related to the stability of the TAHP-stabilised droplets: the droplets coalesce upon being heated, suggesting potential applications in controlled release of active molecules. TAHP and colloidal PMMA particles stabilise emulsions by compatible mechanisms, and can be used to synthesise ('patchy') droplets with an inhomogeneous particle coverage, and ('hairy') droplets, from which long, tendril-like aggregates extend.

Finally, the temperature-responsive nature of TAHP is applied to the composite interfaces. As the droplets are heated the lipid film dissolves, and the PMMA particles become mobile at the interface. The electrostatic interactions between the particles lead to competition between the ordering that the electrostatics would favour, and the defect structure favoured by the topology of the spherical surface. I investigate the freezing transition on a spherical surface, and show the emergence of hexagonal order as particle density is increased.
Lay Summary

In this thesis I study emulsions. Emulsions consist of small droplets of oil in water (or water in oil). Normally, oil and water do not mix. Often, such as when making a salad dressing, it is important that they do mix. The two liquids can be made to mix by adding a third ingredient: an emulsifier. Emulsions appear in a huge range of different products: cosmetics, pharmaceuticals, and fertilisers all use emulsions in one form or another. Sometimes the emulsifier just mixes together the two fluids. Other times, it is actually used to do something. Mustard, for instance, doesn’t just make the oil and vinegar in a salad dressing mix; it also makes the mixture thicker and changes the flavour. Sometimes emulsifiers do things that we don’t want, such as irritate our skin. Given how useful emulsions can be in industry, a lot of research looks at what emulsifiers can be used to do.

The emulsifier I use is unusual: it builds itself at the surface of the water droplets. It is made of one chemical that only dissolves in oil, and another that only dissolves in water. These chemicals meet each other at the surface of the water drops, stick together, and quickly build thick films that coat the droplets. In the first two chapters I learn about the structure of these films and why they form. I will show that the films are useful emulsifiers, and that the emulsions they stabilise separate out when I heat them up. This means that they could be used for releasing ingredients when a mixture gets to a certain temperature.

In the second half of the thesis I study what happens when I add a second emulsifier to my system. This makes things more complicated because the two emulsifiers can affect each other. It is interesting because a lot of emulsions we encounter on a daily basis, such as milk, contain many different emulsifiers, all of which have an effect upon each other. The second emulsifier I use consists of very small, spherical particles of perspex. These particles coat the droplets and stop the water and oil separating out. I show that I can easily control the relative amounts of the two emulsifiers that coat the droplet. When I dissolve off the film, only the particles are left at the surface of the droplet. The particles are then free to move, and arrange themselves in beautiful patterns. When there aren’t many particles on the droplet surface, they form a disordered arrangement that looks like a liquid. When there are lots of particles, they form a repeating pattern that looks like a crystal. Studying the particles on the surface of a sphere adds a new feature as well: arrangements of pentagons and heptagons that are present by mathematical necessity, which one would not normally find on a flat surface.
Chapter 1

Introduction and Thesis Outline

In this thesis I investigate films formed at an oil-water interface by the reaction between two components - tetradecylamine (TDA) and hydrogen phosphate. Tetradecylamine is insoluble in water, and so confined to the oil (in this case, dodecane). Hydrogen phosphate is insoluble in oil, and so confined to the water. These components therefore only interact with one another at the interface between the two fluids. A picture illustrating this is drawn in Fig. 1.1. The material formed by this reaction is Tetradecylammonium Hydrogen Phosphate - I will refer to it throughout this thesis as TAHP.

This reaction quickly forms films with a hierarchical structure. On the molecular level, the TAHP molecules self-assemble into lamellar structures. The lamellae themselves self-assemble into crystallites with a range of shapes, which are most often needle-shaped. These crystallites, which are trapped at the oil-water interface, then aggregate into very strong films. This hierarchical, self-assembled structure is illustrated in Fig. 1.2. The chemistry, conditions for formation, and the kinetics of TAHP film formation are the main focus of Chapter 4.

The films that this reaction forms are unusual in many ways. Its constituent components (the crystallites) are large enough to be seen using light microscopy. The TAHP films are unusually strong, and have a very large elastic modulus. The elastic modulus of the film can be easily tuned from 0.1 N/m to 10 N/m by varying either the pH of the aqueous phase (which changes the structure) or by varying the amount of TDA used. This combination of a structure that can be directly visualised, along with an excellent experimental signal-to-noise ratio, make TAHP very easy to work with from an experimental perspective. I use the
Figure 1.1  (Top) Chemical structure of tetradecylamine. (Bottom) Schematic illustrating the interfacially mediated bonding between the water-insoluble tetradecylamine (TDA) and the dodecane-insoluble hydrogen phosphate. This reaction rapidly forms thick, multi-layer films - as discussed later in Chapter 4.

The tunable structure of the TAHP film, first shown in Chapter 4, to show a direct relationship between the structure of a TAHP film and its interfacial rheology. This is the main focus of Chapter 5, and I have published the results from these chapters in a paper [1].

The TAHP films are then applied to study emulsions. The films stabilise emulsions formed using both extrusion (which forms small amounts monodisperse capsules) and shear (which forms large amounts of polydisperse emulsion droplets). These emulsions provide a stable system to perform scattering experiments on. These show that the TAHP crystallites have a lamellar structure in which the ammonium and phosphate groups are bound together extremely strongly. The emulsions also have potential applications in the controlled release of chemicals that are used in agriculture, such as pesticides and fertilisers. It is found that the TAHP’s stabilisation mechanism shares some characteristics with that of Pickering emulsions, such as a high stability against coalescence and a mean droplet radius that is inversely proportional to the amount of TDA present. The TAHP-stabilised emulsions also share some properties more common, though not exclusive, to molecularly-stabilised emulsions, such as response to external stimuli (i.e., temperature). These emulsions are studied throughout Chapters
Figure 1.2 Illustration of the hierarchical, self-assembled structure formed by TAHP at the oil-water interface. Macroscopically, the TAHP forms sheets at the oil-water interface. Mesoscopically, these sheets can be seen to consist of aggregated, needle-shaped crystallites. Microscopically, these crystallites consist of repeating patterns of lamellae with a well-defined repeat distance and stoichiometry.

Sterically-stabilised PMMA particles are then also added to the emulsions to yield droplets coated with a composite interface, which consists of colloidal PMMA particles and TAHP crystallites. The colloidal PMMA in these interfaces is embedded in an elastic TAHP matrix, which prevents the particles from moving. It is shown that the emulsification mechanisms of the two stabilisers can act synergistically, yielding a stable emulsion even in a region of parameter space in which neither component would typically stabilise an emulsion. The PMMA particles and the TAHP also compete with one another to cover the droplet interface. In the first two chapters I show that the rate which at which the TAHP film forms can be controlled by changing the pH of the aqueous phase. I go on to show that varying the rate at which the TAHP coats the water droplets allows it to be used as a molecular stopwatch, which controls the density and arrangement of the particles at the interface. This is the focus of Chapter 6.

Finally, in Chapter 7 the composite TAHP-PMMA particle interface is used to synthesise droplets coated only by PMMA particles. By varying the particle volume fraction, the density of particles at the droplet interface can be controlled without significantly altering the size of the droplets. I then use the temperature-responsive properties of TAHP to dissolve off the TAHP coating, leaving only the colloidal PMMA particles at the interface. This gives me a novel system...
to investigate the freezing transition in two dimensions on a spherical surface. I show the emergence of an ordered lattice as the density of particles at the interface increases. The system being present on a sphere is not simply a novelty - it is useful to both fundamental physics and the study of Pickering emulsions. The spherical topology enforces the presence of the very controlled number of structural defects. The system I introduce in Chapter 7 could lead to a deeper understanding of the role that defects play in the physics of colloidal systems.
Chapter 2

Background

Throughout this work I present results and their discussion alongside each other. For the most part, this also contains a discussion of the relevant literature. For certain sections, however, reference to significant bodies of work is required to discuss the results more fully. In this chapter I present the background literature on a number of topics relevant to my results. I will outline the chemistry of primary amines and their interactions with counter-ions, both in the bulk and at the interface. I discuss the work already performed on similar, fatty acid-based systems, in particular the broad range of structures that these systems form. These subjects are most relevant to the results in Chapters 4 and 5. I then briefly review some aspects of emulsions, in particular Pickering emulsions. This is relevant to the work in Chapter 6. Finally, I introduce some basic concepts governing the behaviour of charges near surfaces, and the electrostatic interactions they cause between colloidal particles at interfaces. This puts the description of the behaviour of the amines on a more rigorous footing, and describes the mechanism by which the colloidal spherical crystals in Chapter 7 form. Finally, I give an overview of some of the relevant aspects of topology to colloidal systems on a sphere. Again, this is relevant to the behaviour of the colloidal spherical crystals studied in Chapter 7.
2.1 The Aqueous Chemistry of Phosphate and Primary Amines at Varying pH

This work introduces thick films formed by a fatty primary amine (tetradecylamine) and hydrogen phosphate. Both of these components exhibit pH-dependent behaviour, both in bulk solution and at the interface. This pH-dependence determines the conditions under which the films form. I will briefly review some of the pH-dependent behaviour of both amines and phosphate, and then look at the interface-specific behaviour of fatty amines.

2.1.1 Phosphoric Acid and Phosphate Ions

Hydrogen phosphate anions are used with tetradecylammonium cations in this thesis as a reagent to form an interfacial film. Phosphate in an aqueous solution exists in a number of different protonation states simultaneously. \( \text{PO}_4^{3-} \), \( \text{HPO}_4^{2-} \), \( \text{H}_2\text{PO}_4^- \), \( \text{H}_3\text{PO}_4 \) (in general: \( \text{H}_n\text{PO}_4^{3-n} \)) are all present to some degree at all pH values. The ratio of the populations of these ions in an aqueous solution depends on the pH. At low pH (i.e., high \( \text{H}^+ \) ion concentration) chemical potential favours highly protonated phosphate anions. At higher pH, the phosphate donates protons to the aqueous phase, and the lower protonation state becomes the most populous species. In general, the ratio of associated and dissociated ionic species in a solution at equilibrium is related by a constant \( K_a \), where [12]:

\[
K_a = \frac{[A^-][H^+]}{[HA]}. \tag{2.1}
\]

\( K_a \) is known as the acid dissociation constant. Re-arranging equation 2.1 yields the Henderson-Hasselbach equation:

\[
\frac{A^-}{HA} = 10^{\text{pH}-\text{pK}_a} \tag{2.2}
\]

where \( \text{pH} = -\log([\text{H}^+]) \) and \( \text{pK}_a = -\log(K_a) \). In the case of phosphate, the hydrogen phosphate anion has four possible protonation states. The relative concentration of each of these four different ions exists in a ratio defined by the
acid dissociation constant, $K_a$, for three separate dissociation reactions [12]:

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3} \quad (pK_{a1} = 2.12)$$

$$K_{a2} = \frac{[H^+][HPO_2^-]}{[H_2PO_4^-]} = 6.2 \times 10^{-8} \quad (pK_{a2} = 7.21)$$

$$K_{a3} = \frac{[H^+][PO_3^-]}{[HPO_2^-]} = 2.14 \cdot 10^{-13} \quad (pK_{a3} = 12.67)$$

At pH = $pK_a$, the pH of a solution containing phosphate changes only slightly when an acid (i.e., H$^+$ ions) are added. This is because most of the H$^+$ ions go towards changing the protonation state of the phosphate ions rather than changing the pH. Combining equations 2.2 and 2.3 yields the following equations:

$$[H_3PO_4] = \frac{[PO_4]}{1 + 10^{pH-pK_{a1}} [1 + 10^{pH-pK_{a2}} (1 + 10^{pH-pK_{a3}})]}$$

$$[H_2PO_4^-] = [H_3PO_4]10^{pH-pK_{a1}}$$

$$[HPO_2^-] = [H_2PO_4^-]10^{pH-pK_{a2}}$$

$$[PO_3^-] = [HPO_2^-]10^{pH-pK_{a3}}$$

This allows the relative concentration of the ions in the aqueous phase to be calculated, as shown in Fig. 2.1.

### 2.1.2 Long-chain Primary Amines at Interfaces

In this thesis I use the binding of long-chain primary amines to counter-ions at an oil-water interface to build novel, temperature-responsive films. Long-chain primary amines consist of a single, long, aliphatic chain, terminated at one end by a -CH$_3$ group, and at the other by an amine (-NH$_2$) group. Throughout this thesis I will use tetradecylamine (TDA, CH$_3$(CH$_2$)$_{13}$NH$_2$), which I have drawn in Fig. 2.2, but I have also found that hexadecyl- and octadecylamine produce similar results. Tetradecylamine has an extremely low solubility in water, and so
Figure 2.1  The relative concentration of different phosphate anions as a function of pH, as a fraction of the total phosphate within the system.

Figure 2.2  Schematic showing the chemical structure of tetradecylamine, the primary amine used in this work. Its constituent molecules are hydrogen (white), carbon (grey), and nitrogen (blue).

In this work is confined to the oil-water interface and the bulk oil.

**Effect of Primary Amines Upon pH**

Primary amines (e.g., octadecylamine, tetradecylamine) in an aqueous solution act as proton acceptors, and so increase the pH of any aqueous solution that contains them [13]. As in the case of phosphate discussed previously, charged and uncharged species of primary amine exist in a dynamic equilibrium. The reaction describing this equilibrium is:

\[
\text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3^+ + \text{OH}^- 
\]
The ratio of the concentrations of the charged and uncharged species is given by a constant, $K_b$ (the base dissociation constant), which is defined as:

$$K_b \equiv \frac{[\text{RNH}_3^+] [\text{OH}^-]}{[\text{RNH}_2^+]}.$$  \hspace{1cm} (2.5)

Given the basic relations:

$$K_a K_b = K_w$$

$$K_w = [\text{H}^+] [\text{OH}^-]$$

where $K_a$ is the acid dissociation constant and $K_w$ is the autoprotolysis constant, we can express this reaction in the more familiar terms of acidity and pH as:

$$K_a = \frac{[\text{H}^+] [\text{RNH}_2^+]}{[\text{RNH}_3^+]}. \hspace{1cm} (2.6)$$

Finally, using $\text{pH} = -\log[\text{H}^+]$ and $\text{pK}_a = -\log[K_a]$ we find that:

$$\frac{\text{RNH}_3^+}{\text{RNH}_2^+} = 10^{\text{pK}_a - \text{pH}}. \hspace{1cm} (2.7)$$

In the case of primary amines with a saturated aliphatic tail, $\text{pK}_a = 10.5$ \cite{13}. This value is practically independent of chain length. Eqs 2.3 and 2.7 are rather instructive. They tell us that significant quantities of $\text{RNH}_3^+$ and $\text{PO}_4^{3-}$ cannot co-exist in the bulk, and that in general the phosphate anion bonds to no more than two fatty primary amines.

**Interfacial Behaviour of Amines**

The effect of the amine being present at an interface (be it air-water or oil-water) has a very large impact upon its charging behaviour and, hence, surface activity. This was observed in the 1930s \cite{2,15} as a pH-dependence of the surface tension of oil-water interfaces containing primary amines. The result most relevant to this work, Fig. 4 from \cite{2}, is shown in Fig. 2.3. This shows the surface tension measured for a 5.4 mM dispersion of hexadecylamine in benzene against an aqueous buffer containing HCl and glycine. It shows that as the pH of the aqueous solution is decreased, a very large drop in surface tension from 34 mN/m to 2 mN/m is observed. This graph allows us to conclude that the
Figure 2.3  

Fig. 4 from Ref. [2]. This shows the surface tension between water and hexadecane as a function of pH. The hexadecane contains 5.4 mM hexadecylamine, pH was adjusted using a buffer containing glycine and hydrochloric acid. Differently shaped data points correspond to different preparation methods of hexadecylamine.

The concentration of primary amine at the interface (its ‘surface excess’) is increasing as the pH is decreased. The mechanism for this is the charging of the amine head group, changing it from RNH$_2$ to RNH$_3^+$, as described in Eq. 2.7. This increased charge increases the solubility of the head group in the aqueous phase, and so increases the surface activity of the molecule [16].

Curiously, the amine charges at a pK$_a$ of approximately 7.8, far below what would be expected in the bulk. This effect can be described by considering Fig. 2.4 and the following calculation. Consideration of the energy required to bring a point charge from infinity up to a surface of electrostatic potential $\psi_s$, and the effects of thermal noise, allow this effect be quantified. At thermal equilibrium, the surface concentration of hydrogen ions, $[H^+]|_{z=0}$, is related to the concentration in the bulk, $[H^+]|_{z=\infty}$, by a Boltzmann relation

$$[H^+]|_{z=0} = [H^+]|_{z=\infty} \exp \left( \frac{-e\psi_s}{k_B T} \right),$$

where $k_B$ and $T$ correspond to the Boltzmann constant and the absolute temperature respectively and $e$ is the fundamental unit of charge. This is re-stated more generally later in the discussion of the Poisson-Boltzmann equation in Eq. 10.
It tells us that at a positively charged interface there will be an excess of negatively charged (OH\(^-\)) ions, and a corresponding scarcity of positively charged (H\(^+\)) ions. I’ve drawn a schematic showing this in Fig. 2.4. Taking logarithms to the base 10 and applying the definition pH \(\equiv -\log_{10}[H^+]\), yields the relation \(16\ 17\):

\[
pH_s = pH_b + \frac{e\psi_s}{k_BT} \log_{10}e \approx pH_b + \frac{e\psi_s}{2.3k_BT}
\]

where pH\(_s\) and pH\(_b\) correspond to the pH at z = 0 and z = \(\infty\) respectively. Note that the sign of \(\psi_s\) can be both positive or negative, meaning that positively charged interfaces (such as fatty amine monolayers) will lead to a basic pH shift and negatively charged surfaces (such as fatty acid monolayers) will lead to an acidic pH shift. This also leads to an equivalent shift in the effective pK of the system, which explains the form of the graph in Fig. 2.3. The pK at the interface, pK\(_s\), and the pK in the bulk, pK\(_b\), are related by \(17\):

\[
pK_s = pK_b - \frac{e\psi_s}{2.3k_BT}.
\]

This makes the connection between the pH-dependent surface activity of the amine shown in Fig. 2.3, the pH of the bulk solution, and the charge of the head group explicit. The lower the pH of the aqueous sub-phase, the higher the surface activity of the amine. This leads to an equivalent shift of the pK\(_a\) of the amine to more acidic values - approximately 7.8 - which implies a surface potential of approximately 200 mV. This value has been measured by multiple observers \(18\ 19\).

This calculation is not limited simply to hydroxyl ions, but is relevant to all monovalent ions. If large or multivalent ions such as phosphate are present the situation is complicated somewhat. The finite size of the ions reduces their concentration near the interface, and the interactions between multiple monovalent head groups and a single multivalent ion (such as the interaction between RNH\(_3^+\) and HPO\(_4^{2-}\)) means corrections to the form of the electric field near the interface are required \(18\).
2.1.3 Analogous Systems: Acid Soaps, Crystallisation, and the Effect of Counter-ions

The interaction between charged lipids and counter-ions is not limited to amines. A great deal of work has also focused on the binding of acid soaps to a variety of counter-ions, and the stoichiometries and structures these interactions yield [20, 21]. This work is motivated to a great degree by the use of fatty acids and acid soaps in the production of personal care and household cleaning products. The importance of inducing or inhibiting crystallisation during product processing makes knowledge of these systems, and similar ones, economically valuable [22–25]. The literature on this subject is vast, and not covered here, but the recent work of Fameau et al. makes for an instructive case study [3, 26, 27].

This work looked at the interaction between a number of fatty acids and the structures they formed when bound to various organic counter-ions in aqueous solution. The majority of this work focused on the result of binding between 12-hydroxy stearic acid and ethanolamine (or hexanolamine). These systems exhibited a rich range of phase behaviour. At room temperature, they typically form needles. The needles formed are typically hollow, with an internal diameter on the order of 300 nm, and a thickness on the order 200 nm [28]. Remarkably, in spite of this thickness, they contain only 3 or 4 lamellar layers, each separated

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Figure 2.4 Schematic showing the concentration of negative ions near a positively charged insoluble monolayer. The concentration of negative ions decays to the bulk concentration as we move away from the surface.
Figure 2.5  The reversible transition between needle-shaped crystallites to micelles induced by heating and cooling a system of 12-hydroxy stearic acid needles bound to ethanolamine or hexanolamine, described by Fameau et al. [3]. This mechanism is different from the temperature response exhibited by the TAHP studied in this thesis, which is solubility-driven.

by roughly 35 nm. The ordering of the system over such a long distance implies rather strong, long-range interactions between the lamellae. The bending moduli of the lamellae were estimated to be correspondingly stiff: of the order $50 \ k_B T$ [28]. The tubes exhibit a temperature-tunable thickness [29, 30], and when heated above a critical temperature of approximately 65°C they undergo a phase transition from needles to a micellar conformation. This reversible phase transition has been illustrated in Fig. 2.5. This change in conformation was directly related to the stabilisation of the foams stabilised by the needles [3], suggesting potential applications for controlled release of pharmaceutical compounds [31]. The range of conformations offered by these systems has led some workers in the field to propose that lipid-counterion binding may be a fruitful avenue for investigation in a whole range of contexts, from foam destabilisation to synthetic biology [31]. Investigation of analogous systems, such as the temperature responsive fatty ammonium-phosphate system presented in this thesis, offers the chance to extend the applications and relevance of the already-large body of work performed on fatty acids and counter-ions.

2.2 Emulsions

Oil and water do not mix. This immiscibility is characterised by a free energy cost per unit area of contact between the two fluids: the surface tension [32]. Shaking a jar of immiscible fluids does work on the system, leading to the creation of
liquid-liquid surface area and the formation of droplets of one liquid inside the other. This dispersion of droplets soon separates out due to collisions between the droplets. The separation can be prevented by adding a third component, which sits at the interface between the two fluids. This yields a thermodynamically unstable mixture of fluids that is prevented from separating out, in some cases for years. A consequence of this is that emulsions have a very large amount of surface area and a history dependent structure. The component that prevents the liquids from separating out governs, to a great extent, the physics of the resulting system. A great many substances exist that can stabilise an emulsion.

In one of the seminal works on particle-stabilised emulsions, Ramsden noted that proteins, surfactants, and colloidal particles are all capable of stabilising emulsions to one to degree or another [34]. It is the particle-stabilised emulsions that Ramsden first observed that are most relevant to this work, and that I will review here.

2.2.1 Particle-Stabilised Emulsions

Pickering emulsions are emulsions stabilised by solid colloidal particles. They were first observed in the work of Ramsden, and later Pickering, at the turn of the 20th century [34, 35]. They occur when excess surface area is created in a system, and adsorption of colloidal particles onto that interface leads to the formation of a steric barrier to droplet coalescence [36]. Two simple quantitative relations go a long way to describing this phenomenon: the equilibrium height at which a spherical particle sits on an interface, and the energy binding it to the interface. The first of these is determined by the three relevant surface tensions: oil-water surface tension $\gamma_{ow}$, water-particle surface tension $\gamma_{wp}$, and oil-particle surface tension $\gamma_{op}$. Consideration of these three values yields a characteristic angle, the contact angle, $\theta$, which describes the angle at which the three phases (oil, water, a particle) meet. The contact angle is given by [37]:

$$\cos \theta = \frac{\gamma_{op} - \gamma_{wp}}{\gamma_{ow}}. \quad (2.11)$$

The contact angle is, by convention, drawn through the aqueous phase. If $\theta$ is greater than 90°, like for the PMMA particles used in this work, the particles

---

1One consequence of this is the lack of hard-and-fast rules in emulsion science: the chapter on “Unifying concepts...” in surface science in Ref. [33] is 14 pages long. The textbook contains 660 pages.
The contact angle of a particle at a planar oil-water interface. The contact angle is measured through the aqueous phase by convention - in this case the particle is slightly hydrophobic.

A simple argument considering the amount of (energetically expensive) liquid-liquid surface area removed, and the amount of (energetically cheaper) particle-liquid surface area added, leads to an estimate of the attachment energy $\Delta G$ of a colloidal particle at a fluid-fluid interface as [38]:

$$\Delta G_p = \pi r_p^2 \gamma_{ow} (1 - |\cos \theta|). \tag{2.12}$$

This excess surface area can be created by extrusion [39], mixing by shear [40], or liquid-liquid phase separation (either via spinodal decomposition or nucleation) [41]. The structure and surface rheology of the particle layer which surrounds the droplets can be extremely varied. Clegg and co-workers extensively studied the particle multi-layers which jam at the fluid-fluid interfaces, leading to the formation of interfaces in which relaxation to a spherical shape was arrested by the jamming of particles [41-43]. By contrast, Vignati and co-workers found that particle coverages as low as 5% led to the formation of stable Pickering emulsions, provided the particles were free to move at the interface [44].

Despite the complex, history-dependent nature of emulsions, a number of fairly simple qualitative relations can be written down that describe the behaviour of Pickering emulsions under certain ideal conditions. In general, hydrophobic particles stabilise water-in-oil emulsions, whilst hydrophilic particles stabilise oil-in-water emulsions [45]. A simple scaling argument, based on the amount of surface area that a particle dispersion can cover (i.e., the number of particles times
the cross-sectional area of those particles), yields an estimate for the expected scaling of the average droplet radius, $r_d$. This predicts that $r_d$ depends on the volume fraction of particles $\phi_p$ and the volume fraction of dispersed phase $\phi_d$ as:

$$r_d \sim \frac{\phi_d r_p}{\phi_p}.$$  \hspace{1cm} (2.13)

The effects of creating a large excess of surface can also be understood qualitatively, as was most recently investigated by French et al. \cite{47}. If the quantity of surface area created during emulsification far exceeds the amount of surface area that can be stabilised by the particles, partially-coated droplets can share particles. These are referred to as particle bridges. This covers up energetically expensive liquid-liquid surface area on both droplets and binds them together, which results in the formation of large aggregates of droplets \cite{47, 48}. The effect is rather fine-tuned: the particles must protrude sufficiently far from the surface such that they can be shared by both droplets without the liquid-liquid interface touching, but if the contact angle gets too high, the energy in Eq. \ref{eq:2.12} will not be sufficient to bind the particles to the interface.

In Chapter \ref{chap:pickering-emulsions} I investigate Pickering emulsions, and induce droplet aggregation systematically via particle bridge creation. I show that this can be trivially inhibited by adding TAHP to the system, which acts as molecular stopwatch that coats any remaining surface area before the droplet aggregates can form.

### 2.3 The Electrostatics of Colloidal Particles at Fluid-Fluid Interfaces

The broken symmetry of a fluid-fluid interface leads to behaviour that is qualitatively different from that of colloids in the bulk. Many of these interactions are rather long-ranged, with an effective distance on the order of microns or more. Such interactions can be both repulsive and attractive, and give rise to a rich range of phase behaviour. Here I briefly discuss the spatial variation in the concentration of ions near a charged surface, which is necessary to understand the reaction between the phosphate in the amines in Chapter \ref{chap:electroosmosis}. I discuss the long-range, repulsive, dipole-dipole interaction that this leads to for particles trapped at fluid-fluid interfaces, which is necessary to understand the behaviour of the ordered particles in Chapters \ref{chap:ordered-particles} and \ref{chap:ordered-aggregation}.
2.3.1 Electrostatics and Charged Interfaces in a Solvent

Colloidal particles have a propensity to sit on the interface between two immiscible fluids. Typically, one of these fluids is polar and the other is not. The polar fluid has a high dielectric constant $\epsilon_{\text{high}}$, and non-polar fluid has a low dielectric constant $\epsilon_{\text{low}}$. We now have two things to consider: the broken symmetry of the interface, and a colloidal particle that traverses the interface. In the polar fluid, charge groups on the surface of a particle can dissociate from one another. This gives rise to an electrostatic potential at the surface of the particle, $\Phi_s$, that differs from that in the bulk fluid. This attracts (and repels) charges already present in the water to the interface of the colloidal particle. On the non-polar side, charge groups cannot dissociate. This leads to an asymmetric charge distribution around the particle. This is shown schematically in Fig. 2.7 [4].

In such a system, the density of charge groups on the non-polar side is treated as zero.\footnote{This is an idealisation. Effects due to partial dissociation of surface charge groups on the aqueous side the minimum charge concentration possible is 100 nM,}
due to auto-dissociation of water. I will start by considering the electrostatics of the system on the aqueous side of the colloid, and the structure of the charges near its surface. I will then go on to discuss the implications this asymmetric charge distribution has when two colloids are near each other.

The charge density as a function of distance from the particle surface can be modelled by considering the electrostatic interactions between the charged surface groups, the ions in the bulk, and the effects of temperature. At equilibrium, for an ion of valence $z_i$ with bulk concentration $c_{i,0}$, the concentration of a charged species $i$ at a point at electrostatic potential $\Phi$ deviates from the concentration in the bulk as \[ c_i(r) = c_{i,0} \exp\left(\frac{-z_i e \Phi}{k_B T}\right) \] (2.14)

where $k_B$ and $T$ and the Boltzmann constant and the absolute temperature, and $e$ is the fundamental unit of charge. This makes explicit the balance between interaction energy and entropy in this system. Interaction energy between the ions and the charged surface favours structure, and either an increase or a depletion of the concentration of that ionic species near the particle. By contrast, it is entropically favourable for the ions to disperse homogenenously into the solvent. This change in the local concentration of ions near the surface has an effect upon the local electrostatic potential. This can be quantified by considering Poisson’s equation and Eq. 2.14 Consider a solution containing $N$ different ionic species of valency $z$. The Poisson-Boltzmann equation describes the spatial behaviour of the electrostatic potential $\Phi$ in a salt-containing aqueous solution near the surface of a charged particle \[ \frac{d^2 \Phi}{dr^2} = -\frac{e}{\epsilon_0 \epsilon_{high}} \sum_i z_i c_{i,0} \exp\left(\frac{-z_i e \Phi}{k_B T}\right). \] (2.15)

This leads to a rather structured region of both positively and negatively charged ions at the surface of the particle, referred to as the ‘electrical double layer’. A number of lengthscales exist to describe the physics of the electrical double layer. In Fig. 2.7 I’ve drawn the Debye length $\kappa^{-1}$ and the Guoy-Chapman length $l_G$. The Debye length is the lengthscale over which the electrostatic potential near a charged surface in a solution decays (this is shown in the next few equations) \[ [51, 52]. \] The Guoy-Chapman length refers to the lengthscale over which the non-polar side, as well as partitioning of the charges between the polar and non-polar phase can be observed under certain conditions, and lead to a wealth of effects (see e.g., Refs. [49] and [50]). I discuss some of these effects in Sec. 2.3.3
concentration of ions decays to bulk values away from the surface \[53, 54\]. A number of equations can be written to down that quantify the structure of the double layer and the electrostatics related to it.

If the potential at the surface of the particle is sufficiently weak, the concentration of the charge sufficiently low, and the particle is not porous (i.e., we can treat it as a hard, impermeable surface), the right-hand side of Eq. 2.15 can be re-written as \[51, 52\]:

\[
\frac{d^2\Phi(r)}{dr^2} = \kappa^2 \Phi(r) 
\]

(2.16)

and Eq. 2.15 can be solved. The electrostatic potential as a function of the distance from the surface of the particle can be written as:

\[
\Phi(r) = \Phi_s \exp(-\kappa r) 
\]

(2.17)

where \( \kappa^{-1} = \left( \frac{\epsilon_0 \epsilon_{\text{high}} k_B T}{\sum_i (z_i e)^2 c_i,\text{bulk}} \right)^{-1/2} \).

Eqs. 2.15 and 2.18 describe most of the physics shown in Fig. 2.7. They tell us that ions in solution are attracted to charged surfaces, which explains the behaviour of the amines in Sec. 2.1.2. The presence of these charges at the surface make the apparent electrostatic potential die off more rapidly than would be expected. The Debye length, \( \lambda^{-1} \), shown in Fig. 2.7, is the characteristic lengthscale of the exponentially decaying electrostatic potential. This tells us that adding salt to a solution reduces the strength of the repulsive interactions between the particles. The presence of this layer of charges has important consequences for when two colloids are near each other at an interface, as I will discuss in the next section.

### 2.3.2 Dipolar Interactions Between Particles at the Fluid-Fluid Interface

A particle trapped at a fluid-fluid interface has an asymmetric distribution of charges surrounding it, like the one shown in Fig. 2.7. This arises from charge groups on the surface of the particle being able to dissociate more freely in a polar solvent than in a non-polar one.\(^3\) The asymmetric charge distribution gives

\(^3\)This statement, whilst certainly true in some cases, is a matter of some controversy - as I discuss in Sec. 2.3.3.
Figure 2.8  Schematic showing the repulsive dipole-dipole interactions between two colloidal particles whose dipole moments cannot re-orientate. The resulting interaction is repulsive, and described by Eq. 2.19. After Fig. 4 in Ref. [5].

Each particle an effective electrostatic dipole moment. For particles trapped at the fluid-fluid interface, with identical surface chemistry, these dipole moments cannot re-orientate and so the pair-potential between two particles due to this interaction is repulsive. This has been drawn schematically for a pair of colloidal particles in Fig. 2.8.

At long distances, where \( \kappa r \geq 10 \), the interaction potential between two colloidal particles separated by a distance \( r \) at the interface is described by [4, 55]:

\[
\Phi(r) = \frac{1}{8\pi\epsilon_0\epsilon_{low}} \frac{p_{\text{eff}}^2}{r^3} \tag{2.19}
\]

where \( p_{\text{eff}} = \frac{2\epsilon_{\text{high}} q \epsilon_{\text{low}}^{-1}}{\epsilon_{\text{low}}} \) is the effective dipole moment of the particles, and each particle carries a surface charge \( q \). This has a number of notable features. The interaction potential behaves like that of repulsive dipoles in air, with the dipole moment of each particle related to the surface charge density and the size of the particles. The potential depends explicitly on the dielectric constant of the non-polar medium, \( \epsilon_{\text{low}} \). Electrostatic interactions in non-polar media (i.e., ones with a low dielectric constant) are significantly stronger than in polar ones, and the resulting dipole-dipole interactions between the particles are correspondingly more powerful. Distilled water which, due to auto-dissociation of \( \text{H}_2\text{O} \), has a minimum ionic concentration of 100 nM and so a Debye length \( \kappa \approx 0.7 \, \mu\text{m} \) makes for a good case study of this. Spreading colloidal particles at an air-water interface leads to ordered 2-dimensional crystals. Lattice spacings in these crystals can be as large as 10 \( \mu\text{m} \) for particles of diameter 240 nm, implying an
interaction potential of order 100 $k_B T$ \cite{5}. As in the bulk, adding salt to the water screens the electrostatic interactions between the particles. Eq. 2.19 also predicts scaling of $\Phi(r)$ on the Debye screening length as $\Phi(r) \sim \kappa^{-2}$, suggesting that the repulsive interactions can be weakened by adding salt into the solution, driving aggregation. I discuss the experimentally observed behaviour of colloidal particles at the fluid-fluid interface in the next section, along with examples of where their behaviour deviates from that described by Eq. 2.19.

### 2.3.3 Experimental Studies and Deviations from Expected Behaviour

For a system of particles at air-water interfaces with a monovalent salt present in the aqueous phase, Eq. 2.19 is often quantitatively correct \cite{4,5,55}. Multiple workers over the last 3 decades have found that colloidal particles, when placed at an interface, order over very long length scales on the order of 1 - 10 $\mu m$ \cite{5,56,57}. Eq. 2.19 also shows that the addition of salt to the aqueous sub-phase will lead to the aggregation of the particles. This was shown to be the case in a number of papers in the 1990s, in which addition of salt to the aqueous sub-phase induced the aggregation of the particles into clusters with fractal dimensionality \cite{56,58,59}.

When the non-polar phase is not air, but rather a non-polar oil, deviations from the behaviour described by Eq. 2.19 are observed. Horozov et al found that reducing the contact angle of colloidal particles at the octane-water interface from $129^\circ$ to $115^\circ$ resulted in aggregation of previously ordered particles \cite{57}. It was argued that the stability of the colloidal monolayer in this case arose not from the repulsive dipole-dipole interactions due to charge asymmetry, but from long-range Coulombic interactions from dissociated charge groups trapped on the particle surface. It was predicted that the potential from such an interaction would exhibit scaling with the particle radius $r_p$ as $\Phi(r) \sim r_p^4$. Masschaele et al argued that the origin of the discrepancy is a failure of Eq. 2.15 to account for the finite size of ions, and the effect this has upon the screening of the electrostatic interactions \cite{60}. This led to a reduced scaling exponent of the inter-particle potential with $\kappa$. Regardless of the origins of the anomalous effects, both of these groups report that the interaction between the particles scales as $\sim r^{-3}$ \cite{4,61}. Eq. 2.19 is therefore still qualitatively true, but the correct treatment of the effective dipole moment $p_{\text{eff}}$ in Eq. 2.19 particularly its dependence on particle
size and salt concentration, is an open problem in need of model systems with which it can tackled. In Chapter 7 I develop such a system.

2.3.4 Colloids, Topology, and Curved Surfaces

On a flat surface, repulsive particles arrange themselves hexagonally, with the particles spaced by a single characteristic distance [62]. Two factors will prevent this from happening. Firstly, if there are insufficient particles it will be entropically favourable for the system to undergo a transition to a disordered state [63]. Secondly, if the interface is no longer flat, but rather curved, the lattice must distort to accommodate the curvature. Here I discuss the second feature. It is known that any hexagonal patterning of a sphere must include at least 12 pentagonal defects. Curiously, this fact is relevant to the structure of lattices of colloidal particles on a spherical droplets. In the next few sections I will show why this is, and how these defect patterns manifest themselves when there are large numbers of colloidal particles in the system.

The Euler Characteristic and Triangulations of a Sphere

Hexagons tile on a flat surface, they do not tile on a sphere. A mixture of pentagons, hexagons, and heptagons, however, does. This is familiar from both the arrangement of tiles on a football, and the arrangement of molecules in a buckyball. This occurs as a consequence of 3 important quantities: the angular defect, $\delta$, of a single vertex, the total angular defect, $\Delta$, of a closed polygon, and the Euler characteristic, $\chi$, for that closed polygon.

The angular defect of a vertex of some closed, convex polyhedron $P$, which is connected to $E$ edges, is given by [64]:

$$\delta_n = 2\pi - \sum_{E} \phi_i$$

where $\phi_i$ is the $i$th dihedral angle between the edges. This has been drawn for the case of a tetrahedron in Fig. 2.9. The sum of the dihedral angles at each vertex is always less that $2\pi$. The total sum of $\delta$ for all vertices, $V$, is always equal to $4\pi$ [64]:

$$\Delta = \sum_{V} \delta_n = 4\pi.$$
Remarkably, this quantity is related directly to the numbers of edges, $E$, vertices, $V$, and faces, $F$, that the polyhedron has by the Euler characteristic, $\chi$, which is given by [65]:

$$\chi = V - E + F. \quad (2.22)$$

Euler showed that, if the polyhedron is closed and convex, like in Fig. 2.9, then $\chi = 2$. Pólya later related these two statements explicitly, finding [64, 65]:

$$\Delta = 2\pi (V - E + F) = 2\pi \chi. \quad (2.23)$$

The relevance of this statement to the locations of repulsive particles on a sphere now needs to be made explicit. This requires two things. The first of these is a fundamental theorem of topology, that any polyhedron which is both closed and convex may be continuously deformed into a sphere [65]. That is, the Euler characteristic of a polygon which occupies the surface of a sphere is the same as that of a sphere ($\chi = 2$). The second of these is the mechanism by which the strength of a defect in the structure of a lattice can be quantified. For the case of a hexagonal lattice (i.e., one with 6-fold rotational symmetry) this is given by the charge of the defect [66]:

$$q = 6 - c \quad (2.24)$$

where $c$ is the local co-ordination number of the defect (5 for a pentagon, or 7 for a heptagon). The appearance of these arrangements of particles has been drawn, along with their values of $q$ and $c$, in Fig. 2.10. Each pentagon and heptagon-shaped defect contributes an angular defect, $\delta$, of $\frac{\pi}{3} \times q$ to the total angular
defect of the polygon, $\Delta$ [67, 68]. We know from Eq. 2.23 that $\Delta$ is constrained to a total value of $4\pi$. Arranging the particles is then a case of adding sufficient pentagons and heptagons such that $\Delta$, for the polygon the particles form, adds up to $4\pi$.

This makes explicit the constraints placed upon the geometry of the points at a spherical surface, but does not tell us what arrangements the particles will take, only the ones they can’t take. Constructing lattices with a number of particles, $n$, where is $n$ rather small, is fairly easy. A spherical football, for instance, requires 12 pentagonal tiles and 20 hexagonal ones ($q = 6 - 5$, $\chi = \frac{\pi}{3} \times q \times 12 = 4\pi$). However, Eq. 2.23 permits any combination of tilings, so long as the condition $\chi = 4\pi$ is satisfied. The question of finding the minimum energy arrangement of repulsive particles on a sphere is rather more difficult, and was first (unsuccessfully) tackled by Thomson in 1904 [69]. Monte Carlo methods allow the minimum energy arrangement of order 100 particles to be found [70]. However, for a larger number of particles the number of metastable states separated by less than 0.01% of the total elastic energy of the system proliferate, and the problem becomes rather challenging [6, 70, 71]. Recent developments by a number of groups have succeeded in tackling the problem for very large ($n \approx 10^5$) particles both on a sphere [6, 72, 73], and on complex, non-spherical curved geometries such as capillary bridges of both positive and negative Gaussian curvature [7]. I do not review the methods used here, but I will give a brief overview of the phenomenology of the systems for comparison with my results in Chapter 7.

The way in which the particles on a sphere satisfy the condition in Eq. 2.21 depends on the area density of particles $\phi_a$, and the stiffness of the lattice that
they form. For fairly small numbers of particles (order 100 or fewer), 12 isolated defects of charge 1 are found \[71\]. For a large number of particles, the lattice structure becomes rather complicated. Some of the features characteristic of a spherical lattice with large numbers of particles are shown in Fig. 2.11. The creation of extra pairs of 5-7 defects lowers the elastic energy of the system, whilst ensuring Eq. 2.21 remains satisfied \[6\]. As the number of particles is increased to order 400 and above, the total number of defects grows, and the defect pairs aggregate into large grain boundaries which terminate inside of the lattice \[6, 72, 73\]. The emergence of this behaviour with increasing numbers of particles is shown in Fig. 2.11. Theoretical results suggest that, for lattices with a sufficiently low stiffness, pentagonal motifs (such as that shown in Fig. 2.11a) emerge. Such patterns have not yet been seen experimentally, suggesting scope for further study of such systems, and the need for model systems to investigate them.

**Figure 2.11** Comparison of the theoretically (a. from Ref. \[6\]) and experimentally (b. from Ref. \[7\]) observed structures of colloidal particles confined to a spherical geometry. Highlighted regions in both images correspond to defects in the hexagonal lattice. The systems contain a.) 5882 and b.) approximately 200 particles.
Chapter 3

Methods

In this chapter I give the technical details of some of the experimental methods used in this thesis. I include a methods section that describes how the experiment itself was performed in the relevant section of each results chapter.

3.1 Rotor Stators

The emulsions studied in this system were dispersed by applying high shear rates to the fluids. Rotor-stators were used to do this due to their portability, the small volume of the samples used (1-5 ml), and the control over shear rate that they afford.

A rotor-stator, shown Fig. 3.1, works by rotating the inner rotor at high angular velocities, generating high shear rates in the gap between the rotor and the stator. The rotor has a radius \( r_{in} \), a rotor-stator gap distance \( \delta \). It rotates with angular frequency \( \omega \), and the shear rate in the gap is given by \( \dot{\gamma} = \frac{\omega r_{in}}{\delta} \). For a rotor stator in which the mean flow speed in the shear gap is \( v = \frac{\omega r_{in}}{2} \) with a continuous phase fluid of density \( \rho \) and viscosity \( \eta \), flow is turbulent if \( Re \gtrsim 1000 \) \[74\], where \( Re \) is the Reynolds number:

\[
Re = \frac{v\delta \rho}{\eta}.
\]  
(3.1)

At the shear rates studied in this thesis, \( Re \leq 1000 \), and droplet break-up occurs in the laminar flow regime. In this flow regime viscous shear stresses act on (and parallel to) the droplet-fluid interface \[74\] \[75\]. Under these conditions semi-
Figure 3.1  Left: Typical rotor-stator setup used for the experiments. Shear rate can be varied between 0 and 40000 s\(^{-1}\) using the control box; the sample is raised into the flow field of the rotor-stator attachment using the lab jack. Right: Close-up of the rotor stator-attachment, showing the inner rotor and the outer stator. The inner diameter of the stator is 5 mm, the gap width between the rotor and the stator is 150 \(\mu m\).
quantitative relations can be made between the shear rate and the size of the droplets present in the system. These quantities are related by the dimensionless capillary number, Ca:

\[
Ca = \frac{\eta \dot{\gamma} r}{\gamma_{ow}}
\]  

(3.2)

where \(\gamma_{ow}\) is the oil-water surface tension, \(\dot{\gamma}\) is the applied shear rate, \(\eta\) is the viscosity of the continuous phase, and \(R\) is the radius of a droplet. Above a critical value for the capillary number, \(Ca_c\), viscous shear stresses cause droplets larger than a critical radius, \(r_c\) to break up. For a water-dodecane (\(\gamma_{ow} = 52 \text{ mN/m}\)) system in a two-dimensional, simple shear flow such as that in a rotor-stator, \(Ca_c\) is on the order 0.1 - 1. This yields \(r_c = 0.25 - 1.4 \text{ mm}\) for \(\dot{\gamma} = 8000 - 40000 \text{ s}^{-1}\) [75]. This relation, however, is only semi-quantitative; complications arise due to interfacial elasticity due to the presence of surface active materials [76], and the formation of smaller droplets upon the subjection of a very large droplet to a stress far greater than that required to cause break-up [77].

Two different rotor-stators were used to make emulsions in this work: a Polytron PT-3100 (Kinematica) with a 5mm internal diameter attachment, as shown in Fig. 3.1 and an IKA Ultra-Turrax S10N with a 5G attachment. The characteristics of both of these rotor-stators are shown in Table 3.1 and outlined in Ref. [78].

<table>
<thead>
<tr>
<th></th>
<th>Polytron</th>
<th>Ultra-Turrax</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap Width (mm)</td>
<td>0.15</td>
<td>0.1</td>
</tr>
<tr>
<td>Rotor Outer Radius (mm)</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Operating RPM</td>
<td>5000 - 25000</td>
<td>8000 - 30000</td>
</tr>
<tr>
<td>Shear Rate (s(^{-1}))</td>
<td>8200 - 41000</td>
<td>16000 - 60000</td>
</tr>
</tbody>
</table>

Table 3.1 Operating parameters of the two rotor-stators used in this work.

The two models are broadly comparable. The overwhelming majority of the emulsions studied in this work were made using the Polytron, as it offers greater control over the applied shear rate. In the case of the neutron scattering study, the Ultra-Turrax was used due to the higher shear rates that can be attained. The Ultra-Turrax also has the added benefit of being significantly smaller, and so is more portable than the Polytron.
### 3.2 Surface Tension

Two different methods are used to measure liquid-liquid surface tension in this work. For most systems, where the droplet can be visually distinguished from the surrounding fluid, the pendant drop shape analysis method has been used. For fluids with matching refractive indices, the maximum droplet volume method was used. I discuss the technical aspects of both of these methods here, along with some relevant aspects of surface tension.

#### 3.2.1 Pendant Drop Tensiometry

Pendant drop tensiometry is a method for obtaining the surface tension of a fluid-fluid interface by measuring the shape of a droplet and its distortion due to buoyancy. In the case of a droplet suspended from a needle, and in the absence of any interfacial elasticity, surface tension will pull the droplet into a spherical shape. The buoyancy force due to the difference in density \( \Delta \rho \) between the two fluids will elongate the droplet. Young and Laplace showed that at a curved fluid-fluid interface described by radii of curvature \( R_1 \) and \( R_2 \), there is a pressure difference, \( \Delta P \) which is balanced by the surface tension, \( \gamma \), and buoyancy such that: [18]:

\[
\Delta P = 2\gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right). \tag{3.3}
\]

The effect of the radii of curvature upon the shape of a droplet is shown in Fig. 3.2. Both of these droplet shapes are relatively easy to realise experimentally. A spherical droplet can be formed by creating a sufficiently small droplet (the term ‘sufficiently small’ is quantified using the capillary length, and is discussed later in this section) or using fluids with a sufficiently high surface tension. A capillary bridge may be formed by sandwiching a droplet between two glass cover slips, or by depositing a droplet on a cover slip that has had specific regions treated with a superhydrophobic coating. Examples of these two methods are shown in Fig. 1 of Ref. [11] and Fig. 1 of Ref. [10].

Introducing a term for deformation of the droplet geometry due its weight yields
the Young-Laplace equation of capillarity \[79\]:

\[
\frac{2}{R_0} - y \frac{\Delta \rho g}{\gamma} = \frac{1}{R_1} + \frac{1}{R_2}.
\]  

Equation (3.4)

In the absence of significant interfacial elasticity, this equation completely describes the profile of pendant and sessile droplets. Eq. (3.4) has a number of rather important consequences for the results contained in this thesis. At the apex (bottom) of a pendant drop, at \( y = 0 \), the gravity-dependent term \( \frac{\Delta \rho g}{\gamma} \) disappears, leaving \( \frac{2}{R_0} = \frac{1}{R_1} + \frac{1}{R_2} \). That is, the apex of any pendant or sessile drop, no matter how large, may be approximated as a sphere. Secondly is that any sufficiently small droplet with a sufficiently high surface tension will be negligibly deformed by gravitational forces, and so will have the shape of a spherical cap.

**What Does ‘Sufficiently Small’ Mean?**

For any pendant or sessile drop with sufficiently small radii of curvature, gravity will not significantly deform the drop, and so any sufficiently small drop,

\footnote{Pendant as ‘pendulous’ (or hanging), sessile as in ‘sitting’}
independent of contact angle, will have the geometry of a truncated sphere. Quantitatively, the extent of deformation of the droplet due to weight is described by the Bond number, Bo, where:

$$Bo = \frac{\Delta \rho g R_0^2}{\gamma}. \quad (3.5)$$

For a successful pendant drop measurement, it is preferable that the Bond number is large (i.e., $Bo \gg 1$). This is because the method measures the deviation of the drop profile from that described by surface tension alone, and so maximal gravitational distortion is preferable. Equivalent to the Bond number, one can define a lengthscale, $\lambda_c$, called the capillary length:

$$\lambda_c = \sqrt{\frac{\gamma}{\rho g}}. \quad (3.6)$$

In this thesis, $\lambda_c = 1 - 2.6 \text{ mm}$, and $\gamma = 10 - 50 \text{ mN/m}$. If $R \gg \lambda_c^2$, then the droplet will be significantly deformed from a spherical cap geometry, and it is possible to determine the surface tension from the droplet profile.

The experimental set-up for measuring surface tension via pendant drop profile is shown in Fig. 3.3. This shows a drop of water, suspended from a 1.83 mm diameter stainless steel needle, in a bath of dodecane. The drop has a volume of approximately 10 $\mu l$, and so a radius of approximately 1.3 mm. This corresponds to a Bond number of 63.7. For a bare dodecane-water interface ($\gamma \approx 53 \text{ mN/m}$ [80]), $\lambda_c = 2.6 \text{ mm}$. This is, therefore, a suitable droplet volume for a surface tension measurement, though measurements performed on a droplet much smaller than this will yield significant errors.

The droplet profile is extracted using an edge detection algorithm, which numerically calculates the first spatial derivative of the intensities. The droplet profile is then expressed in terms of x- and y-coordinates. The local curvature at each section of the droplet profile is then found using the relation [79, 80]:

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{x \left(1 + \left(\frac{dy}{dx}\right)^2\right)^{1/2}} - \frac{d^2x}{dy^2} \frac{1}{1 + \left(\frac{dx}{dy}\right)^{3/2}} \quad (3.7)$$

The right-hand side of Eq. 3.7 is extracted from the droplet shape. Eqs 3.4
Figure 3.3  Photograph of a pendant drop during experiment (left) and schematic of same system (right). The system is a 10 µl water droplet in dodecane, the needle diameter is 1.83 mm.

3.2.2 Adsorption Kinetics and Interfacial Elasticity

Surface tension is a dynamic quantity. At very short times, before any surface active molecules have adsorbed onto the droplet surface, the surface tension is simply the bare fluid-fluid surface tension. At long time scales, once the system has equilibrated, the presence of surface active molecules significantly reduces the surface tension. The change in the surface tension with time can be used to infer the rate of adsorption of surface active molecules on to the interface, and their final concentration. If the adsorption of the molecules on to and off the interface is governed by diffusion alone, the following expressions can be used to describe the surface tension of the system at very short and very long time scales \[^{83, 85}\]:

\[^{2}\]This, along with some extra steps not discussed here, are covered more fully in Refs. \[^{81, 82}\].
\( \gamma(t) \sim \gamma_0 - 4RTc \left( \frac{D_{\text{short}}t}{\pi} \right)^{\frac{1}{2}} \) for \( t \to 0 \) (3.8)

\( \gamma(t) \sim \gamma_{\text{eq}} + \frac{RTT^2}{c} \left( \frac{\pi}{D_{\text{long}}t} \right)^{\frac{1}{2}} \) for \( t \to \infty \) (3.9)

where \( D \) is the diffusion constant of the surface active molecules, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( c \) is bulk concentration of the molecules. \( \Gamma \) is called the surface excess, and is the amount by which the concentration of surface active molecules at the fluid-fluid interfaces exceeds that of some equivalent slice in the bulk. The differing diffusion constants at differing timescales account for back-diffusion of molecules from the interface at long timescales, which is assumed to be negligible at short times. These relations are used in Sec. 6.3.3 to describe the behaviour of the surface tension of TAHP-stabilised emulsion droplets at the short timescales relevant to emulsification.

**The Effects of Interfacial Elasticity**

Eq. 3.4 is only valid in the absence of significant interfacial elasticity. This makes it suitable for measuring the surface tensions of most simple fluids in the presence of low molecular weight surfactants. However, presence of a rigid interface due to, for instance, proteins or insoluble surfactants, complicate the physics of the system and often makes the drop shape history-dependent [86, 87]. This allows droplet shape analysis to be used both as a *quantitative* tool for studying the surface tension of simple fluid-fluid interfaces, and as a *diagnostic* tool to ascertain the presence of physics not described by the Young-Laplace equation. The extent to which the droplet profile deviates from a shape described by the Young-Laplace equation is given by the fit error (units of length), which is simply the RMS horizontal distance between the model drop shape and the measured drop shape. The effects of interfacial elasticity, and its effects upon droplet shape, are studied experimentally in Secs. 4.4 and 5.4 of this work.

### 3.2.3 Alternative Method: Maximum Drop Weight

A number of factors can make drop shape analysis unsuitable for measuring surface tension. If the density difference between the two fluids is too small the
deformation of the drop will be negligible. If the surface tensions between the fluids are small then the droplet will be too small to measure. Finally, if the refractive indices of the fluids are sufficiently similar, then the droplet profile cannot be obtained by imaging the samples. Several alternative methods exist to measure the surface tension in these instances. A brief summary of these can be found in Chapter 2 of Ref. [18]. In the case of the system studied in Chapter 7, in which the refractive indices of the fluids are matched, the maximum weight method can be used to estimate the surface tension between two fluids to within ±10%.

The maximum detachment weight method uses the same apparatus as the pendant drop method. Pendant drops suspended from a needle are shown in Fig. 3.4. One of the drops (Fig. 3.4, right) has fluids with approximately matched refractive indices. For a needle with inner diameter \( r_n \), the maximum drop volume that can be suspended from the needle is given by the force balance between the surface tension, \( \gamma \), and the effective weight of the drop, \( V_{\text{max}}\Delta \rho \): [18]

\[
V_{\text{max}}\Delta \rho g = 2\pi r_n \gamma
\]

where \( g \) is the local acceleration due to gravity. This method can be first calibrated using index-mismatched fluids for comparison of results using the drop shape analysis method. The water droplet in air shown in Fig. 3.4, left has a surface tension of 72.5 mN/m as measured using the pendant drop method,
in good agreement with literature values \[18\]. The needle in Fig. 3.4 has an inner diameter of 1.59 ±0.13 mm, and the maximum drop volume which remains attached to it was found to be 32.3 ±0.8 µl, yielding a surface tension of 63.5 ±7.9 mN/m. Repeating this experiment using a water drop in dodecane yielded surface tension values of 43 ±4 mN/m (compared with a drop shape measurement of 47.2 ±0.1 mN/m). This suggests that the drop volume method, using the set-up applied here, yields surface tensions in reasonable agreement with the values obtained using drop shape analysis, albeit with much larger errors on the order of 10%. Whilst unsuitable for precision measurements of surface tension, for which a Blodgett trough and a Wilhelmy plate would be required, the accuracy and precision of the measurements performed here are more than sufficient for the experiments performed in Chapter 7.

### 3.3 Interfacial Shear Rheology

Interfacial shear rheology is a method that measures the viscoelasticity of an interface in response to an applied shear strain. It functions in a very similar way to bulk shear rheology, which is described extensively in the literature \[88\]. The major difference between bulk and interfacial shear rheology is dimensionality: bulk stresses are measured in units of force per unit area, whilst interfacial stresses are measure in units of force per unit length.
Interfacial shear rheology uses a probe to apply a sinusoidal shear strain $\gamma(t)$ and measures the resulting stress $\tau(t)$. These are described by [89, 90]:

\[
\gamma(t) = \gamma_0 \sin \omega t \\
\dot{\gamma}(t) = \omega \gamma_0 \cos \omega t \\
\tau(t) = G^*_s \gamma_0 \sin (\omega t + \delta).
\]

$G^*_s$ relates the amplitude of the applied to strain to the amplitude of the measured stress. The latter relation is analogous the similar expression relating the Young’s modulus, $E$, to the stress and strain in an elastic material: $E = \frac{\tau}{\gamma}$. Applying the trigonometric relation $\sin(\omega t + \delta) = \cos(\delta)\sin(\omega t) + \sin(\delta)\cos(\omega t)$ allows the stress to be broken into two components:

\[
\tau = \gamma_0 G'_s \sin(\omega t) + \gamma_0 G''_s \cos(\omega t) \quad (3.14)
\]

where: $G'_s \equiv G^*_s \cos(\delta)$ and $G''_s \equiv G^*_s \sin(\delta)$. Two contributions to the stress in the system can now be seen. One of these is the in-phase, elastic stress, which is related to the applied strain by $G'_s$. The other of these is the out-of-phase, viscous stress, which is related to the applied strain by $G''_s$. Dividing the definitions of $G'_s$ and $G''_s$ by one another yields the measure of the extent to which the material is viscous or elastic:

\[
\frac{G''_s}{G'_s} = \tan(\delta). \quad (3.15)
\]

This makes explicit the relation between the physics of the material and the forces applied by the rheometer. The input strain is known, the resulting stress is measured, and the phase angle, $\delta$, between the two is measured, giving us $G'_s$ and $G''_s$. The relative extent to which the elastic and viscous forces contribute to the total stress is then quantified by $\delta$. For the very elastic films I study in this thesis, $\delta$ can be as small as 1°.

### 3.3.1 Sub-phase flows in interfacial shear rheology

When an interfacial geometry applies a strain to an interface, it also applies a strain to the surrounding sub-phases. This means that the sub-phases

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3In practice, the machines used in this work do the reverse: they apply a stress and measure the strain. An equally valid mathematical formalism can be derived by reversing the in-phase and out-of-phase components in Eq. 3.13, resulting in a complex viscosity rather than a complex elastic modulus.
also contribute to the apparent rheological parameters of the interface. This
is undesirable, and removing the contribution from sub-phase flows to the
measured rheological parameters of the interface can require extensive numerical
calculations [91]. In general, interfacial shear measurements are very sensitive to
this effect [92, 93]. This is because the rheological moduli of the interface are
typically rather small, with interfacial viscosity, \( \eta_s \) typically on the order \( 10^{-2} \)
mN s / m. In this thesis I study very strong, elastic interfaces, and it is not
necessary to correct for sub-phase flows. However, a brief discussion of sub-phase
flows is necessary to determine the relative merits of the geometries discussed
in the next section. For measurements on simple viscous systems, the extent
to which interfacial effects contribute to a measurement performed on a system
is described by the ratio of interfacial viscosity, \( \eta_s \), and the average sub-phase
viscosity, \( \eta_b \). This ratio is expressed as a dimensionless number known as the
Boussinesq number, Bo [91, 94]:

\[
Bo = \frac{\eta_s \frac{v}{L_s} P_s}{\eta_b \frac{v}{L_b} A_b} = \frac{\eta_s}{\eta L} \tag{3.16}
\]

This contains a number of length scales. \( L_s \) and \( L_b \) are the length scales over
which velocity field decays at the interface and in the bulk, respectively. \( A_b \) is
the surface area of the geometry that penetrates into the bulk fluids, and \( P_s \) is
the perimeter length of the geometry at the interface.

An interfacial geometry sensitive to interfacial effects, then, will minimise surface
area and maximise perimeter length. Equivalently, it will minimise the length
scale \( L = \frac{L_s A_b}{L_b P_s} \). Interfacial effects dominate the measurement when \( Bo \gg 1 \). In
certain cases, expressions \( L_s \) and \( L_b \) can be derived analytically by solving the
Navier-Stokes equation for low Reynolds numbers. These length scales have been
calculated numerically for the Double Wall Ring (DWR) geometry using finite
difference methods in Ref. [91] and analytically for the bicone in Ref [95]. Both
of these geometries are described in the next section and are used in this work.
More details discussions of the drag on interfacial objects and the flow fields near
them can be found in Ref. [96]. For elastic interfaces Bo is a complex number.
This is fully discussed in [94], but the large rheological moduli of the TAHP film
make it an unnecessary consideration here.
3.3.2 Experimental Method

Two different interfacial shear rheology set-ups are used in this work: a bicone and a Double Wall Ring (DWR). They are made of different materials: the DWR is made of Pt-Ir alloy, whilst the bicone is made of stainless steel. Both geometries are two-dimensional Couette geometries with a circular symmetry that generates rotational strains.

Pt-Ir Double-Wall Ring (DWR)

The DWR is a double-Couette geometry which consists of a 1.5 mm thick Pt-Ir ring (shown in Fig. 3.6). The set-up is fully described by Vandebril et al. in Ref. [91] and the relevant patent paper [97]. It maximises the Boussinesq number (defined in Eq. 3.16) by having both an interior and exterior contact line with the interface. It also has a large radius, which maximises contact line length. This makes it sensitive to interfacial viscosities on the order $10^{-5}$ N s / m [91]. It also has the added benefit of being compatible with commercial rheometers. Numerical calculations show that for steady shear experiments on an air-water interface, $L_s$ corresponds approximately to the dimensions of trough (i.e., 3.5 mm for the inside channel, 4 mm for the outside channel), and that $L_b \sim 4$ mm [91]. The interfacial geometry was attached to a DHR-2 Hybrid Rheometer. The DHR-2 is a controlled stress rheometer, but is also fitted with a feedback loop that allows it to effectively operate in a controlled strain mode. This gives the apparatus rather poor performance compared to a true controlled strain rheometer when probing strongly non-linear properties of a material (i.e., in the brittle region of the TAHP film studied later).

Stainless Steel Bicone

The bicone is a single Couette geometry that consists of a 22 mm diameter stainless steel biconical disk. Like the DWR, this is then lowered onto the air-water interface (shown in Fig. 3.7). If required, a second sulphate is then added on top. The sub phases are contained within a 44mm diameter glass trough. The geometry was attached to a TA AR-G2 rheometer which could operate in both strain-controlled and stress-controlled mode. The large relative ratio of surface area to perimeter length of the bicone means that the data obtained
are significantly noisier than for those obtained using the DWR. This makes it suitable for studying elastic films, but unsuitable for studying rather weak viscous films.

### 3.4 Confocal Fluorescence Microscopy

Confocal fluorescence microscopy is an optical fluorescence microscopy method used in this work to record both 2-dimensional and 3-dimensional images of the sample. The confocal microscope used in this work is a Zeiss LSM T-PMT/LSM700 inverted confocal laser scanning microscope. I give details of the experimental set-up in Sec. 4.2.6 and so I only give an overview here of some of the image analysis and reconstruction methods.

The microscope illuminates a specimen using a monochromatic, polarised laser light source. The optics in the microscope contain a pinhole, which scans the image line-by-line, so that only a very small area of the specimen is imaged at one time. This excludes light from outside of the optical plane, leading to increased effective spatial resolution and an improved signal-to-noise ratio in the resulting image [98]. The intensity transmitted through the pinhole is recorded using two photomultiplier tube detectors (PMTs). One PMT records the fluorescence

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**Figure 3.6** Photograph and diagram showing the DWR geometry attached to the rheometer and the dimensions of the set-up. The centre of the trough is on the left-hand side of the diagram.
signal emitted back through the objective lens, and the other measures the signal transmitted through the sample. The image taken then contains information with a depth of field on the order of the dimensions of the pinhole [98]. The imaging stage is moved in the vertical direction by means of an electric motor, which means a depth in real space can be assigned to each slice of the image, and a three-dimensional image reconstructed. This is illustrated in Fig. 3.8.

Acquiring a fluorescence micrograph requires that the sample be tagged with a fluorophore. The excitation and emission spectra of the fluorophores used in this work vary significantly [99, 100]. This variation need not be due to the presence of several different fluorophores: the excitation and emission spectrum of a single fluorophore can depend on the physical and chemical properties of the sample in which it is embedded [99]. The differing emission and excitation spectra allow fluorescence signals to be isolated by illuminating at specific frequencies. Passing the emitted fluorescence signal through a band-pass filter and a dichroic mirror, as applied in this work, then allows only a range of light wavelengths to reach the PMT. This permits the separation of fluorescence signals from fluorophores in different regions of the sample, and so determination of the sample structure from its fluorescence signal. Some examples of this in this thesis can be found in Figs. 4.14 (NBD-tagged TAHP) and 6.22 (NBD-tagged PMMA).
Figure 3.8  The construction of a 3-dimensional image using confocal micrographs. 144 individual slices (3 of which are shown in the image) are summed together to produce the composite image at the bottom. Image acquisition took 20 minutes.
3.4.1 Reconstructing Three-Dimensional Images

The image in Fig. 3.8 now contains spatial information in three dimensions that corresponds to the spatial density of fluorophores in the sample. This can be used to generate projections of the sample at various angles. I have presented two examples of this, taken using different imaging parameters, in Figs. 3.9 and 3.10. Here, the individual volume pixels ('voxels') that make up the image can be seen as individual slices. The voxel depth 317 nm in Fig. 3.8 and 500 nm in Fig. 3.9. A comparison of the qualities of the two images is informative as to the methods used in this work.

Fig. 3.9 was taken using an air-immersion objective with a relatively low numerical aperture (NA = 0.6, 40× magnification). The system consists of two fluids which have matching refractive indices ($n_{\text{fluids}} = 1.421$), and particles with a refractive index that differs from the fluids ($n_{\text{particles}} = 1.489$). There are two notable distortions present in the rotated image in Fig. 3.9. The droplet shown in Fig. 3.9 is a spherical cap, yet its initial projection in Fig. 3.9b, shows it to be an oblate spheroidal cap. This is due to the so-called ‘goldfish tank’ effect, in which the apparent contraction or expansion of an object occurs due to the refractive index of the medium that surrounds the microscope objective being bigger or smaller than the refractive index of the sample. In samples with a homogeneous refractive index, using objectives with a comparatively low numerical aperture, the depth moved by the microscope objective must be multiplied by a factor $k$, where [101–103]:

$$k = \frac{n_{\text{sample}}}{n_{\text{medium}}}$$  \hspace{1cm} (3.17)
where \( n_{\text{medium}} \) is the refractive index through which the objective is moved (\( n_{\text{medium}} = 1 \) for air). This recovers the original spherical geometry of the droplet, as shown in Fig. 3.9c.

The second notable effect is the significant axial distortion of the particles. This, again, is due to refractive index mismatches in the system, both within the sample and between the sample and the medium in which the objective is contained \([98, 101]\). The resulting intensity profile of the particles is a convolution of the true shape of the particles and the point spread function of the set-up \([98, 104]\). This second effect leads to significantly larger distortions in the z-direction of the sample. In the case of the air-immersion objective used in Fig. 3.9, it renders the axial location of the individual particles difficult to determine, but allows for a reasonable estimate of the droplet aspect ratio.

Both of the effects discussed above are sensitive to both the numerical aperture of the objective used and the refractive indices of the components of the system. Both can be mitigated by minimising the difference in the refractive index of the sample and the medium in which the objective is contained. A droplet imaged using a 40× magnification, oil-immersion objective (\( n_{\text{medium}} = 1.518, n_{\text{sample}} = 1.421 \)) to image a sample with same parameters as in Fig. 3.9 is shown in Fig. 3.10.

The objectives used to image Figs. 3.9 and 3.10 have a number of advantages and disadvantages. The oil-immersion objective (40× magnification, NA = 1.3) yields images with excellent lateral resolution and minimal axial distortion, but is unsuitable for imaging specimens at the elevated temperatures, as this can warp the lenses and damage the glue used to seal the objective. This makes it suitable for imaging the samples at room temperature, which I mostly study in Chapter 6. Using the air-immersion objective causes significant distortion of the image, but can be used at elevated temperatures. This makes it unsuitable for acquiring images with full 3-dimensional information when micron-scale axial resolution is required. It can, however, be used to assign 3-dimensional coordinates if the geometry of the system being imaged is known, and the sample is sufficiently sparse. It is used to this end to track micron-sized colloidal particles on a droplet surface in Chapter 7 at a range of temperatures, between 20 and 65°C.
Figure 3.10  Reconstructed 3-dimensional confocal image (left) of fluorescent PMMA particles at the oil-water interface of a water droplet. The image can rotated (right) to display the z-coordinates of the particles at the interface, and to reconstruct the droplet geometry. The drop in intensity between each slice on the rotated image is an imaging artefact caused by the depth resolution being approximately one-half that of the lateral resolution. This can be corrected by interpolation for presentation purposes, but this adds no information.
3.4.2 Combining Transmission and Fluorescence Signals to Determine Sample Geometry

In most of this work, the objects studied are confined to a surface with a well-defined geometry (i.e., the surface a spherical emulsion droplet), and so the shape of the object can be inferred simply from the fluorescence signal. In other specimens, such as those in which the only fluorescently tagged objects in the sample a sparsely distributed, the signal from the transmission PMT can be used to give further structural information about the sample. An example of this is shown in Fig. 3.11. The fluorescence micrograph shows fluorescent PMMA particles, which are located at the surface of a water droplet. The transmission PMT signal clearly shows the water droplet. Both images have been reconstructed from a series of confocal scans at increasing depth through the sample, as described in Fig. 3.8.

3.4.3 Construction of Imaging Chambers

This thesis images samples over the course of up to 1 hour. Open samples are typically extensively perturbed by air flow in the room and flow from the subphases. To minimise this effect, custom-built imaging chambers were made. This was achieved by removing the bottom of a 7 ml glass vial using a precision glass cutter, and attaching a ground glass cover slip of approximately 100 µm thickness to the bottom. The samples are imaged at elevated temperatures (up to 70°C) in a continuous phase of dodecane. Extensive efforts were therefore made to choose a glue that did not contaminate the sample. Many block copolymer epoxy resin glues, such as Araldite, dissolve in organic solvents or melt at elevated temperatures. This results in micelles forming in the continuous phase, which leads to the formation of bulk colloidal crystals. Whilst visually arresting, this is undesirable. It was also necessary to hydrophobise the cover slip to minimise wetting of the cover slip by the aqueous emulsion droplets. The use of a continuous non-polar phase also makes this challenging. Treatments with tri(methoxy)octadecyl-silane (TMODS) again lead to the dissolution of the coating at elevated temperatures, and anomalous charging of colloidal particles in the bulk dodecane. Treatment with TMODS also often led to large quantities of precipitate coating the cover slip, giving it poor optical qualities.

The following combination of methods was found to make imaging chambers that
Figure 3.11  Confocal micrograph of an emulsion droplet showing both fluorescent (white) PMMA particles at the interface and the transmission PMT signal. a.) The fluorescence image shows the signal from the particles only. b.) The transmission-PMT image shows the droplet geometry. c.) Combining the two by summing and renormalising the intensity values shows both.
Figure 3.12 Imaging chambers used for confocal microscopy experiments. a.) Side view and b.) bottom view of chamber is shown.

did not contaminate the sample. Imaging chambers were sealed using Norland Optical Adhesive 61, a UV-curing glue, that was exposed to UV light for 20 minutes. To prevent dissolution of the glue in the dodecane, the imaging chambers were then heat-hardened in an oven at 50°C for one week. This was found to cause no contamination of the sample. Sintered glass fluorimetry cuvettes were used as a control to confirm this. The imaging chambers were then hydrophobised using a solution of 20% v/v dichlorodimethylsilane (DCDMS, Sigma Aldrich, ≥ 98.5% purity) in hexane for 3 hours. After treatment, the chambers were then rinsed gently with hexane. Finally, the chambers were placed in a drying oven overnight at 50°C to remove any residual hexane from the rinsing process. The imaging chambers used are shown in Fig. 3.12.

3.5 Fluorescamine as an Assay for Primary Amines

Measuring the quantity of TAHP formed at the interface allows a number of inferences to be made about the nature of the interfacial reaction. In the case of a planar interface, separating the TAHP from the fluid sub-phases is trivial and achieved by pouring the sample through filter paper. In the case of the emulsion system, an fluorimetric chemical assay was used to determine the residual concentration of primary amine in the dodecane. This was achieved by dispersing emulsion supernatant in a concentrated 10 mM solution of fluorescamine in acetone. The chemical structure of fluorescamine is shown in Fig. 3.13. Fluorescamine is a non-fluorescent compound that binds to primary amines. The resulting compound is fluorescent and, if a saturating concentration
of fluorescamine is used, yields a fluorescence signal that is proportional to the primary amine concentration in a suspension or solution [105, 106].

### 3.6 Single Particle Tracking

Particle tracking of confocal images is performed using trackpy, the Python implementation of the Crocker-Grier particle tracking algorithm [107, 108]. A full description of the Crocker-Grier particle tracking algorithm can be found in Ref. [108], and so I will only briefly review some of the technical aspects of it here.

In this technique, an image is treated as a 2- or 3D array of values between 0 and an upper limit (255 for 8-bit images), which correspond to measured intensity. The algorithm takes an input time-series of images $A(x, y, t)$, and numerically applies a band pass filter to it. The lower and upper lengthscales of the bandpass filter typically correspond to 1 pixel and the diameter of the particles respectively. The algorithm then locates in each image a set of local maxima, $f(x, y, t)$ that correspond to the initial guesses of the particle locations. These initial guesses are then refined by finding the centre of mass of each particle. This allows the particle centres to be located to within 0.5 pixels ($x, y \rightarrow x', y'$). Finally, the algorithm links together particle centres in each images by performing a search algorithm between frames, yielding the particle trajectories $p(x', y')$. This is outlined in Figure 3.14.
Small Angle Neutron Scattering (SANS)

Small angle neutron scattering is a scattering technique that allows the structure of a material to be probed on a wide range of lengthscales (approximately 1-150 nm). It has a number of advantages over small-angle x-ray scattering. Arguably the most important of these is the facility with which the scattering length densities of samples can be tuned, most simply by varying the ratio of hydrogen and deuterium present in the system. It also has certain disadvantages. It requires large, specialised facilities such as nuclear reactors or spallation sources, and neutron sources typically have a much lower luminosity than synchrotron radiation facilities. The SANS2D facility at the ISIS spallation source was used in this work to probe the structure of the TAHP film at molecular lengthscales.

A schematic of the geometry of the small-angle neutron scattering experiment performed in this work is shown in Fig. 3.15. I here discuss some of the relations between the structure of the sample and the experimental geometry shown in the figure. I begin by considering the case of a beam of neutrons with flux $I_0(\lambda)$.
neutrons m⁻², and a detector at an angle \( \theta \). The number of neutrons detected at a detector which occupies solid angle \( \Delta \Omega \), is given by [109]:

\[
I(\lambda, \theta) = I_0(\lambda) \Delta \Omega \eta(\lambda) T V \frac{d^2 \sigma}{d \Omega d \lambda}(q)
\]  

(3.18)

where \( \eta \) is the detector efficiency, \( T \) is the fraction of neutrons transmitted by the sample, \( V \) is the sample volume, and \( \frac{d^2 \sigma}{d \Omega d \lambda}(q) \) is known as the ‘differential cross-section’. The first five terms in the equation are machine-dependent, and not discussed here. More important is the differential cross-section, which contains the structural information contained in the sample.

\[
\Delta q = \frac{4 \pi}{\lambda} \sin \frac{\theta}{2}
\]

Figure 3.15  *The geometry of a scattering experiment, in which a beam of neutrons each with momentum \( \hbar q \) is incident upon a sample. The momentums a scattered from the sample with momentum \( \hbar q' \). The scattering is assumed to be elastic (i.e., \( q = q' \)), and so the change in momentum of the neutron, \( \Delta q \), due to interaction with the sample only changes its direction.*

It can be shown [62] that the differential cross-section (and, hence, the neutron flux detected at a given angle) and the structure of the material that scatters the neutrons are related by [110]:

\[
\frac{d \sigma}{d^2 \Omega}(q) = \left| \left| \int_V \rho(\mathbf{r}) e^{i \mathbf{q} \cdot \mathbf{r}} d^3 \mathbf{r} \right| \right|^2
\]  

(3.19)

where \( \rho(\mathbf{r}) \) is the scattering length density of the sample. If the particles in the sample are point particles, this corresponds to a set of delta functions located at the positions of the particle centres, multiplied by a numerical factor that describes how strongly the particles scatter the incident beam. In words: the intensity detected by a scattering experiment is proportional to the modulus-
squared of the time-average of the Fourier transform of the structure of the material being studied.

In the case of the individual scatterers having a non-point-particle form, it is convenient to break $\rho(r)$ into two different functions: $\rho_{\text{form}}$, which describes the structure of the individual particles, and $\rho_{\text{structure}}$ which is a set of delta functions located at the particle centres. $\rho(r)$ can then be re-expressed as the convolution of $\rho_{\text{structure}}(r)$ and $\rho_{\text{form}}(r)$:

$$
\rho(r) = \rho_{\text{structure}}(r) \ast \rho_{\text{form}}(r) = \int d^3r' \rho_{\text{structure}}(r') \rho_{\text{form}}(r - r')
$$

(3.20)

The expected intensity detected in an experiment (Eq. 3.19) is then given by the Fourier transform of Eq. 3.20 multiplied by its complex conjugate. Applying the convolution theorem one can perform Fourier transforms on $\rho_{\text{structure}}(r)$ and $\rho_{\text{form}}(r)$ separately, and express the differential cross-section as the product of the two Fourier transforms:

$$
d\sigma = \langle S(q)P(q) \rangle.
$$

(3.21)

$S(q) = \mathcal{F}(\rho_{\text{structure}}(r))$, is referred to as the structure factor, $P(q) = \mathcal{F}(\rho_{\text{form}}(r))$, as the form factor. $\mathcal{F}$ denotes the Fourier transform operator.

### 3.7.1 Modelling TAHP Scattering: Caillé Theory

In the following sections I briefly derive the structure and form factors of the material studied in this thesis (i.e., TAHP), discuss the effects of q-resolution smearing of the data, and give a brief overview of the key features of Caillé theory.

The TAHP is modelled as a set of strongly-interacting lamellar sheets that undergo thermal fluctuations in the structure factor. The intensity is modulated by a form factor that accounts for interference effects due to the non-zero thickness of the lamellae. Whilst both paracrystalline and Caillé theories are apt for

---

4This can be stated as: $\mathcal{F}(f \ast s) = \mathcal{F}(f) \cdot \mathcal{F}(s)$, where $f$ and $s$ are functions (in this case the form and structure factor or our scatterer), $\mathcal{F}$ is the Fourier transform operator, and $\ast$ denotes convolution. In words: ‘The Fourier transform of the convolution of two functions is equal to the product of the two functions Fourier transformed separately’.

51
studying such systems, here I apply the Modified Caillé Theory (MCT) developed by Nallet et al to study surfactant bilayers, which has been used more recently on a system similar to the one studied in this thesis.

**Powder Averaging and Treatment of Fluctuations**

Caillé theory neglects fluctuations in the form factor, $P(q)$, considering only fluctuations in the structure factor. This amounts to assuming that fluctuations in the bilayer thickness are uncoupled from fluctuations in the separations of the bilayers. Further, uncoupling in-plane and out-of-plane form factors ($P_\perp(q_\perp)$ and $P_z(q_z)$, respectively) means Eq. 3.21 can be re-written as:

$$\frac{d\sigma}{d^2\Omega}(q) = P_\perp(q_\perp)P_z(q_z)\langle S(q) \rangle$$

(3.22)

In the case of the system consisting of a single crystal, or containing some non-zero average degree of orientation, one expects the intensity detected to depend upon the axis around which the detector is rotated. In this thesis, a sample with no net inter-crystallite orientation is studied and so the powder-average of the expected intensity must be calculated. Applying the powder-averaging theorem of Wilson leads to a scattering signal that is azimuthally averaged in reciprocal space, and allows the TAHP to be effectively modelled as a one-dimensional system, multiplied by a factor of $\frac{2\pi}{d} q^{-2}$ to account for the scattering due to in-plane form factor of the lamellae. Eq. 3.21 can thus be re-written in terms of a normalised, thermally-averaged, 1D structure factor $S_1(q_z)$, and a 1D form factor $P_z(q_z)$:

$$\frac{d\sigma}{d^2\Omega}(q) = \frac{2\pi}{d} P_z(q_z) S_1(q_z) \frac{1}{q^2}.$$  

(3.23)

The derivation of the terms $S_1(q_z)$ and $P_z(q_z)$ is briefly outlined in the next section.

**Structure Factor $S_1(q_z)$**

Caillé theory models the structure factor of the system a set of N thin sheets, spaced along the z-axis by an average repeat distance, d. Caillé modelled the effect
of thermal fluctuations by allowing the $n^{th}$ lamella to undergo small fluctuations in positions around position $nd$ \cite{116}. The displacement of that layer at transverse position $r_\perp$ is referred to as $u_n$. This corresponds to a real space density function of the form:

$$\rho(r_\perp) = \delta[z - u_0(r_\perp)] + \delta[z - d + u_1(r_\perp)] + ... + \delta[z - (n - 1)d + u_{n-1}(r_\perp)]$$

$$= \sum_{0}^{N-1} \delta[z - nd - u_n(r_\perp)].$$

(3.24)

Performing the Fourier transform directly, thermally averaging, and multiplying by the complex conjugate yields the 1-dimensional structure factor:

$$S_1(q_z) = N + 2 \sum_{n=1}^{N-1} (N - n) \cos(n q_z d) \langle e^{-i q (u_n - u_0)} \rangle.$$  

(3.25)

The terms to the left of the $\langle ... \rangle$ term make up the structure factor for a perfectly ordered one-dimensional lattice of points spaced by distance $d$. This yields a set of equally spaced peaks of equal height. The effect of the term within the angled brackets is to introduce the effect of paracrystalline disorder into the lattice. The consequence of this is an exponential decay in the height of the higher-order peaks and the presence of diffuse scattering which alters the scaling exponent of the scattered intensity near the Bragg peaks.

Assuming that the fluctuations are small and Gaussian-distributed, the thermally-averaged term in Eq. 3.25 can be modelled as $\langle e^{-i q (u_n - u_0)} \rangle = e^{-\frac{q^2 d^2}{2}} \langle (u_n - u_0)^2 \rangle$. Performing the integral detailed in Ref. \cite{116} yields the normalised 1-dimensional structure factor for the system \cite{112, 119}:

$$S_1(q_z) = 1 + 2 \sum_{n=1}^{N-1} \left(1 - \frac{n}{N} \right) \cos(n q_z d) e^{-\frac{q^2 d^2}{2}} \langle (u_n - u_0)^2 \rangle.$$  

(3.26)

Here:

$$\langle (u_n - u_0)^2 \rangle = \frac{\eta d^2}{2 \pi^2} (\gamma + \ln(\pi n))$$  

(3.27)

\footnote{Ref. \cite{116} is not widely available: an English translation has been included in the back in the form of an appendix. The model is also discussed in detail in Ref. \cite{117}, in Chapter 2 of Ref. \cite{118}, and summarised in Ref. \cite{111}.}
and:
\[
\eta = \frac{h^2 q_h^2 k_B T}{8\pi \sqrt{K B}}, \quad \gamma \approx 0.577. \tag{3.28}
\]

$B$ and $K$ are, respectively, the compressional and bending moduli of the system, and $h$ is the order (1, 2, ...) of the Bragg peak being studied. It can be shown that \cite{112, 116, 117}, in the region of a Bragg peak situated at $q_h$, the structure factor leads to divergence of the scattered intensity as:
\[
S_1(q_z) \sim |q - q_h|^{-1+\eta}. \tag{3.29}
\]

By fitting the data to the above model in the region of the $h$th-order Bragg peak located at $q_h$, the scaling exponent near the peak can be determined. This scaling exponent is modified by the Caillé parameter, which contains information about the mechanical moduli of the bilayers. Typical values for the Caillé parameter range from 0.03 for tightly bound acid soap bilayers to 0.4 for surfactants in a dilute lamellar phase \cite{26, 112}. In oriented samples, or samples in which one of the moduli is known, this allows the mechanical moduli to be calculated \cite{120, 121}. In the case of the powder system studied in this thesis, it allows changes in the mechanical moduli to be studied by comparing the scaling exponent of the intensity (in the vicinity of a Bragg peak) at different temperatures.

**Finite Lamellar Thickness: the Form Factor $P_z(q_z)$**

The structure factor discussed in the previous section is apt for lamellar systems in which $d \gg \delta$ (i.e., the spacing between the lamellae is much bigger than their thickness). In the case where $d \approx \delta$ the non-zero thickness of the lamellae leads to a decrease in the intensity of the Bragg peaks. This is accounted for using the form factor introduced by Nallet and co-workers \cite{112}.

The form factor of the TAHP crystallites is modelled as a square wave of length $\delta$ and height $\Delta \rho$. $\delta$ corresponds to the lengthscale over which there is contrast in the scattering length density (SLD), and $\Delta \rho$ is the difference in SLDs of the polar and non-polar regions of the lamellar system. This assumes that the main contribution to the scattered intensity is due to the contrast in SLD between the polar region and the non-polar region of the bilayer, and that fluctuations in the
Figure 3.16  Schematic illustrating the square wave profile of the scattering length density across a single lamella. The choice of structure drawn is rather arbitrary - head groups need not be clearly distinct from one another. Water molecules (shown here) may not be present between the lamellae; likewise, non-polar solvent molecules (not shown here) may be present in the non-polar region.

form factor are negligible compared to those in the structure factor. Explicitly:

$$\rho_{\text{form}}(z) = \begin{cases} 
\Delta \rho : -\delta/2 < z < \delta/2 \\
0 : \text{elsewhere}
\end{cases} \quad (3.30)$$

The polar region consists of the ammonium phosphate ‘head groups’ of the TAHP, plus any water present in the system (SLD = \(\rho_{\text{polar}}\)). The non-polar region consists of the aliphatic tails of the tetradecylamine, along with any dodecane which has been incorporated into the TAHP (SLD = \(\rho_{\text{non-polar}}\)). The height of the square wave is then the difference in SLD between the polar and non-polar regions, \(\Delta \rho\). This ‘box-model’ form factor is illustrated in Fig. 3.16.

The Fourier Transform of Eq. (3.30) is

$$\mathcal{F} (\rho(z)) = \int_{-\infty}^{\infty} \rho(z) e^{-iqz} dz$$

$$= -\frac{\Delta \rho}{iq} \left( e^{-iq\delta/2} - e^{iq\delta/2} \right)$$

$$= \frac{2\Delta \rho}{q} \sin \frac{\delta}{2q}.$$  

(3.31)
Multiplying this by its complex conjugate yields the form factor:

\[ P_z(q_z) = 4(\Delta \rho)^2 \frac{\sin^2 \frac{\delta}{2}}{q^2}. \]  
(3.32)

The form factor contains two key elements: the modulation of the intensity of the Bragg peak due to the oscillations in the sine wave, and the scaling of scattering intensity at low-q. Maxima in scattered intensity will be absent where \( \delta = d \), and reduced significantly if \( \delta \approx d \). The form factor also predicts that the scattered intensity scales as \( q^{-2} \), however accounting for powder-averaging leads to a predicted scaling in the scattered intensity of \( q^{-4} \).

### 3.7.2 Effects of thermal motion at high-q

On top of the scattering described by the form and structure factors, scattering was observed at intermediate- and high-q values \( (q \geq 0.1 \text{ Å}^{-1}) \) due to the thermal motion in the sample. This takes the form of an intensity that decays with increasing \( q \), and which is not described by a single power law. The structure factor (Eq. 3.26) already accounts for thermal motion within the TAHP crystallites, however the aliphatic chains of the amines will also project from the TAHP-dodecane interface, which is the most likely source of this diffusive motion. The scattering from such motion is well-described by a Lorentzian of the form:

\[ I(q) = \frac{1}{1 + (Lq)^2} \]  
(3.33)

where \( L \) is the lengthscale over which correlations in the diffusive motion decay.

### 3.7.3 Accounting for Finite \( q \)-Resolution

The model described above is used to extract the physical parameters of the system by fitting the model to the measured data. Before this can be done, the limited wavelength resolution of the experimental set-up must be accounted for. This is has the effect of smearing out some features predicted by the model. Smearing of the scattering data due to the finite \( q \)-resolution of the experimental apparatus is taken in to account using the procedure described by Pedersen and Barker [122], in which the modelled scattering intensity at \( q_0 \) is convolved with a
Gaussian smearing function $R(q, q_0)$, described by:

$$I(q_0) = \int_{q_{\text{min}}}^{q_{\text{max}}} R(q, q_0) I(q) \, dq$$

$$R(q, q_0) = \frac{1}{\Delta q \sqrt{2\pi}} \exp \left[ -\frac{(q - \bar{q})^2}{2(\Delta q)^2} \right].$$

(3.34)

where $\bar{q}$ is the mean scattering vector and $\Delta q$ is the q-resolution of the instrument.

**3.7.4 Summary**

The final equation is obtained by inserting Eqs. 3.32 and 3.26 into Eq. 3.23, adding on the Lorentzian in Eq. 3.33, and performing the convolution according to Eq. 3.34. The physical parameters $\delta$ and $\eta$ are then extracted from fits to the data. During analysis, this formula is then multiplied by a scale factor obtained from fitting to account for the volume fraction of scatterers in the sample. The features of MCT may be summarised as follows:

- At low-$q$, the intensity scattered from a powder-averaged sample scales as $q^{-4}$.

- Thermal fluctuations lead to Bragg peaks exhibiting a power-law divergence in the structure factor of the form $S_{\text{MCT}}(q) \sim |q - q_0|^{-1+\eta}$. [116]

- The scaling exponent of the scattered intensity in region of the $h^{th}$ order Bragg peak at $q_h$ is related to the mechanical moduli of the lamellae by $\eta = \frac{h^2 q_h^2 k_B T}{8\pi \sqrt{BR}}$, where $m$ is the integer order of the Bragg peak. [114, 123]
Chapter 4

TAHP: Molecular and Mesoscopic Structure, Stoichiometry, Formation Kinetics

In this chapter I discuss the properties of a thick, elastic film that forms at the oil-water interface due to the attraction of negatively charged phosphate ions to positively charged fatty amines. The film consists of tetradecylamine, a water-insoluble primary amine, and hydrogen phosphate, an oil-insoluble salt, and is referred to as tetradecylammonium hydrogen phosphate (TAHP). This chapter focusses on the chemical and structural aspects of the film: the conditions under which it forms, the rate at which the film forms, its structure, and its chemical constituents. I also introduce the emulsions that the film stabilises, and relate their stability directly to the properties of the film. Finally, I will use the emulsions to probe the microscopic structure of the film. I argue that on molecular length scales the film structure is identical at both spherical and flat interfaces, and that the scattering results describe the film structure under both conditions. Once the properties of the film are established, I will go on to study its rheology, temperature response, and applications in encapsulation in Chapter 5.
4.1 Introduction

Interfacial films appear in a great many shapes and sizes. The interfacial films that prevent emulsions coalescing can consist of low molecular weight surfactants, insoluble surfactants, proteins, polysaccharides, colloidal particles, and even viruses. The formation of interfacial films plays a role in particle synthesis, energy storage, the synthesis of anti-reflective coatings, and allowing us to breathe. In spite of the relative simplicity of most synthetic interfaces, at least compared to their biological counterparts, important qualities can be introduced by the presence of a single interfacial component. These qualities include the lowering of the fluid-fluid surface tension, the emergence of an interfacial elasticity, and a selective permeability. One rather under-explored topic in this area are the films formed by components that are contained in separate, immiscible fluids, and that react with one another only at the fluid-fluid interface. In this chapter I introduce such a system: the thick, elastic films formed by condensation of oil-insoluble phosphate anions on to a charged layer of water-insoluble tetradecylamine molecules.

Interactions between multiple components, mediated by an oil-water interface, can be used to create complex interfacial films with novel properties [124, 125]. The mechanisms by which such interfacial layers are formed include polyelectrolyte complexation [126, 127], interfacial polymerisation [128, 129], and particle-surfactant complexation [130, 131]. These mechanisms typically lead to the formation of an insoluble, rather elastic layer that is confined to the interface and can sustain non-equilibrium droplet shapes [132, 133]. Such elastic multi-layer films have received recent attention for their potential applications in encapsulation and controlled-release of active molecules for uses in the food and pharmaceuticals industry [134, 135]. These films are often stimulus-responsive and provide a high stability against aggregation and coalescence, but can require rather intensive multi-step processing such as layer-by-layer film formation [126, 136]. One method of avoiding layer-by-layer film fabrication is by dispersing two components in separate, immiscible phases, such that they interact only at the interface [137, 138]. However, encapsulation and film-formation by this method has been explored using only a narrow range of materials. Given the potential range of applications of such systems, a cheap material which creates temperature-responsive films with tunable interfacial rheological properties, and that is suitable for large-scale production, is rather desirable.
In this chapter, the physical and chemical properties of Tetradecylammonium Hydrogen Phosphate films formed at the dodecane-water interface and the emulsions that this film stabilises are studied using Fourier transform infrared spectroscopy (FTIR), small angle neutron scattering (SANS), confocal fluorescence microscopy, and pendant drop analysis. Below a critical pH value (approximately pH 8) and in the presence of hydrogen phosphate in the aqueous phase, tetradecylamine can be seen by visual inspection to form thick films at the dodecane-water interface. Light microscopy shows that these thick films consist of micron-sized, predominately needle-shaped crystallites, which aggregate together to form elastic sheets. Using drop shape analysis, the pH is shown to affect both the kinetics of film formation and the mass of material formed at the interface. This dependence can be directly related to the amount of amine at the interface that is protonated. FTIR spectroscopy shows that the stoichiometry of these films, between pH 5 and 8, is independent of pH, and that the films consist almost entirely of two tetradecylammonium cations bound to one HPO$_4^{2-}$ anion. SANS is then used to infer the molecular properties of the TAHP film by studying TAHP-stabilised water-in-oil emulsions. It is found that the TAHP contains lamellar order at the molecular scale, with a lamellar repeat distance of 37.9 Å. The layers that make up the film interact with one another very strongly, and are found to undergo only rather small fluctuations in position, as shown by the scaling exponent of the scattered intensity in the region of the main Bragg peak. As the system is heated, the scattered intensity at low-q decreases, suggesting dissolution of the TAHP into the liquid phases. Another, co-existing, lamellar lengthscale is observed in the TAHP above 40°C. It is found that this corresponds either to untilting or de-interdigitation of the TAHP molecules, rather than swelling due to solvent incorporation.

4.2 Materials and Methods

The oil used throughout this work is dodecane. Dodecane is a non-polar hydrocarbon with a very low dielectric constant, $\epsilon_r$, and vapour pressure, $V_p$ ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$, $\epsilon_r = 2.0$, $V_p = 18 \text{ Pa}$). Due to its low vapour pressure, it evaporates very slowly, and so is suitable for long studies lasting several days. The water contains 100 mM of phosphate ions. Due to the low dielectric constant of the oil, water is immiscible with the dodecane and phosphate is soluble only

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1 The solubility of dodecane in water is 0.0037 mg/l at 25°C. [139]
in the aqueous phase. The oil contains 1-5 mM of tetradecylamine (TDA, CH$_3$ (CH$_2$)$_{13}$ NH$_2$) which, due to its comparatively small polar head group and large non-polar aliphatic chain, is effectively insoluble in the water. I will vary the pH of the aqueous phase from 5 to 9. This is achieved by using two species of sodium phosphate salt, NaH$_2$PO$_4$ and Na$_2$HPO$_4$, mixed in ratios calculated using Eqn. 23. Minor corrections to the pH were made using 1 M solutions of NaOH or phosphoric acid. Changing the pH has two effects: it varies the relative quantities of HPO$_4^{2-}$ and H$_2$PO$_4^{-}$ in the water, and it increases the concentration of primary amine at the oil-water interface. A schematic showing the early stages of the interfacially mediated reaction, in which only a monolayer is formed at the interface, has already been shown in the introduction, in Fig. 1.1.

### 4.2.1 Sample Preparation

Tetradecylamine ($\geq 95\%$) and dodecane (ReagentPlus, $\geq 99\%$) were purchased from Sigma-Aldrich, UK, and used as obtained. Water was de-ionised and filtered through a Milli-Q reverse osmosis unit (resistivity $> 10^{18} \Omega$m). Sodium hydrogen phosphate salts (monobasic monohydrate and dibasic dihydrate, $\geq 99\%$, Sigma Aldrich, UK) were used as the source of phosphate ions. Minor adjustments to pH were made using 1 M NaOH and 1 M phosphoric acid. All experiments presented here were performed using an aqueous solution of 100 mM H$_n$PO$_{(3-n)}$$^-$$^4$, with the ratio [HPO$_4^{2-}$] / [H$_2$PO$_4^{-}$] in the aqueous phase controlled by varying the initial pH. Salts and primary amines were dispersed in their solvents using a warm ($T \approx 40^\circ$C) ultrasonic bath to ensure complete homogenisation of the samples. This method is also used for samples in all other chapters (Sections 5.2 and 6.2).

### 4.2.2 Fluorescence Methods

Fluorescent doping of the fatty amine film was achieved using 4-chloro-7-nitrobenzofurazan (NBD-Cl, $\geq 98\%$ purity, Sigma-Aldrich, UK), which is known to form fluorescent compounds upon reacting with primary amines [140]. A small quantity ($\leq 5$ mg / 20 ml) of NBD-Cl was added to the phosphate solution and dispersed thoroughly on an ultrasonic bath for several hours at approximately 50$^\circ$C, hand shaking of the vial during this process was also found to aid dispersion. To remove any large, residual aggregates of NBD-Cl, the solution was then passed through a Millex syringe-driven polyethersulfone filter unit with a pore size of
200 nm. Addition of this aqueous solution to a dispersion of tetradecylamine in dodecane led to the formation of fluorescent interfacial films with rheological and solubility characteristics very similar to those of films formed with no NBD present. Fluorescence microscopy images were taken 24 hours after emulsification to allow the fluorophore to react.

In order to measure the residual quantity of primary amine remaining in the emulsion supernatant a fluorimetric assay was used. This consisted of a 10 mM solution of fluorescamine (obtained from Sigma Aldrich UK, ≥ 98% purity) in acetone. 0.67 ml of emulsion supernatant was added to 1.23 ml of fluorescamine solution. Fluorescamine and its use as an assay have been discussed in Sec. 3.5. The mixture was left in a sintered borosilicate glass fluorimetry cuvette to react for one hour. The fluorescence signal from the sample was measured using a Varian Cary Eclipse fluorescence spectrophotometer. The sample was excited at 390 nm, and the peak emission intensity was measured at 483 nm. A calibration was performed for tetradecylamine concentrations between 10 and 300 µM to ensure linearity in the range being studied.

### 4.2.3 Pendant Drop Tensiometry

Pendant drop images were obtained using the Krüss Easy Drop apparatus and accompanying software, which allows for controlled rates and volumes of droplet
injection. Some of the technical aspects of pendant drop analysis have been outlined in Sec. 3.2.1. Measurements were performed in an air-conditioned room at 19±1°C. The dodecane was held in a 6 ml cubic borosilicate glass cuvette. The needle was lowered into the dodecane bath and a pre-determined volume of water was injected at 0.5 ml min⁻¹. Surface tension was measured every 10 seconds.

4.2.4 Fourier Transform Infra-Red Spectroscopy

The functional groups present in the TAHP was determined using all-reflection objective Fourier transform infrared spectroscopy (FTIR). FTIR measurements were performed in reflection mode using a Smiths IlluminatIR spectrometer mounted on top of a Renishaw inVia Raman microscope equipped with a non-contact all-reflection objective (ARO, 10x magnification, Smiths Detection). TAHP synthesis for these experiments was carried out over 60 hours in the crystallisation dishes shown in Figure 4.4. After synthesis, the materials from the dishes were isolated by filtration, washed consecutively with ethanol and hexane, and dried. Samples were prepared by dispersing a small quantity of TAHP (≈ 5 mg) of TAHP powder in 1 ml pentane using an ultrasonic bath, drop casting them on to IR-reflective low-E glass slides (Smiths Detection), and performing the measurement after the pentane had evaporated. A linear baseline subtraction procedure was applied to the spectra after the measurements were performed.

4.2.5 Cryo-Scanning Electron Microscopy

Cryo-scanning electron microscopy was performed using a Hitachi S-4700 Cold Field-Emission Scanning Electron Microscope (Hitachi High-Tech. Europe GmbH, Krefeld, Germany) fitted with a Gatan Alto 2500 cryo-specimen system (Gatan UK, Abingdon, Oxon, UK), using a method adapted for imaging biological specimens [141]. The samples were mounted on brass specimen stubs. The specimen stub was plunged into slushed nitrogen at -210°C, and then rapidly transferred into the preparation chamber and microscope to achieve best sample preservation. The specimen was fractured in the cryo-preparation chamber using a mounted scalpel, and then sputter-coated with ~10nm of 60%:40% gold:palladium alloy for 3 min at 10 mA. Specimens were manually rotated for part of the coating period, to allow for even sputter-coating of rough surfaces, which were almost at right angles to the plane of the stub. An accelerating voltage
of $\sim$5 kV was used to image the sample in the microscope, and both upper and lower detectors were used for imaging.

### 4.2.6 Confocal Fluorescence Microscopy

Confocal microscopy measurements were performed on a Zeiss LSM T-PMT/LSM700 confocal laser scanning inverted microscope with Zeiss ZEN software (Carl Zeiss AG). This set-up can illuminate a sample with up to 4 lasers simultaneously. 405 and 639 nm wavelength 5 mW lasers, and 488 and 555 nm wavelength 10 mW lasers are used to illuminate the samples in this work. Confocal micrographs were obtained using a 40x magnification, planfluorite-corrected, oil-immersion objective (NA = 1.3). Some of the technical aspects of confocal microscopy relevant to this work have been discussed in Sec. 3.4. Images were taken using custom-made imaging chambers which consisted of a 7ml glass vial with the base removed, and attached to a ground glass coverslip using Norland 61 UV-setting optical adhesive. These have been described in detail in Sec. 3.4.3.

### 4.2.7 Small Angle Neutron Scattering (SANS)

Small-angle neutron scattering experiments were performed at ISIS on the SANS2D instrument using TAHP-stabilized water-in-dodecane emulsions. Dodecane with a scattering length density matched (5% v/v h-dodecane, 95% v/v d-dodecane) and off-matched (100% d-dodecane) to D$_2$O (98-atom %, d-dodecane, QMX Laboratories; D$_2$O, Sigma Aldrich) was used. Aspects of small angle neutron scattering have been reviewed to some extent in Sec. 3.7. To maximise surface area and scattering signal, 6.5 mM h-tetradecylamine was used and emulsions were formed at 60000 s$^{-1}$ for 1 min using an UltraTurrax T10 Basic rotor stator with S10N-5G stainless steel attachment (IKA). These values were both somewhat higher than those used in other experiments (typically 1-5 mM and 20000-30000 s$^{-1}$). This yielded droplets qualitatively similar in appearance from those used elsewhere in this work, albeit with a smaller droplet diameter (approximately 20 $\mu$m). The emulsions were then pipetted into 0.5 ml volume, 2mm path length quartz cuvettes held in a temperature-controlled rack (see Fig. 4.17 for the typical appearance of the samples). Incoherent background scattering from the solvents was corrected for by measuring the background scattering from an empty quartz vial, as well as from vials containing the
appropriate ratio of d- and h-dodecane or D$_2$O. Scattering from the solvents was measured at 25, 40, 55, and 65°C with scattering for intermediate temperatures calculated by interpolation. Background subtractions were calculated using relative volume fractions in each phase, which was measured after the experiment by weighing the mass of the two fluid phases after the emulsions had coalesced in response to heating to 80°C. In the case of the measurements performed above 45°C, coalescence and sedimentation of the samples led to over-subtraction of incoherent background, and a small (∼ 5%) reduction to the background subtraction was made.

The SANS2D instrument used in this work, described elsewhere [142], uses a white beam containing neutrons with wavelengths in the range 1.75 - 16.5 Å, where $q$ is determined by time-of-flight. $\Delta q/q$ is taken to be 5%, in line with estimates used elsewhere for the same instrument [142, 143]. Scattering data was reduced using Mantid, with measured intensity being placed on an absolute scale using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene) in accordance with established procedure [144].

Data was modelled using the modified Caillé theory described by Nallet et al [112, 116], which models the powder-averaged scattering from a system of lamellar sheets with a separation, $d$, and bilayer thickness, $\delta$, undergoing thermal fluctuations in the structure factor. I also add a Lorentzian term to describe background scattering at high-q. Details of the model used to describe the data, with particular focus on Caillé theory, can be found in Sec. 3.7, in particular Sec. 3.7.1. When fitting the data, the low-q region of the data was used to fit the scale factor and number of sheets. A further 2 parameters, the Caillé parameter $\eta$, and the lengthscale of the non-polar region $\delta$, are then found from fits to the data in the region of the Bragg peaks. Fits were performed by using the implementation of the Levenberg-Marquardt non-linear fitting algorithm and the NIST SANS data analysis macros in Igor PRO [145] to minimise the value

$$\chi^2 = \frac{1}{N_{\text{points}} - N_{\text{parameters}} - 1} \sum_{N_{\text{points}}} \frac{(I_{\text{obs}} - I_{\text{cal}})^2}{\sigma_{\text{obs}}^2}$$

where $N_{\text{points}}$ is the number of data points, $N_{\text{parameters}}$ is the number of parameters in the model, $I_{\text{obs}}$ and $I_{\text{cal}}$ are the measured and calculated intensities, respectively, and $\sigma_{\text{obs}}^2$ is the variance of the measured value. Least-squares fits and

See Figs. 5.11 and 6.30 for examples of heat-induced coalescence in TAHP-stabilised emulsions.
data analysis for scattering experiments was performed in Igor Pro using the NIST SANS data analysis macros. Scattering length densities for the polar region were estimated using the density of diammonium phosphate, assuming full deuteration of the salt, and for the non-polar region using the volume of an aliphatic chain, \( v \), using the empirical formula obtained by Tanford, \( v = 27.4 + 26.9n_c \) \(^{[146]} \), with \( n_c = 14 \), yielding \( \rho_{\text{polar}} = 3.85 \cdot 10^{-6} \text{Å}^2 \) and \( \rho_{\text{non-polar}} = -4.73 \cdot 10^{-7} \text{Å}^2 \).

4.3 TAHP Film Formation

Initially, the films are studied by visual inspection. This is done using a 7 cm diameter crystallisation dish. 25 ml of water, containing 100 mM phosphate ions at pH 7, is first added to the dish. 25 ml of dodecane, containing 5 mM tetradecylamine, is then gently added on top. As a control experiment, de-ionised water containing no phosphate ions is also used in an identical experiment in a different crystallisation dish, and 25 ml of dodecane containing 5 mM tetradecylamine is added on top. A photograph of the crystallisation dishes, after the films have been left to form for 60 hours, is shown in Fig. 4.2, along with a schematic of the experimental set-up.

The difference in appearance of the crystallisation dishes in Fig. 4.2 is striking. In the absence of hydrogen phosphate, the system does not appear to have changed. If hydrogen phosphate is present in the aqueous phase, a white film of TAHP can be seen to form. Visual inspection shows that this film forms at the oil-water interface. Gently agitating the crystallisation dish causes the film to crack and break into large, plate-shaped crystallites, as shown in Fig. 4.3. Leaving the cracked film for 24 hours does not lead to a change in appearance of the film. This suggests that the layer has a very low solubility in either fluid phase, and that the film is solid. Agitating the dish in which no phosphate is present leads to no change in the appearance of the interface. Given that, under these conditions, some tetradecylamine is expected to be present at the interface, this implies that the presence of the phosphate leads to the formation of the solid material.

4.3.1 Film Appearance - Effect of varying pH

In Sec. 2.1.2 the effect of aqueous pH upon the surface activity of primary amines was discussed. It has long been known that the pH at which fatty amines charge
Figure 4.2  Top: Schematic showing the experimental setup of the crystallisation dish experiments. Bottom: Photographs of crystallisation dishes 60 hours after the phosphate solution and tetradecylamine were brought into contact. One sample contains 100 mM phosphate ions at pH 7, whilst a control dish contains MilliQ water. Bright regions in the dish containing no phosphate are reflections from the light source.
The TAHP film formed at pH 7, as shown originally in Fig. 4.2, before (left) and after (right) the dish was gently agitated. Dish diameter is 7 cm.

depends on whether they are at a fluid-fluid interface or in a bulk fluid. The effective pK$_a$ of a primary amine at an oil-water interface is approximately 7.8, meaning that increasing the pH past this value ought to affect the system in Fig. 4.2 significantly - most obviously through reducing the number of charged amine groups present at the interface.

Photographs of the TAHP films formed at different pH values after 60 hours at a flat, macroscopic, water-dodecane interface are shown in Fig. 4.4. The structure of the film is strongly dependent on the pH of the aqueous phase, and varies from a thick sheet that strongly scatters light at pH 7, to a self-affine, lace-like structure at pH 8. No film can be seen by eye to form at pH 9, and the appearance of the dish is identical to the case shown in Fig. 4.2 in which there is no phosphate present. This shows that both a primary amine and a counter-ion, in this instance phosphate, must be present for the thick film to form, confirming that the film does, indeed, consist of tetradecylammonium hydrogen phosphate (TAHP).

Micrographs of the films formed at pH 7 and 8 are shown in Figs. 4.5 and 4.6 respectively. At pH 7, significant variations in film thickness and heterogeneities in structure can be clearly seen in the micrographs in Fig. 4.5a. Rupturing the film using a glass pipette reveals the hierarchical nature of the TAHP films; individual needle-shaped crystallites can be clearly seen at the oil-water interface in Fig. 4.5b and c.
Figure 4.4  *TAHP films formed at a dodecane-water interface at various pH values, photographed after 60 hours of formation. The pH of the aqueous phase is given in the images. Films were also formed at pH values 5 and 6 for chemical analysis, and were identical in appearance to the film formed at pH 7. The diameter of the crystallisation dishes is approximately 7 cm.*

At pH 8 the lace-like structure seen in Fig. 4.4 can be seen to consist predominantly of aggregated needle-shaped TAHP crystallites. The fractal structure of the film means that the crystallites can be directly visualised without rupturing the film. The needles have a large aspect ratio, similar to those formed at pH 7, and can be as long as 200 μm. Qualitatively, no large lengthscale orientational order or the crystallites has been observed under any conditions. The crystallites can be seen to significantly deform the interface, most clearly at pH 8 where the TAHP crystallites are largest, as shown in Fig. 4.6c. This suggests that aggregation of these clusters, driven by capillary interaction which minimise the free energy cost of oil-water interfacial curvature, play a significant role in the self-assembly of these films [38].

At both pH 7 and 8 the TAHP films formed at the dodecane-water interface are found to consist predominantly of aggregated crystallites. At pH 7 and below, the crystallites form a continuous skin. Rupturing this skin with a pipette reveals the individual crystallites that make up the skin, which are found to look similar to the crystallites formed at pH 8, albeit significantly smaller. The greater crystallite size at pH 8 is likely a consequence of the retarded TAHP formation kinetics at higher pH-values. The lower surface coverage of the film at pH 8 also suggests a lower mass of material being formed at raised pH. Both the film formation kinetics and the yield of the interfacial reaction are discussed in the next sections.
4.4 The Effect of the TAHP Film Upon Pendant Drops

The crystallisation dishes in Fig. 4.4 give information about the final state of the interface after the TAHP has been formed. In order to study what happens to the interface during TAHP formation, pendant drop tensiometry has been used. The technical aspects of pendant drop tensiometry have been outlined in Sec. 3.2.1.

In an initial control experiment, a drop of MilliQ water, with a volume of approximately 10 µl, was injected into a dodecane bath containing 2.5 mM tetradecylamine. The system was imaged, and the surface tension was measured using the Krüss Easy Drop Software. The effect the of presence of the TDA, with no phosphate present, is shown in Fig. 4.7. Surface tensions and fit errors were measured by comparing the oil-water surface tensions of dodecane with (red line) and without (blue line) 2.5 mM TDA.
Both systems have drops with profiles that are well described by the Young-Laplace equation, such as that shown in Fig. 3.3 in the Methods section. The error of fit to the Young-Laplace equation is correspondingly low for dodecane both with and without 2.5 mM TDA, with the error of fit being below 1 µm in both cases. This shows that interfacial elasticity is negligible in both cases. In the first 10 minutes, the system containing no TDA undergoes a slight (1 mN/m) increase in surface tension before converging on a surface tension value of 46 mN/m after approximately one hour. This is slightly lower than the literature values for a water-dodecane interface (52.87 mN/m at 20°C, according to Ref. [80]), which can be attributed to the presence of polar impurities in the dodecane.

The effect of the TDA is to lower the surface tension of the system by adsorbing on to the dodecane-water interface. In the presence of 2.5 mM TDA in the dodecane, the surface tension decreases over time, reaching 22 mN/m after one hour, after which a steady-state value has still not been reached. Two separate regimes of surface tension decrease can be seen. In the first 5 minutes of the experiment, surface tension decreases rapidly. This is followed by a regime of very slow decrease after 15 minutes, which has still not terminated after one hour of observation. In the case of a change in surface tension being driven purely by diffusion, the surface tension decreases as $\Delta \gamma \sim -(Dt)^{1/2}$ at short times. At very long timescales, a slower decrease in surface tension with the functional form $\Delta \gamma \sim (Dt)^{-1/2}$ is expected (see Sec. 3.2.2 for a discussion of this). The first regime in Fig. 4.7 in the presence of 2.5 mM TDA is well described by the curve $\Delta \gamma \sim -(Dt)^{1/2}$, whilst at timescales greater than 15 minutes decrease in surface tension slows significantly. This suggests that at these timescales processes such
as back-diffusion must be accounted for to describe the surface tension [147, 149].

Given the rather extensive work already performed upon the surface activity of fatty amines, the inelastic monolayers formed under the conditions of Fig. 4.7 are not discussed here. Of primary interest is the effect the phosphate counterions have upon the characteristics of the interface, which is discussed in the next section.

### 4.4.1 The Effect of Phosphate and pH upon the Dynamics Film Formation

Thus far it has been shown that a system containing dodecane, water, and a water-insoluble primary amine (tetradecylamine) can be radically altered by adding hydrogen phosphate to the aqueous phase (see e.g., Fig. 4.2). It has been shown that this is due to interactions between the primary amine and the counter-ion at the interface, and that these films consist for the most part of needle-shaped crystallites. The effect of pH upon the final structure of the film has also been found to be significant (see e.g., Fig. 4.4). The film structure varies from a thick, solid sheet at pH 7 and below, to a lace-like assembly of crystallites at pH 8. No solid film was observed to form at pH 9. These two observations lead to a number
of questions: why does the film structure depend on the pH of the aqueous phase? Does the pH of the aqueous phase affect the quantity of material formed, as well as the film’s structure? Finally, how does pH affect the kinetics of the formation of the film? It is the last of these phenomena, the kinetics of film formation, that I study in this section. I do this by using pendant drop shape analysis, which is suitable for studying film formation on time scales on the order 1 second to 1 hour.

Images of the effect of including both phosphate in the aqueous phase and tetradecylamine in the dodecane upon the appearance of a pendant drop are shown in Fig. 4.8. Here, the change in appearance of the TAHP film during the first 30 seconds of film formation, and how this is affected by the pH of the aqueous phase can be directly seen. A drop of aqueous hydrogen phosphate solution at pH 5 or 7 is injected into a dodecane bath containing tetradecylamine. Measurements were begun as soon as the droplet was injected into the oil bath, meaning the first second of film formation is not observed.

The difference in appearance between the appearance of the pendant drops in Fig. 4.8 and Fig. 4.7 is striking. The difference in the rate at which the films form at differing pH is particularly noteworthy. At pH 5 a TAHP film is visible from the start of the experiment, leading to significant deformation of the droplet shape and, hence, a significant error in the fit to the Young-Laplace equation. The film is seen to thicken and wrinkle over the course of 30 seconds. Experiments lasting 2 hours have shown that this thickening continues, resulting in an opaque droplet (shown later in Figure 4.9). At pH 7, the droplet is seen to ‘dance’ during the first 5 seconds, suggesting local fluctuations in surface tension due to adsorption of interfacially active molecules [18]. The error of fit is initially much smaller than in the case of the pH 5 droplet, and it takes approximately 1 second for this to reach a significant value (≥ 1 µm). After 5 seconds, the droplet has adopted a significantly asymmetric profile, corresponding to a large error in the fit. At pH 7 there is significantly less visible structure on the droplet interface at the higher pH. As will be shown later (see Fig. 4.10), the mass of TAHP formed in the crystallisation dishes after 24 hours is the same at both pH 5 and 7. In the TDA concentration range probed (1.5 - 6.5 mM), reducing the pH below 7 accelerates the kinetics of film formation, but does not affect the amount of interfacial TAHP formed. At the shorter timescales studied here, the amount of material formed is smaller at pH 7. This is a consequence of retarded formation kinetics at higher pH.
Figure 4.8 (a.) Droplets of aqueous hydrogen phosphate solution (volume = 10\(\mu\)l) at (i.) pH 5 and (ii.) pH 7 imaged directly after injection into a bath of dodecane containing 2.5 mM TDA. Images were taken directly after injection, and 9, 17, and 27 seconds afterwards. The drops took approximately 1 second to inject. (b.) The error of fit of the droplet profiles to the Young-Laplace equation as a function of time. For this apparatus, an error of fit greater than 1\(\mu\)m indicates a poor fit to the droplet profile. The diameter of the needle (the black bar above the droplets) is 1.83 mm.

The ageing of the TAHP film at the dodecane-water interface was studied visually for time scales up to 1 hour using the imaging set-up used in the droplet shape analysis experiments. The arrest of interfacial dynamics due to the elastic TAHP film means that the system cannot be studied quantitatively using this method, but the visible ageing of the droplet allows some qualitative observations to be made. The results are shown in Figure 4.9. A rather thick film, similar in
appearance to that shown in Fig. 4.8 is shown to significantly deform the interface. Over the course of an hour, the film is seen to darken, with very little light transmitted through the droplet after an hour. This suggests that, in spite of the rather thick layer already present at the rather short time scales studied in Fig. 4.8 the TAHP film continues to age. Given the interfacial mechanism by which the TAHP is formed, this is rather surprising. I discuss the mechanisms by which this phenomenon could occur later, in Sec. 4.4.4.

Figure 4.9 A water droplet at pH 5 containing 100 mM PO₄ after being injected into a bath of dodecane containing 2.5 mM Tetradecylamine. Images are taken 1, 5, 15, and 60 minutes after the droplet was injected. The needle from which the droplet is hanging has an external diameter of 1.83 mm.

4.4.2 Yield of the Interfacial Reaction

The pH of the aqueous phase affects both the structure of the TAHP films and the amount of TAHP formed. In order to study the dependence of the mass of material formed on the pH of the aqueous phase, the solid material (i.e., the TAHP, shown in the crystallisation dishes in Fig. 4.4) was separated from the solvents by pouring the contents of the dishes through filter paper. The remaining solid material was rinsed with ethanol and hexane, dried, and then weighed. The dry mass of material formed as a function of pH is shown in Fig. 4.10. The y-axis shows the yield of the reaction, calculated as a fraction of the mass of primary amine added to the system, assuming perfect stoichiometry of one HPO₄²⁻ ion to two RNH₃⁺ ions, as implied by the FTIR results in the next section. At pH 7 and below, the value plateaus at approximately 90%, suggesting that nearly all of the tetradecylamine added to the system is present as solid TAHP in the interfacial film. Above pH 7, the yield is found to decrease, reaching zero at around pH 9.
Figure 4.10  a.) Photograph of vials (diameter = 7 mm) containing TAHP obtained from the crystallisation dishes in Fig. 4.4, after isolation by filtration, rinsing, and drying. b.) Yield of TAHP formed by a reaction at the dodecane-water interface as a function of pH (black circles) and the calculated concentration of $\text{HPO}_4^{2-}$ (red) and $\text{RNH}_3^+$ (green) ions in the bulk of the aqueous solution. Yields calculated assuming films have perfect stoichiometry of two fatty amines bonded to one $\text{HPO}_4^{2-}$ ion, and that the solid mass isolated by filtration is pure TAHP. Error bars give the standard error from 3 measurements.
The yield measurements in Fig. 4.10 show good agreement with the qualitative observations inferred from the crystallisation dishes in Fig. 4.4, and show that the film thickness can be varied by changing both pH and quantity of primary amine added. They also allow an important distinction to be made between the kinetics and quantity of TAHP formation. Increasing the pH from 5 to 7 was found in the pendant drop experiments (shown in Fig. 4.8) to slow the rate at which the TAHP film formed. This change in pH does not, however, result in a drop in the amount of TAHP synthesised; doing this requires the pH of the aqueous phase to be shifted above pH 8. I investigate this phenomenon quantitatively in the next chapter using interfacial shear rheology. I will find that the elastic modulus of the film, and the timescale on which interfacial elasticity emerges, can be tuned by varying both the pH of the aqueous phase and the concentration of the fatty amine.

4.4.3 FTIR Analysis of TAHP Films

Fourier Transform Infra-Red spectroscopy was used to give information about the chemical constituents of the films. This allows the presence or absence of functional groups (particularly amines) to be ascertained by measuring the adsorption of light in the infrared spectrum due to excitation of the bonds present in a molecule\(^3\), which allow for comparison of spectra with a range of results obtained from the literature. By comparing the IR spectra of TDA, hydrogen phosphate, and TAHP, the extent of phosphate and TDA incorporation into the solid material was determined. Of particular interest is the dependence of the stoichiometry of the films (i.e., do the RNH\(^3\)\(^+\) groups bind to the HPO\(^4\)\(^−\) groups in a particular ratio), the speciation of the phosphate in the TAHP (i.e., the relative quantities HPO\(^2\)\(^−\) or H\(_2\)PO\(^−\) is present), and how these quantities are affected by the pH of synthesis. This is achieved here by using two different methods. Firstly, the FTIR spectrum for TDA, prior to binding with phosphate, was measured. The FTIR spectra for ammonium phosphate salts (dibasic ((NH\(_4\))\(_2\)HPO\(_4\)) and monobasic (NH\(_4\)H\(_2\)PO\(_4\))) were obtained from the NIST Webbook, an online repository\[152\]. Comparing the peaks in the IR spectra before and after TAHP synthesis, followed by comparison of these peaks with those observed in the literature, allowed the molecular origin of the peaks to be determined and the

\[^3\]A description of the method can be found in a number of general textbooks on chemistry, such as Refs. [13] and [150]. Look up tables containing characteristic frequencies of adsorption bands can be found in e.g., [151].
material constituents identified. Secondly, monolayers of TAHP formed at the air-water interface have been well-studied and characterised using both FTIR and neutron activation analysis [153, 154], which provides results with which the TAHP formed at the oil-water interface can be compared directly.

FTIR spectra for powder TAHP and TDA samples are compared with FTIR data for dibasic ((NH₄)₂HPO₄) and monobasic (NH₄H₂PO₄) ammonium phosphate dispersions in Nujol (obtained from the NIST Webbook [152]) in Fig. 4.11. Peaks characteristic of HPO₄²⁻ at 1077 cm⁻¹ (νₐs,HPO₄²⁻), 965 cm⁻¹ (νₛ,HPO₄²⁻), and 900 cm⁻¹ (νₛ,HPO₄²⁻) can be clearly identified in samples formed at pH 5 and pH 8, as seen elsewhere in the literature [153,154]. The bands in the region between 3000 and 2800 cm⁻¹ originate from C-H stretching vibrations in the aliphatic chains that are present in both the TDA and the synthesised TAHP. The sharp band in the synthesised TAHP at 1470 cm⁻¹, present in both the ammonium phosphate salts as a broad peak, and in the TDA as a sharp peak, arises from the collective ν₄ stretching vibration of the NH₄⁺ groups [155–157]. The sharpening of this band for the TAHP and the organic cations appears to be due to the change in the symmetry of the ammonium moiety, in which only 3 hydrogens participate in the vibration, as opposed to 4 in the case of the inorganic salt. Work performed on monolayers of short-chain organic ammonium ions adsorbed on to montmorillonite, by Fripiat et al., showed that this peak was absent after exposure of the system to water vapor, suggesting that little, if any, water is present in the dried TAHP films [157].

The labelled peak at 3340 cm⁻¹, present in the TDA and characteristic of free amino groups, is absent from the TAHP powder samples. This does not entirely exclude the possibility that free tetradecylamine adsorbs on to the interfacial film during formation, and is then removed when the film is rinsed (tetradecylamine’s solubility in ethanol and hexane being far higher than TAHP’s). However, as noted, the TAHP yield at pH 7 and below is 90% of all the TDA added to the system, meaning the measurements performed here correspond to the majority constituents of the film. Measurements were also performed at pH 7, but are not shown due to their similarity with those taken of films formed at pH 5. The results show that the interfacial film consists largely of two tetradecylammonium molecules bonded to a single HPO₄²⁻ anion, in good agreement with results obtained for monolayers formed at the air-water interface in other work [158,159].
4.4.4 Discussion

What is the mechanism by which the TAHP film forms?

It has been found that, in order for a thick elastic film to form at the oil-water interface, both tetradecylamine and hydrogen phosphate must be present in the system, and that the rate at which the film forms decreases as pH is increased from 5 to 8. As discussed in the Background section (see Fig. 2.3), the surface activity of primary amines at the oil-water interface decreases by a factor of approximately 90% between pH 7.5 and 8.5 [2, 15]. This can be directly related to a drop in the surface potential of the amine monolayer over this pH range, showing that a positively charged tetradecylammonium layer is required to be present at the interface for the film to form. In the case of air-water monolayers, it has been observed by several groups that the presence of a divalent counter-ion, such as HPO\(_4^{2-}\) or HAsO\(_4^{2-}\), then leads to the formation of insoluble monolayers [158, 160]. The presence of the phosphate at the oil-water interface studied here leads to condensation of the phosphate anions at the positively charged tetradecylammonium layer, leading to the formation of
tetradecylammonium phosphate (TAHP). The potential reactions governing this process, as observed by Petrov, are [159]:

\[
\text{RNH}_3^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{RNH}_3\text{PO}_4 \quad (4.2)
\]

\[
2 \text{RNH}_3^+ + \text{H}_2\text{PO}_4^{2-} \rightleftharpoons (\text{RNH}_3)_2\text{HPO}_4 \quad (4.3)
\]

\[
3 \text{RNH}_3^+ + \text{PO}_4^{3-} \rightleftharpoons (\text{RNH}_3)_3\text{PO}_4 \quad (4.4)
\]

The FTIR spectra in Fig. 4.11 show that, between pH 5 and 8, it is the reaction in Eq. 4.3 that leads to the formation of TAHP, and that the films have a well-defined stoichiometry of two tetradecylammonium cations to one hydrogen phosphate anion.

**Why do the yield and formation kinetics depend on the pH of the aqueous sub-phase?**

The pH-dependence of both the yield and the kinetics of the film’s formation is a consequence of the local pH increasing near a positively charged interface [2, 18]. This shift in pH reduces the surface activity of the amine. It is *not* due to the change in phosphate ion speciation due to pH.

The pH at a charged air-water interface, pH\(_s\), is related to the pH in the bulk aqueous solution, pH\(_b\), by the relation pH\(_s\) = pH\(_b\) + \frac{e\psi_s}{k_BT} \cdot \frac{1}{2.3026}, \text{ where } k_B \text{ and } T \text{ are the Boltzmann constant and absolute temperature respectively, } e \text{ is the fundamental unit of charge, and } \psi_s \text{ is the surface potential [18]. This explains both the apparent contradiction of the high mass TAHP formed even though at pH 5 the HPO}_4^{2-} \text{ concentration is extremely low, and the decrease in TAHP yield and the slowing of the formation kinetics as the pH increased above pH 7. The acid dissociation constant of tetradecylamine is 10.6 [14], and the increased pH near the (positively charged) interface leads to a reduced concentration of tetradecylammonium cations. This trend was observed as long ago as the 1920s [2, 15], and more recently in work studying the stoichiometry of fatty ammonium phosphate and fatty ammonium arsenate monolayers [153, 158]. Our results for TAHP films formed at the oil-water interface show an interfacial pH shift of approximately 3 towards more basic values, in good agreement with the
other work mentioned here. This implies an effective interfacial $pK_a$ of the tetradecylamine at the interface of approximately pH 7.5, and a surface potential on the order of 200 mV, in line with values obtained for monolayers of primary amines [16, 17].

**Why does the TAHP form a thick film, rather than a monolayer?**

Monolayers of long-chain primary amines, carefully spread at the air-water interface and in the presence of a divalent counter-ion, form high-quality monolayers [160]. Contrastingly, the TAHP at the *oil*-water interface studied in this work forms a thick film, which consists to a great degree of aggregated, needle-shaped crystallites. The presence of a monolayer in some regions of the film cannot be ruled out, however the majority of the mass of the TAHP is clearly present as crystallites. The reasons for the formation of a thick film, rather than a monolayer, are not entirely clear. The 2D-3D transformation of amphiphilic monolayers has been extensively studied, both experimentally and theoretically, for insoluble monolayers at the air-water interface [153, 161, 163]. This 2D-3D transformation is referred to as monolayer collapse, and remains the subject of much study, particularly with regards to the behaviour of lung surfactants [164].

Monolayer collapse has been studied in similar, fatty acid-based systems at the air-water interface [165], which suggests that monolayer collapse may play an important role in the nucleation of the TAHP crystallites at the oil-water interface. However, the importance of the sparing solubility of the TAHP in the dodecane, along with the speciation of the phosphate ions, are also likely to be important factors, especially given the importance of ionic strength, ion speciation, and head group ionization in governing monolayer collapse behaviour [166]. Whilst monolayer collapse is often undesirable in certain processing applications involving monolayers [167], it is found in this thesis that the formation of thick TAHP films at the oil-water interface leads to both highly stable water-in-oil emulsions and novel interfacial rheological properties, as discussed in the next chapter.
Figure 4.12  Top: 4 ml dodecane containing 2.5 mM TDA and 1 ml deionised water (left) and deionised water containing 100 mM phosphate (right) at pH 7. System was sheared for 1 min using a rotor-stator operated at 24000 s$^{-1}$. Bottom: Light micrograph of the white substance at the bottom of the vial in the system containing 100 mM phosphate (showing that it is an emulsion) and, inset, confocal fluorescence micrograph in which 1 mg / 20 ml Nile Red has been added to the dodecane (showing that it is a water-in-oil emulsion).

4.5 TAHP-stabilised Emulsions

In previous sections it was shown that both phosphate ions and tetradecylamine are required for primary amines to assemble into rigid films at the dodecane-water interface. It has been shown at pH 5, this process happens more rapidly than can be observed using the apparatus used to study film formation thus far. As the pH of the aqueous phase is increased to 7, the film formation kinetics are observed to retard, but the quantity of interfacial material formed after long time periods (60 hours) remains the same, with at least 90% of the primary amine used present in the system as an interfacial TAHP film. As pH is increased to pH
8, the film formation kinetics are retarded further, and the mass of TAHP formed drops by approximately 30%. In this section I will show that the TAHP film can be used to stabilise water-in-oil emulsions, and that the emulsions form under the same conditions that the thick films form, showing that the rigid TAHP film provides a steric barrier to droplet coalescence. I will image the interface of the emulsions using both fluorescence microscopy and scanning electron microscopy techniques. I will show that the structure of the TAHP film coating the droplets consists predominantly of aggregated, needle-shaped crystallites, much like at a planar interface. Emulsions are used in the next section to study the structure of TAHP at the molecular scale by using small-angle neutron scattering.

As with previous sections I begin with a control experiment, in which it is shown that both tetradecylamine and hydrogen phosphate are required for a stable water-in-oil emulsion to be formed. This is shown in Fig. 4.12. The vial on the right-hand side of Fig. 4.12 has had 100 mM phosphate added to the aqueous phase. The water in the vial on the left-hand side is de-ionised, and contains no phosphate. Both vials also contain 4 ml of 2.5 mM TDA dispersed in dodecane. Both vials were sheared using a rotor-stator operated at 24000 s\(^{-1}\) for 1 min. In the vial on the left, in which no phosphate ions are present, the fluids have separated. In the vial on the right, in which 100 mM phosphate ions have been added to the aqueous phase, the bottom third of the vial is opaque. Light micrography (Fig. 4.12, bottom) shows that this is due to the present of an emulsion. Testing of the non-aqueous supernatant of the emulsion using a fluorimetric assay found a residual primary amine concentration of approximately 150 \(\mu\)M at pH 5. This implies a similar, or slightly higher, uptake of primary amine compared to films formed at a planar interface.

The emulsions are water-in-oil emulsions, as shown in Fig. 4.12 inset. The dispersed phase is identified by adding a small quantity of hydrophobic fluorescent dye to the dodecane and imaging using fluorescence microscopy methods. Here, a 1 mg / 20 ml solution of Nile Red dye in dodecane, which is insoluble in water, has been added to the system. Imaging the system using confocal fluorescence microscopy, exciting the system using the 488 nm laser, reveals a strong fluorescence signal emitted by continuous phase. This shows that TAHP stabilises water droplets in dodecane.
4.5.1 Emulsion Stability and pH of Aqueous Phase

Water-in-oil emulsions stabilised by a TAHP film, formed at various aqueous pH values, are shown in Fig. 4.13. This shows the importance of pH in determining emulsion stability. At pH 8 and above, insufficient interfacial material is formed on the time scale of coalescence for stable emulsions to form. At pH 7 and below, highly stable water-in-oil emulsions drops are formed. TAHP-stabilised water-in-oil emulsions formed between pH 5 and 7 have been found to be stable against coalescence for over 2 years.

![Figure 4.13](image)

The TAHP-stabilised emulsions and the TAHP films exhibit very similar trends in pH dependence. At pH 7 and below, TAHP stabilises water-in-oil emulsions. At pH 8 and above, TAHP is ineffective as an emulsifier. This is informative as to the mechanism by which the TDA and phosphate stabilise the emulsions. The change in physical properties of the TAHP film in the pH range in which emulsification is studied in Fig. 4.13 (a rigid film that forms rapidly at pH 7 and below, a slow-forming, lace-like film at pH 8, and little-to-no film found to form at pH 9) suggests that the thick TAHP film provides a steric barrier to droplet coalescence, rather than emulsifying via electrostatic effects or reduction in surface tension due to amine adsorption. There is a slight difference in the behaviours of the two systems, however, in that no emulsion is stabilised at pH 8, even though a significant quantity of TAHP is found to form at this pH. This can be understood by considering the grossly retarded formation kinetics of TAHP at
pH 8 (which will be studied quantitatively using interfacial rheology in the next chapter). Separation of the fluids occurs on the time scale of seconds, and so at pH 8 insufficient TAHP is formed on these timescales to yield a stable emulsion. Droplet coalescence therefore proceeds unarrested.

4.5.2 Imaging the TAHP Interface

A key topic of this thesis is the study of the relationship between the structure of an interface and its physical properties. In this section I use a number of methods to probe the TAHP film on the lengthscale of its mesoscopic building blocks: the individual crystallites. To do this, I will image the TAHP interface using laser scanning confocal fluorescence microscopy and freeze-fracture scanning electron microscopy (Cryo-SEM). The two techniques are complementary. Cryo-SEM allows for high-resolution images of the system to be obtained, but at the expense of introducing imaging artefacts via the freezing process used for sample preparation. Confocal fluorescence microscopy has a spatial resolution limited to approximately 210 nm, but allows for the sample to be imaged without extensive manipulation.

Water-in-oil emulsions with fluorescent TAHP interfaces were made by adding NBD-Cl, a fluorophore, to the aqueous phase. Primary amines react with NBD-Cl to form a fluorescent compound, TDA-NBD [140]. Adding a small quantity (1 mg / 20 ml) of NBD-Cl to the aqueous phase leads to the formation of fluorescently doped films on the droplet surfaces. These films can be directly imaged using fluorescence microscopy. The crystalline TAHP also exhibits birefringence under crossed-polarisers, allowing for the structure of the droplet interfaces to be studied using both birefringence and fluorescence microscopy methods. The TAHP-stabilised droplets, with no fluorophore added, are visualised using an analyser with a plane of polarisation at 90° to the incident laser light.

Results using these two methods, along with a schematic indicating the locations of the various phases in the emulsion, are shown in Fig. 4.14. Using the fluorescence methods to image the emulsion, a signal from both the interface (green) and the bulk dodecane (red) can be detected. The signals are obtained by exciting the system using lasers of different frequencies. The excitation and emission spectrum of NBD-based fluorophores depends strongly on the dielectric constant of the surrounding phase [99], meaning that the fluorescence signals from the dodecane and the interface can be readily separated (shown in Fig. 4.14a).
Exciting the system at 408 nm yields a bright signal from the bulk oil, whilst exciting at 488 nm gives a bright signal from the interface. No fluorescence signal is obtained from the aqueous solution, as expected given the extremely limited solubility of TAHP in water at room temperature. When viewed under crossed polarisers, no signal is obtained in the fluids above background noise (grey in Fig. 4.14). Bright regions can, however, be seen at the interface of the droplets, indicating the presence of bulk quantities of material and a degree of spatial ordering.

Figure 4.14  a.) Confocal fluorescence micrograph showing the signal from both the TDA-NBD at the interface (green) and in the bulk dodecane (red). b.) Birefringence confocal micrograph showing the transmission image after the light has passed through a polariser oriented at 90° to the polarisation of the incident laser light. Intensity has been increased in post-processing (by multiplication) for clarity.

The high elasticity of the interfacial TAHP film prevents re-arrangements of the interface on the experimental timescale (in this case, ≈ 1 hr). This allows for high-quality, high-resolution confocal z-stacks with an imaging time of up to 30 minutes to be taken, as shown in Fig. 4.15. The droplets are seen to be coated with crystallites of TAHP of a range of shapes, most of which are needle-shaped. The needle-shaped crystallites are seen to be as long as 10 µm, and so large enough to be directly imaged by the microscope. Emulsions formed using high-shear show TAHP films consisting of both large plates (small droplet, Figure 4.14c) and needle-shaped crystallites (large droplet, Figure 4.14c). The total imaging

4As will be shown in the next chapter, at elevated temperatures (50°C), a weak fluorescence signal is obtained from TDA-NBD, suggesting it is sparingly soluble in the aqueous phase.
time of Fig. 4.14c was 7 minutes, during which time no motion of the plates was observed. Further observations lasting an hour have also detected no movement in the interfacial films of stable emulsion droplets. A weak fluorescence signal can also be seen in the inter-plate regions, suggesting continuous or near-continuous interfacial coverage.

4.5.3 Cryo-SEM Images of the Droplets and the TAHP Film

In the previous section, confocal fluorescence microscopy was used to image the TAHP film. Imaging the samples using this method has a number of advantages: the samples are easy to prepare, and the experiment is relatively easy to carry out. However, studying the film using crossed-polarisers only serves to confirm
the presence of bulk quantities of material at the interface, whilst imaging using fluorescence methods requires a fluorophore to be added to the system, which will disturb the structure of the film. Furthermore, even using a high numerical aperture lens (such as the 63× magnification oil-immersion lens, NA = 1.4) both of these methods have a spatial resolution limited to \( \Delta l = \frac{0.61 \lambda}{NA} = 210 \text{ nm} \) by the Rayleigh criterion [168]. One method to improve spatial resolution is to use shorter wavelength particles, such as electrons, to image the samples. As such, Cryo-SEM, the technical aspects of which are outlined briefly in Sec. 4.2.5, has been used to image the system at smaller length scales.

Cryo-SEM images of emulsion drops, prepared under similar conditions to both those shown in Figure 4.15 and those used in the neutron scattering experiments (discussed later), are shown in Figure 4.16. Needle- and ribbon-shaped TAHP crystallites, similar in appearance to those seen in the confocal micrographs, can be clearly seen in Figures 4.16 a. and b., showing that these are not artefacts of the freezing process.

![Cryo-SEM images of a TAHP-stabilised water-in-dodecane emulsion at a.) low and b.) high magnification. The region magnified is denoted in each image. \( \dot{\gamma} = 30000 \text{ s}^{-1} \), [TDA] = 5 mM, pH = 5](image)

**Figure 4.16** Cryo-SEM images of a TAHP-stabilised water-in-dodecane emulsion at a.) low and b.) high magnification. The region magnified is denoted in each image. \( \dot{\gamma} = 30000 \text{ s}^{-1} \), [TDA] = 5 mM, pH = 5

The interfacial structures observed using both Cryo-SEM and confocal fluorescence microscopy show good agreement with one another. Both show water droplets covered in a thick layer (rather than a monolayer) of TAHP crystallites. They also show that the structure of the TAHP film that coats the emulsion droplets is very similar to that of a TAHP film at a planar interface (such as in Fig. 4.5). In both cases, the TAHP films consist for the most part of aggregated, needle-shaped crystallites. The interfacial structure of the TAHP is most reminiscent of the crystallites formed by acid soaps, which have been reviewed to some extent in Sec. 2.1.3 [31]. Extensive work has been performed on these
systems to understand the rather complex relationship between the stoichiometry, phase behaviour, and concentration-dependence of the crystallite morphology \[20, 23, 24\]. The marked similarity in crystallite morphology variation suggests that the work presented here is complementary to the extensive body of work already performed on acid soaps.

### 4.6 Molecular-Scale Structure of the TAHP Film

Thus far, the conditions under which TAHP films form, as well as how these formation conditions affect formation kinetics, structure and stoichiometry of the film, have been studied. So far, however, the molecular structure of the film has not been investigated. In this section I will use small angle neutron scattering (SANS) measurements performed on TAHP-stabilised emulsions droplets to analyse the structure of the TAHP crystallites, which Fig. 4.4 shows are the major constituents of the film.

In this section the small-angle neutron scattering (SANS) data obtained from TAHP-stabilised emulsions will be used to infer the molecular structure of the TAHP crystallites, such as those shown in Figs. 4.5 and 4.6. The relevant technical aspects of SANS have been discussed in the Methods chapter (see Sec. 3.7 for the operating principles and theory, and Sec. 4.2.7 for methodology specific to this experiment), whilst sample preparation has been discussed in the materials section of this chapter.

**Is it reasonable to infer the microscopic structure of the TAHP formed at a planar interface from emulsion droplets?**

In order to investigate the molecular structure of the TAHP films (and how the structure is influenced by heating) emulsions, rather than the powder samples shown in Fig. 4.10 were studied. Emulsions are employed as a compromise between the ability to study the TAHP in situ at a fluid-fluid interface, at the expense of both background noise from the solvents present in the emulsion and the effect of interfacial curvature upon crystallite structure. I briefly argue here why the scattering from TAHP films formed at emulsion interfaces is relevant to the TAHP films formed at both planar and curved interfaces studied in this thesis, with reference to some of the microscopy results in Figs. 4.15 and 4.16
The argument can be outlined as having three key points: that the TAHP at both the planar films and the droplet interfaces is known to consist of micron-sized crystallites, that the crystallites in both systems are chemically identical, and that whilst the curvature of the micron-sized droplets will likely affect the geometry of the TAHP crystallites, this curvature is negligible at microscopic length scales. A cuvette, as used in the scattering experiment, filled with TAHP-stabilised water-in-dodecane emulsion is shown in Fig. 4.17.

Figure 4.17  Photograph of a 2mm path length quartz glass cuvette, as used in the scattering experiments, containing a TAHP-stabilised water-in-oil emulsion.

A comparison between the TAHP films formed at the planar interface (in Figs. 4.5 and 4.6) and the confocal fluorescence and scanning electron micrographs of emulsion droplet interfaces (in Figs. 4.14 and 4.15, respectively) is instructive. The crystallisation dishes show that at pH 5, after breaking the film, the film consists primarily of large crystallites up to tens of micron in length (or hundreds, in the case of the film formed at pH 8). Likewise, the confocal fluorescence micrographs of the TAHP-coated droplets formed at pH 5 show needle-shaped crystallites, up to tens of microns long, which coat the droplets. The birefringence signal from the droplet interface in Fig. 4.14 further shows that the interface consists of bulk quantities crystalline or paracrystalline material. It has been found that, much like the case of the planar interface, the emulsions are stable only in the presence of a thick layer of TAHP (this is argued further in the next chapter, in which the temperature response of the system is studied), and that
the conditions for emulsion stability and for film formation at the planar interface are identical. The similarity of film formation conditions for both systems, along with the observation from the FTIR spectra that the chemical constituents of the TAHP films are identical across a broad range of film formation conditions (between pH 5 and 8), suggest that, chemically speaking, the TAHP crystallites at the droplet interface are chemically identical to those formed at a planar interface.

Another important effect that requires consideration is the effect of the droplet curvature upon the internal structure of the TAHP crystallites. It is extremely likely that confinement of the TAHP crystallites to a curved emulsion interface will lead to them having a different macroscopic structure than if they were at a planar interface. This is seen in Fig. 4.15, where the curvature of the emulsion drops is significant on the lengthscale of the crystallites. The droplets, which have radii of 1 µm upwards (typically 10-20 µm in the case of the scattering experiment), are much larger than the largest lengthscale probed by the SANS experiment ($q = 0.005 \text{ Å}^{-1} \rightarrow \lambda \approx 126 \text{ nm}$). The curvature of the droplets is therefore negligible both on the atomic scale of the TAHP molecules, and on the largest lengthscale probed by the scattering experiment. Both the SEM images and the confocal micrographs also show that the TAHP-film is rather thick. The crystallites have a thickness on the order of the roughness of the film in the micrographs; the film thickness can thus be estimated as being of the order 100 nm, but assigning an explicit lengthscale is difficult. Regardless, it is likely that, in the case of the droplets being coated by TAHP crystallites, such as those shown in Fig. 4.16, the scattering signal in the q-range probed is Porod-like surface scattering from the TAHP crystallites at low-q, with structure-specific features characteristic of the TAHP crystallites detected at higher q-values.

**4.6.1 Neutron Scattering from TAHP films**

**Structure at Low Temperature**

Scattering data for a TAHP-stabilised, water-in-oil emulsion, where both solvents are fully deuterated, are shown in Fig. 4.18, along with the fit to the data (red line). The individual contributions from the two different components of the model: the Lorentzian tail (purple line, which dominates at high-q) and Caillé theory (green line, which dominates at low-q and near the Bragg peaks) are also shown. If Caillé theory alone were used to describe the data (Fig. 4.18 green
line), troughs at high-$q$ in the region of the Bragg peaks (due to minima in the form factor), along with scaling of the intensity as $q^{-4}$ would be expected to be observed. These troughs are not observed due to the Lorentzian, which acts as the noise floor for the measurement at high-$q$. At low-$q$ (between $q = 0.005$ and $0.05 \, \text{Å}^{-1}$) the intensity scales as approximately $I(q) \sim q^{-4}$. SLD-matching of the solvents in the next section will show that this is due to the thickness of the TAHP interface, rather than scattering from the oil-water interface. At high-$q$, the scattered intensity is poorly described by a single exponent (this can also be seen in Fig. 4.19 in which the underlying trend shows a curved, rather than straight, line on a log-log scale). This is a consequence of the diffusive thermal fluctuations of the non-deuterated aliphatic chains in the fatty amine, which is described by the Lorentzian (Fig. 4.18, purple line).

The scattering near the main Bragg peak is magnified and put on a linear scale in Fig. 4.18 inset. Bragg peaks can be seen at $q = 0.166$, 0.332, and 0.504 $\, \text{Å}^{-1}$ (i.e., a ratio of 1:2:3), showing that the TAHP film is multi-lamellar in structure. There is also a fainter, rather broad peak at $q = 0.224 \, \text{Å}^{-1}$, which most likely corresponds to short-range order in the plane of the lamellae. The first order Bragg peak corresponds to a lamellar repeat distance of 37.9 Å, which is somewhat smaller than the estimated length of two tetradecylamine molecules ($\sim 41 \, \text{Å}$) [146]. Good fits to the data are obtained for a tail group thickness of $33.7 \pm 0.4 \, \text{Å}$. This corresponds to a polar region, which contains the ammonium phosphate groups, with a thickness of 4.2 Å. The TAHP crystallites, which give rise to this scattering, must therefore contain little-to-no inter-lamellar water, and with the lipid tails either interdigitated or tilted with respect to the surface normal of the bilayer. Similar lamellar structures have been found to be formed by fatty acid soaps (as discussed in Sec. 2.1.3), though the TAHP crystallites incorporate significantly less solvent, and therefore have a much smaller inter-lamellar spacing [169]. Both interdigitation of the tails and tilting has been observed in similar, fatty acid-based systems, in which the tail conformation was dependent upon the structure of the aliphatic chain [26].

The Caillé parameter, $\eta$, and the number of lamellae that must be included in the structure factor, $N$, give information about the strength of interactions between the lamellae that make up the system. In order for good fits to be obtained, correlations from between 40 and 50 lamellae must be accounted for, suggesting a rather high degree of order within the system. As expected from Caillé theory, the first order Bragg peak is the most prominent, with the prominence of the peaks
Figure 4.18  Scattered intensity as a function of wavenumber plotted for a TAHP-stabilised D₂O-in-d-dodecane emulsion at 30°C (black circles). Also plotted are 3 lines corresponding to the models used to fit the data - a Lorentzian with \( \xi = 6 \ \text{Å} \) (purple line), Caillé theory with \( d = 37.9 \ \text{Å} \), \( \delta = 33.9 \ \text{Å} \), \( \eta = 10^{-6} \), \( N = 44 \) (green line), and the sum of the two models (red line). The dashed line shows \( I(q) \sim q^{-4} \). The data in the region of the main Bragg peak has also been magnified and placed on a linear y-scale, inset (error bars smaller than data points).

As shown in Fig. 4.18 inset, the model somewhat underestimates the peak intensity and overestimates the width of the primary peak. This is most likely a consequence of a slight overestimate of the q-resolution (\( \Delta q \)) of the instrument.
and, consequently, an overestimate of the width of the Gaussian with which the predicted intensity is convolved to yield the final, resolution-smeared model. As mentioned in Sec. 4.2.7, estimating the $q$-resolution of a time-of-flight instrument using a white beam of neutrons, such as SANS2D is non-trivial. The results obtained here suggest that the value for $\eta$ should be treated as a lower bound. This does not, however, affect the observation that only very little diffuse scattering can be attributed to thermal fluctuations within the TAHP, suggesting extremely strong interactions between the lamellae.

**Varying Temperature Between 25 and 35°C**

Scattering data in the low-$q$ region for TAHP-stabilised emulsions at low temperature (between 25 and 35°C), where the solvents are fully deuterated, is shown in Fig. 4.19. The similarity between the graphs is striking. All exhibit three Bragg peaks at the same values, showing that the spacing of the lamellae does not depend on temperature below 35°C. The shape of the Bragg peaks does exhibit some temperature dependence. There is no difference in the scaling exponent of $I(q)$ near the primary Bragg peak at 25 and 30°C, however at 35°C the peak appears to broaden, corresponding to an increase in $\eta$ to 0.01, compared to a $q$-resolution-constrained lower bound of 0.001 at lower temperatures. This is still a rather low value, compared with 0.025 for fatty acid needles [28] or of the order 0.4 for lipid bilayers [112], though consideration of the rather small separation of the TAHP lamellae and the scaling of $\eta \sim d^{-2}$ suggests that the mechanical moduli of the TAHP are comparable to those of the fatty acid needles of Fameau et al [27].

At 35°C and below, fitting the data to the first order Bragg peak gives values of the Caillé parameter of 0.001 or less. Decreasing $\eta$ below this value does not significantly alter the shape of the curve, meaning this should be considered an upper bound for $\eta$. In this temperature range, $\eta$ is found to be independent of temperature, suggesting that the elastic properties of the bilayers are not strongly affected by heating at these temperatures. This low value for $\eta$, along with the small repeat distance of the film and the predicted $\eta \sim d^{-2}$ behaviour of the Caillé parameter, suggest that the film has rather large mechanical moduli that can be attributed, at least in part, to the rather strong electrostatic interactions and hydrogen bonding likely present in the polar part of the TAHP film. The models

\footnote{The lamellae of the acid soap needles in Refs. [27] and [28] have a separation 35 nm, compared with 3.7 nm for the TAHP.}
Figure 4.19 (Top) Measured scattering intensity at 25-35°C in the mid-q range for TAHP-stabilized emulsions containing fully deuterated solvents.

used also appear to slightly over-estimate the range over which the scattered intensity diverges near the 1st Bragg peak (as shown in Fig. 4.18), suggesting that q-smearing due to finite instrumental resolution has been slightly over-estimated. This does not, however, suggest that the Caillé parameter has been significantly over-estimated by the fits to the data. Indeed, the large number of Bragg peaks observed (up to four in some measurements), in spite of the relatively low volume fraction of TAHP present in the system (≤ 1%), is in line with the strong interactions between lamellae which the low value for η would suggest.

**Effect of heating upon TAHP structure**

The effect that heating the emulsions above 40°C has on the Bragg peaks is shown in Fig. 4.20. As temperature increases, the Bragg peaks become less prominent due to the reduced quantity of TAHP present at the interface. The third order peak is only visible below 40°C. As the system is heated above 45°C a second lengthscale is observed in the system. This is detected at 40°C as a broadening of the principle peak at $q = 0.166$ Å$^{-1}$, at which point Caillé theory can no longer be used to fit the peaks. This second lengthscale is then present as a shoulder at 45°C and can be resolved as a separate peak at 50°C (shown in Fig. 4.20 inset). The $q$-value of this peak decreases further as temperature increases, reaching
\[ q = 0.114 \text{ Å}^{-1} \text{ at 65°C, corresponding to a real-space repeat distance of 55.1 Å.} \]

Figure 4.20  Measured scattering for the h-TAHP-stabilized D$_2$O-in-d-dodecane (off-match) emulsions measured at 45 (green), 50 (orange), and 55°C (purple). Inset: The same data, in the region of the main Bragg peak, re-drawn on a linear scale.

The emergence of the second, lower-q peak, shows that two co-existing structures are present in the TAHP at these temperatures, corresponding to lamellae with repeat distances of 37.9 and 55.1 Å (at 65°C). The experiments were performed at sufficiently high emulsion volume fraction and fatty amine concentration ([TDA] = 6.5 mM in the emulsions used in the scattering experiment) that the emulsions were stable against coalescence at these elevated temperatures; thus, the appearance of this second, larger lengthscale cannot be directly related to the coalescence of the emulsions. Similar temperature-driven changes in bilayer separation have been observed in multi-layer assemblies of fatty acids, with the change in separation between lamellae being due to incorporation of water into the region between the bilayers [27, 29]. Whilst chemically and structurally somewhat similar to these acid soap systems, the TAHP system studied here exhibits some significant differences. The acid soap needles studied by Fameau et al had a rather large separation between bilayers (often 10-50 nm), with the crystallites containing typically only three or four lamellae. Contrastingly, in the case of TAHP crystallites, the bilayer separation remains rather small (i.e., never greater than the expected length of the fully extended aliphatic chains plus the size of the ammonium phosphate head group), with good fits to the
data obtained when the number of lamellae is between 40 and 50. In the case of the TAHP, the emergence of the second lengthscale at higher temperatures ostensibly corresponds to a change in the conformation of the aliphatic tails, in which the temperature increase drives a transition to either a lower tilt angle or a non-interdigitated phase.

Matching Solvent SLDs

Matching the scattering length densities of the solvents allows inferences to be made about the structure of the interfacial film by studying the scaling of the scattered intensity at small wavevectors. In the absence of any scattering length density contrast between the aqueous and non-aqueous phase of the emulsion, the only contribution to scattering comes from the TAHP. The micrographs, in Fig. 4.16, clearly show that at room temperature the thickness of the TAHP film is of the order of 100 nm or more, and so at the wavevectors studied here only surface scattering will be observed. However, also of interest in this work is the temperature response of the system, the structure of the TAHP film at high temperature, and the extent to which the film thins before significant droplet coalescence occurs. To this end, SLD-matching of the solvents was employed to examine the temperature-dependence of the TAHP film structure. The temperature response of the emulsion system will also be studied in depth in the next chapter. SLD-matching of the solvents was achieved by using a blend of 95% perdeuterated dodecane and 5% h-dodecane, as outlined in Sec. 4.2.7.

The difference between the scattering from samples with the scattering length density of the dodecane matched (black line) and off-matched (grey line) to D$_2$O is shown in Fig. 4.21. Matching the scattering length densities of the solvents leads to a slight decrease in the scattering intensity at low-$q$ (from 360 to 280 cm$^{-1}$) due to reduced scattering from the oil-water interface. It also leads to an increase in incoherent background due to the larger incoherent scattering cross-section of the hydrogenous solvent. Power-law scaling in the low-$q$ region ($q \leq 0.37$ Å$^{-1}$) was determined by fitting the equation $aq^{-b}$ to $q^4I(q)$. Fitting to weighted data prevents the very large, very low-$q$ values from biasing the curve fit. The intensity was found to scale with $q$ as $q^{-3.87\pm0.05}$, and is independent of both sample temperature and, more importantly, h-dodecane concentration.

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For comparison, $\rho$(D$_2$O) = 6.402 $\times$ 10$^{-6}$Å$^{-2}$, whilst $\rho$(95%-d, 5%-h dodecane) = 6.359 $\pm$ 0.13 $\times$ 10$^{-6}$Å$^{-2}$. The error arises due to the finite precision of solvent perdeuteration and mass measurement.
SLD-matched solvents also exhibit a similar change in the value of $I(q)$ at very low-$q$ as temperature is increased. $I(q)$ at higher temperatures (35 - 55°C) from an SLD-matched emulsion at 35, 45, and 55°C is shown in Fig. 4.22, and can be compared with results for non-SLD-matched samples in Fig. 4.20. In the case of the non-SLD-matched solvents, $I(q)$ at $q = 0.005 \text{ Å}^{-1}$ drops from 320 to 90 cm$^{-1}$. In the case of SLD-matched solvents, $I(q)$ at $q = 0.005 \text{ Å}^{-1}$ dropped from 250 to 40 cm$^{-1}$, representing a decrease of similar magnitude.

TAHP-stabilised emulsions exhibit similar temperature-dependence of low-$q$ scaling of $I(q)$ and decrease in $I(q)$ at low-$q$ and near the Bragg peaks, independent of h-dodecane content of the non-aqueous solvent. At all temperatures and h-dodecane concentrations, the intensity scaled as $I(q) \sim q^{-4}$. If the TAHP film were thin, with the scattering length densities of the solvents being matched, the system would yield $q^{-2}$ scaling of the intensity \[170, 171\]. From the $q^{-4}$ scaling measured for the TAHP-stabilized emulsions studied here, it can be inferred that the interfacial TAHP film is rather thick under all conditions studied in these scattering experiments, even at higher temperatures. In the next chapter I confirm this observation by directly imaging the film using confocal fluorescence microscopy. I will further show that a thick coating of TAHP is necessary for droplet stability against coalescence, and that heating the system (and dissolving

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**Figure 4.21** Comparison between the scattering from TAHP-stabilised emulsions with SLD-matched (black) and non-SLD-matched (grey) solvents. Dotted line shows $I(q) \sim q^{-4}$. 
(Top) SANS data for an approximately SLD-matched (5% v/v h-dodecane in oil phase) shown for the full q-range studied. Measurements were performed at 35°C (green), 45°C (orange), and 55°C. Inset: The same data, with only the region near the 1st order Bragg peak shown, same colours as in main figure.
the TAHP film) leads to coalescence of the droplets. It is this dissolution that explains the drop in Bragg peak prominence and scattered intensity at low-\(q\); dissolution of material leads to a reduction in the number of TAHP crystallites coating the droplets, and so fewer objects contributing to the scattering.

### 4.7 Conclusion

The assembly of films of Tetradecylammonium Hydrogen Phosphate (TAHP) at a planar dodecane-water interface has been studied. In a pH range between 5 and 8, FTIR has shown that two tetradecylammonium (RNH\(_3^+\)) cations bind stoichiometrically to a single HPO\(_4^{2-}\) anion, which leads to the formation of thick films consisting of micron-sized crystallites. The key processes guiding the formation of the films are counter-ion condensation at the interface followed by crystallite formation.

The kinetics of film formation and the physical and structural properties of the TAHP film have been studied by drop shape analysis and light microscopy. Increasing the pH of the aqueous phase has been shown to retard the kinetics of film formation, and reduce the quantity of TAHP formed. This has been observed by measuring the mass of dry TAHP formed and by studying the time scale over which significant interfacial elasticity is detected in pendant drops. The pH also directly impacts the mesoscopic structure of the film. Between pH 5 and 7 a TAHP skin, which completely covers the oil-water interface, is formed. At pH 8 a lace-like structure is formed. Light microscopy has shown that both of the structures consist of aggregated TAHP crystallites.

The TAHP film has also been shown to stabilise emulsions. Coalescence of the emulsions is arrested only at the pH at which TAHP is found to form. Using confocal fluorescence microscopy upon fluorescently doped TAHP and Cryo-SEM shows that, much like in the case of the emulsions, the TAHP film at the droplet interface consists predominantly of needle-shaped crystallites. The emulsions were then used in small-angle neutron scattering experiments to study the microscopic structure of the TAHP crystallites. SANS results show that, on the molecular level, the films have a lamellar structure with a repeat distance of 37.9 Å. In order to model the structure correctly correlations between up to 50 lamellae must be accounted for. This suggests there are very strong interactions between the monolayers. Upon heating the TAHP above 40°C, a
second lengthscale is observed in the system, and the scattered intensity and
prominence of the Bragg peaks is observed to drop. The emergence of the second
lengthscale is entropically driven, and corresponds to either de-interdigitation or
untilting of the aliphatic chains in the TAHP. The drop in scattered intensity
ostensibly occurs due to dissolution of the TAHP, and will be discussed more
extensively using an emulsion system in the next chapter.

In the next chapter, the properties of the TAHP film are applied to obtain both a
tunable interfacial rheology which is directly related to the film structure, and to
create temperature-responsive capsules. The relationship between the heating-
induced dissolution of the TAHP and the stability of the droplets is investigated.
Finally, a mechanism for production of TAHP-stabilised, monodisperse capsules
is developed. The wealth of variables that can be varied for this system, along
with the extensive body of work already performed on similar acid soap systems,
means there is significant scope for future work on this system that is not studied
in this thesis. The exact mechanism for formation of the thick TAHP film, rather
than a monolayer, is the major open question of the chapter. The effects of
varying the counter-ion upon the morphology of the crystallites could also lead
to range of structures with potential applications in controlled release of active
molecules.
Chapter 5

TAHP: Temperature Response, Tunable Interfacial Rheology, Emulsions and Capsules

In this chapter I will discuss the relationship between the structure of the TAHP films, their interfacial rheology, and their temperature response. I will then relate these properties to explain both the mechanism by which TAHP arrests coalescence in emulsion droplets, and why heating a TAHP-stabilised emulsion system leads to droplet coalescence. I will use light microscopy and interfacial rheology to show that the structure of the TAHP film and its interfacial rheology are directly connected. When the TAHP film forms a continuous sheet, the film is highly brittle. When it forms a lace-like network (as shown in Fig. 4.4 at pH 8), it deforms plastically when sheared. I will then use pendant drop shape analysis and interfacial rheology to study the temperature response of the TAHP film as the system is heated from 25 to 70°C. It is found that as the system is heated, the TAHP dissolves into the bulk fluid phases. This causes the rheological moduli of the film to drop, eventually becoming undetectable relative to sub-phase contributions. This corresponds to a relaxation in the shape of TAHP-coated pendant drops. It is found that, upon heating, TAHP-stabilised emulsions undergo coalescence. Direct imaging of the emulsion system during heating shows that this is due to dissolution of the TAHP crystallites. This shows unambiguously that it is the steric barrier provided by the thick elastic TAHP film that is the origin of the stability of the droplets, rather than electrostatics or Marangoni flows. Finally, I will show that TAHP is a suitable
stabiliser for preparing monodisperse capsules via a microfluidic method that is both cheap and easy to implement. The temperature-responsive nature of TAHP as an emulsifier, along with its suitability as an emulsifier using a number of production methods, suggest potential applications in water treatment and agricultural chemical encapsulation.

5.1 Introduction

The relationship between the rheology and structure of an interface is of fundamental physical importance. Close-packed, arrested monolayers of particles provide stability against coalescence for Pickering emulsions [39]. Replacement of a single residue can disrupt the network-forming capabilities of proteins essential for biofilm formation in bacterial colonies [172]. The fine-tuned phase behaviour of lung surfactant, a multi-component monolayer made mostly of lipids and proteins, is essential in enabling us to breathe [173]. In all of these systems, the physics of the interface determines the physics of the system. In this chapter, I will use TAHP as a model system to investigate how the rheology of an interfacial film varies from plastic to brittle as the structure changes from a continuous skin to a lace-like, aggregated structured.

In order for the structure and rheology of the interface to be related, two factors must be studied: the response of both the rheological moduli and the structure of the system to an applied stress. A number of techniques exist to do this, the most powerful of which is the combination of a sensitive interfacial shear rheometer, preferably one which allows for surface pressure control, and a method of imaging the structure of the system during shear. Light microscopy is power, easy-to-implement imaging method, but details smaller than 200 nm (or, more practically for the optics on a surface shear apparatus, 1 µm) cannot be resolved by light microscopy. It has, however, seen some success at studying materials that form domains on optically-visible lengthscales. At surface pressures near a phase transition, some lipids such as DPPC form micron-sized domains. This allows fluorescence microscopy to be used to study the deformation of the domains under shear [174]. Fuller and Yim used Brewster angle microscopy, a Langmuir trough, and an interfacial shear apparatus in studies on fatty acids. The phase behaviour of the lipids was studied using Brewster Angle Microscopy to image the film, the Langmuir trough was employed to determine the thermodynamic phase of the lipids, and an interfacial shear apparatus was used to measure the interfacial
viscosity \[175\]. A direct relation between the conformation of the lipids and their surface shear rheology could thus be found. Both continuous and discontinuous increases in surface viscosity were observed with increasing surface pressure, with discontinuous changes corresponding to phase transitions (see e.g., Fig. 9 in Ref. \[175\] or Fig. 6 in Ref. \[176\]). For molecular systems that do not have structure on optically visible lengthscales, determining the structure of the system under flow is challenging. Scattering and reflectometry methods such as grazing-incidence x-ray diffraction (GIXD) allow the structure of a film to be determined on molecular length scales \[177, 178\], but application of these methods to in situ studies of flow upon molecular monolayer systems is experimentally challenging \[176\]. The development of model systems for interfacial rheological studies, which contain structure on a lengthscale that can be visualised with light microscopy, is therefore desirable.

Colloidal particles spread at the fluid-fluid interface fulfil this criterion. Their large size (on the order 0.5 - 5 \(\mu\)m) makes their study with light microscopy trivial, and their interaction potentials can be readily tuned by varying the salt concentration in the aqueous phase. Interfacial rheo-optic shear measurements have been performed upon these systems recently, using a number of apparatuses \[179–182\]. The use of colloidal particles as model systems for interfacial rheology allows for the structure of the system to be tuned relatively easily (by varying e.g., aqueous salt concentration, particle radius, and particle surface chemistry), whilst simultaneously being able to implement particle tracking of a representative portion of the system \[89, 183\]. Such systems have a number of disadvantages, however. Interfacial shear moduli are typically on the order of 1 - 1000 \(\mu\)N/m \[184\], meaning rather sensitive equipment is required to perform measurements. Convective motion in large, 2-dimensional monolayers of colloidal particles, caused by flows in the bulk sub-phases, can also make imaging the system challenging.

In this chapter, I find that TAHP, which has been shown to have structural features large enough to be easily visualised using light microscopy, also has a notably large elastic modulus \(G_s' \sim 10 \text{ N/m}\). This, combined with its tunable structure, allows a direct relationship between the film’s structure and interfacial rheology to be made. I will compare interfacial rheological measurements with pendant drop images and confocal fluorescence microscopy to link together the

\[1\] See Sec. 2.3 for a more extensive discussion of the conditions under which this statement is, and isn’t, true.
structure and interfacial rheology of the TAHP. With an aim of developing TAHP towards applications of encapsulation and emulsion stabilisation, I will show how these properties result in the formation of temperature-responsive water-in-oil emulsions.

5.2 Materials and Methods

The chemical components used in this chapter are identical to those described Chapter 4: Tetradecylamine (≥ 95%) and dodecane (ReagentPlus, ≥ 99%) were purchased from Sigma-Aldrich, UK, and used as obtained. Water was de-ionised and filtered through a Milli-Q reverse osmosis unit (resistivity > 10^{18} \Omega m). Sodium hydrogen phosphate salts (monobasic monohydrate and dibasic dihydrate, ≥ 99%, Sigma Aldrich, UK) were used as the source of phosphate ions. Minor adjustments to pH were made using 1 M NaOH and 1 M phosphoric acid. All experiments presented here were performed using an aqueous solution of 100 mM H_nPO_4^{(3-n)-}, with the ratio $\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$ in the aqueous phase controlled by varying the initial pH. Salts and primary amines were dispersed in their solvents using a warm ($T \approx 40^\circ C$) ultrasonic bath to ensure complete homogenisation of the samples.

5.2.1 Interfacial Rheology

Interfacial rheology results were taken using a TA DHR-2 Rheometer (TA Instruments) equipped with a Pt-Ir DWR (Double Wall Ring) interfacial geometry. The technical aspects of interfacial rheology, including a brief overview of the experimental set-up used here, have been discussed in Sec. 3.3. The Pt-Ir ring was flame-treated between experiments using a butane burner to remove any contaminants. To take measurements the aqueous phase was added into a Delrin trough and the ring was lowered such that the sharp edges of the interfacial geometry were level with both the air-water interface and the lip of trough. 10 ml of dodecane containing a known concentration tetradecylamine was then gently added on top. During film formation, the rheometer was operated in controlled strain mode to prevent damage to the film, with a small amplitude oscillatory strain (typically 0.01%) applied at 0.5 Hz. In experiments probing the yielding behaviour of the film, the rheometer was operated in controlled
stress mode, as the abrupt drop in the film’s rheological moduli in the non-linear region resulted in large strain overshoots. An increasing oscillatory 0.5 Hz stress was applied, with typical values ranging between \( \sigma_s = 10^{-5} - 0.1 \) N/m. For temperature measurements, the trough was covered with an aluminium lid and samples were equilibrated for 2 hours before the measurement was performed. Further measurements were taken using a TA AR-G2 rheometer with a stainless steel 22mm diameter bicone geometry to control for geometry- and instrument-specific effects. Sample preparation and experimental procedure was identical for experiments on both devices. The two geometries have been compared in Sec. 3.3.

5.2.2 Pendant Drop Tensiometry

Pendant drop images were obtained using the Krüss Easy Drop apparatus and accompanying software, described in Sec. 4.2.3. Measurements were performed with the sample inside a temperature-controlled chamber and samples cooled at a constant rate of 0.5°C or, where temperatures are quoted, after the sample had been left for 30 minutes to reach thermal equilibrium. The system temperature was calibrated and measured remotely using a thermocouple attached to a LakeShore 331 Temperature Controller (Lake Shore Cryotronics Inc., US). The dodecane was held in a 6 ml cubic borosilicate glass cuvette. The needle was lowered into the dodecane bath and the pre-determined volume of water was injected at 0.5 ml/min. The injection and ageing of the droplet was recorded at 31 frames per second over time periods less than 1 minute, and at 1 frame per minute for longer experiments.

5.3 The Interfacial Rheology of TAHP

Interfacial shear rheology is used in this thesis both as a tool to study the kinetics of the film formation (as in this section) and as a method for studying the relationship between the structure of the film and its mechanical properties (in the next section). I will begin by studying the effect of the pH of the aqueous phase upon the interfacial rheology of the film during its formation. I showed in the last chapter that, below a critical pH, the combination of tetradecylamine in the dodecane and hydrogen phosphate in the aqueous phase leads to the formation of films at the oil-water interface. The films are expected to be rather elastic, as
shown by the significant deformation of pendant drops (see e.g., Fig. 4.8). The rates at which the pendant drops are deformed, and so the time scale at which a significant interfacial elasticity emerges in the system, was found to depend on the pH. At pH 5, the pendant drop was deformed by the TAHP more rapidly than the apparatus could extrude it. Contrastingly, at pH 7 it took several seconds for the error of the fit of the droplet profile to the Young-Laplace equation to become significant. This was attributed to retarded film formation kinetics. Another pH-dependent feature was also observed: the quantity of TAHP formed. Between pH 5 and 7 the quantity of TAHP formed after 60 hours was identical, and corresponded to approximately 90% of the TDA added to the system. As pH was increased, this number decreased rapidly, and no TAHP was found to form at all at pH 9. All of these features have been investigated quantitatively here using interfacial shear rheology. I find that the percolation time of the TAHP network is connected to the film formation kinetics, and that this time increases with the pH of the aqueous phase. I will also find good agreement between the reduced quantity of TAHP with increasing pH and the final strength of the film.

5.3.1 The Effect of pH Upon Film Formation

The effect of pH upon film formation kinetics is shown in Fig. 5.1. Film formation was observed for 10 hours at pH 5 (green lines), pH 7 (purple lines), and pH 8 (orange lines). Both the elastic shear modulus \( G'_s \) (dark colours) and the viscous shear modulus \( G''_s \) (light colours) are shown.

At pH 5 and 7 a very large elastic modulus is detected from the moment measurements commence. This shows that significant interfacial elasticities are acquired by the TAHP film in under 1 minute. The rheological moduli at both pH 5 and 7 then increase by an order of magnitude over the course of 2 hours, before plateauing at a very large, elastic-dominated value \( G'_s \approx 10 \text{ N/m}, \text{ phase angle} \leq 1^\circ \). The increase in the rheological moduli at short times is more rapid at pH 5 than at pH 7, reflected by the higher value of \( G'_s \) measured at the start of the experiment at pH 5. The longest time over which the systems at pH 5 and 7 were observed was 60 hours. No significant change in the rheological moduli were observed on these timescales.

The formation of the film exhibits markedly different trends at pH 8. The rheological moduli at pH 8 are negligible for the first 2 hours of the experiment, with only the sub-phases detected. This corresponds to rheological moduli of
order $10^{-4}$ N/m. After two hours, the rheological moduli increase sharply. With the exception of the first hour of this increase, $G'_s$ exceeds $G''_s$ by an order of magnitude, showing that the TAHP films are highly elastic even at pH 8. 10 hours after the rheological moduli begin increasing, the rate of increase slows, eventually reaching a value on the order 1 N/m. This final value is found to vary between 0.1 and 3 N/m. Experiments studying the film for longer times show that, after 10 hours, the rheological moduli at pH 8 typically plateau, with a decrease of up to 50% sometimes observed after 60 hours of observation. The system then typically reaches an steady state value after 60 hours.

The results in Fig. 5.1 show that for all systems, independent of pH, the fully-formed films are highly elastic with $G'_s$ exceeding $G''_s$ by over an order of magnitude. This corresponds to a phase angle between the applied stress and strain of approximately 1°. The pH of the aqueous phase affects both the final rheological moduli of the film and the rate at which the film forms. At pH 5, the storage modulus of the film exceeds 100mN/m (and therefore that values at which surface tension would determine the drop shape) more rapidly than can be detected, explaining the significant deformation of the pendant drops in Figure 4.8. At pH 7, the rate of film formation is slowed somewhat, but the final values
of the rheological moduli are similar for both pH 5 and 7. This agrees with the observations made using the pendant drop in the previous chapter. There, a higher pH led to the timescale on which the droplet was deformed being retarded. The interfacial rheology results shown here also allow us to quantify phenomena that the pendant drop does not. It has been shown that the final values of the films’ rheological moduli depend on the pH of the aqueous phase. This is also in agreement with the results obtained in the previous chapter, in which the quantity of TAHP formed was found to decrease with the pH of the aqueous phase. This suggests that thicker TAHP films have larger rheological moduli. I will confirm this directly in the next experiment, in which I measure the dependence of film strength upon the quantity of TDA added to the system.

Between pH 5 and 7 the system gives highly repeatable results. At pH 8 the percolation time, film formation rate, and final value of film strength are highly variable: values for the interfacial storage modulus between 20 and 1000mN/m have been measured. Likewise, the time after which a film can be detected has been observed to range from the order of minutes up to several hours, with some films requiring 60 hours for the interfacial rheological moduli to reach stable values. There are a number of possible reasons for this. The images of TAHP formed in crystallisation dishes (previous chapter, Fig. 4.4) shows that the TAHP film at pH 8 consists of only a partial covering of aggregated TAHP crystallites. The crystallites that make up the film, as observed using light microscopy in Fig. 4.6, are too large to undergo thermal diffusion on a relevant timescale. These two factors suggest that the non-equilibrium structure of the film is being probed. It is therefore reasonable to expect that the rheological moduli will be rather history-dependent, and that the percolation time will be a statistical property, rather than having a single characteristic value. The long time-scale variations, which do not affect the film at pH 5 and 7, are likely to represent large length scale changes in the structure of the film, possibly induced by evaporation of the fluid phases over the course of 60 hours.

The Effect of Varying [TDA]

As noted in the yield measurements in Fig. 4.10, 90% of the TDA added to the system ends up at the interface as solid, insoluble TAHP. The presence of phosphate in the films, shown using FTIR in Fig. 4.11, suggests this is due to a reduction in the solubility of the primary amine in either fluid phase due to
the binding of the primary amine to the phosphate counter-ion. It is therefore reasonable to expect that, the majority of the TDA in the system will be present at the interface as TAHP. This means the quantity of TAHP formed can be quantitatively controlled by varying the TDA concentration ([TDA]).

The effect of varying the amount of TAHP formed by varying [TDA] is quantified here using interfacial shear rheology.

The final values of the interfacial rheological moduli depend on the initial quantity of tetradecylamine used. This is shown for the case of TAHP films formed at pH 5 in Fig. 5.2. Varying the initial TDA concentration between 2.5 and 6.5 mM allows the film strength to be varied by a factor of approximately 3, and the system reaches a steady value for $G'_s$ and $G''_s$ after one hour. At TDA concentrations below 1 mM, the behaviour of the system is somewhat more complicated. The behaviour of the films formed at low TDA concentration during the first hour of the experiment is similar to those formed at high [TDA]. The rheological moduli reach extremely high values more rapidly than the apparatus can detect, and steadily increase up to values of 0.5 - 15 mN/m, depending on the concentration of TDA used. Whilst the films formed at [TDA] ≥ 1 mM then have constant rheological moduli, the films formed at low concentration typically reach a peak in $G'_s$ after 2 hours, before decreasing by up to an order of magnitude over the course of up to 60 hours. This is similar to the behaviour exhibited by the film at pH 8. At very low concentration of TDA, 200 µM or less, no film is observed to form.

Varying the amount of TDA added to the system varies the amount of TAHP formed. The results in Fig. 5.2 shows that increasing [TDA] increases the rheological moduli of the film. This is a direct consequence of the film being thicker. Quantitative work to understand the scaling of the film strength with [TDA], and how that relates to the amount of TAHP formed, has not been undertaken in this thesis. Whilst varying [TDA] clearly has an effect upon $G'_s$, (as shown in Fig. 5.2), the exact mechanism by which the TAHP forms is not known, and the final mesoscopic structure of the skin-like film formed at pH 5 is likely rather history-dependent.

The steady decrease in rheological moduli at both low [TDA] and pH 8 likely have a similar origin. At pH 8, the quantity of TAHP formed is much smaller, and the kinetics of film formation are much slower. Film detection requires the

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2At low concentrations ([TDA] < 0.2 mM) the finite solubility of the TAHP in the dodecane at room temperature will render this assumption invalid, as will be discussed later
TAHP to precipitate or nucleate at the oil-water interface, and for the needle-shaped crystallites shown in Fig. 4.4 to form a percolating network on the length scale of the shear gap of the rheology geometry (about 4 mm in the case of the DWR). In the case of low TDA concentrations at pH 5, whilst the kinetics of TAHP formation are very rapid, the quantity of material formed is still insufficient to completely cover the amount of interface present. Incomplete coverage of the interface may lead to long time-scale rearrangements of the film structure due to convective motion at the interface, explaining the variation of the films’ rheological moduli during formation under these conditions. Determining the exact relationship between [TDA] and $G'_s$ is therefore rather challenging.

The values of the rheological moduli of the films, $G'_s \approx 1 - 10$ N/m are over an order of magnitude larger than typical values for interfacial films. Rheological moduli for elastic films typically range from $10^{-6}$ N/m for particle monolayers [181], up to 0.1 N/m for films consisting of proteins or polysaccharides [185, 186]. The strength of the TAHP film can be attributed to its thick, multi-layer structure: estimating molecular area as 20 Å² (in line with previous work on TAHP monolayers [160]) gives the film an estimated thickness of 300 layers (approximately 1 µm) when using 10 ml of 2.5 mM TDA in the DWR geometry. By contrast, the majority of interfacial shear measurements have been performed

Figure 5.2  Interfacial storage modulus ($G'_s$) of TAHP films formed at constant pH 5 and varying [TDA].
on comparatively thin films, such as those consisting of proteins \cite{187, 188}, and insoluble surfactant monolayers \cite{189}, or comparatively weakly-interacting systems such as colloidal particles \cite{190}. The concentration dependence of the final values of $G'_s$ suggest that the extremely large rheological moduli measured for the TAHP film are a direct consequence of its thickness.

5.3.2 Dependence of Film Rheology Upon Structure and pH

The TAHP films have a macroscopic structure that can be trivially tuned by varying the pH of the aqueous phase. It is expected that changing the structure of the film, from a continuous skin to a lace-like film of aggregates, will affect the way in which the film deforms when a stress is applied. I discuss this effect here, and investigate it using interfacial shear rheology.

The interfacial rheological moduli ($G'_s$ and $G''_s$) of TAHP films formed at different pH values (and, hence, with different structures) at increasing interfacial shear stresses is shown in Figure 5.3. At low strains ($\gamma_s < 0.1\%$), the skin-like pH 5 film behaves like a Hookean solid ($G'_s \gg G''_s$), and the rheological moduli are independent of strain rate. As shear stress is increased, the rheological moduli drop steeply over a very narrow range of stresses. At $\gamma_s \approx 0.5$ the film breaks. The residual rheological moduli measured ($G'_s, G''_s \approx 10^{-5}$ N/m) correspond to contributions from the (bulk oil and water) subphases. After the rheological moduli crash, the raw phase between stress and strain is approximately 180°. This shows that rather than measuring the physics of the interface, the inertia of the instrument dominates the measurement and that the film has been destroyed at high strains \cite{91, 191}.

At pH 8, the rheological behaviour is markedly different. At low interfacial stresses, the film deforms elastically. The deformation required to achieve a certain strain is significantly lower at pH 8 due to the lower rheological moduli of the system. As interfacial stress is increased, the difference in behaviour of the skin-like and lace-like film becomes apparent. Rather than yielding abruptly, the film deforms plastically at increasing strain, exhibiting a small peak in the loss modulus, and a cross-over of $G'_s$ and $G''_s$ at $\gamma_s \sim 0.25\%$.

The data obtained in Fig. 5.3 are re-plotted as $\tau_s$ against $\gamma_s$ (interfacial stress and interfacial strain, respectively) in Fig. 5.4. Doing this yields the stress-strain curves associated with a classical brittle (at pH 5) and plastic (at pH 8) material
Figure 5.3  Top: Macroscopic structure of TAHP films formed at different pH values, shown in the previous chapter. Bottom: Interfacial shear moduli of TAHP films formed at different pH values, measured at increasing interfacial stress.

The lace-like film deforms plastically with increasing stress. In the non-linear region a steadily-increasing ratio of strain to stress can be seen, indicating a weakening of the film. The skin-like film deforms like a brittle material, such as concrete, where the non-linear region is characterised by a very steep increase in strain as a function of stress. This appears to be a direct consequence of the differing structures of the films.

To ensure this was purely a static, structural effect, rather than being due to dynamic relaxation mechanisms in the films, the dependence of the rheological moduli upon the frequency of the applied stress was measured. In the case of there being a dynamic mechanism by which stress is relaxed in this system, frequency dependence of $G'_s$ and $G''_s$ would be expected. As shown in Figure 5.4
inset, the interfacial rheological moduli of the TAHP films are independent of the frequency of the oscillatory stress. Given the chemical similarity of the pH 5 and pH 8 films shown in the previous chapter, the change in yielding behaviour seems to be a direct consequence of the lower interfacial coverage at higher pH values. Complete interfacial coverage at pH 5 appears to inhibit the structural re-arrangements that give rise to plastic deformation at pH 8, and thus brittle behaviour is observed.

Figure 5.4  Strain as a function of interfacial stress at pH 5 and pH 8. Inset: Interfacial shear moduli as a function of frequency at pH 5 and pH 8. The dodecane contains 2.5 mM TDA.

5.3.3 Control Experiment Using a Different Geometry

In order to control for instrument- and geometry-specific effects, the experiments on the pH 5 film were repeated using a stainless steel bicone, single Couette geometry (as oppose to a Pt-Ir, double Couette geometry). A comparison between the two results is shown in Fig. 5.5. The results are qualitatively extremely similar. Both systems show a highly elastic, linear deformation region at low strains, and an abrupt drop (corresponding to the film yielding) in the rheological moduli at $\gamma_s \approx 0.5\%$. After yielding, the results obtained differ significantly in magnitude. This is not due to the physical properties of the film at these stresses (as the film has been irreversibly broken), but instead due to the differing signal-to-noise ratios of the two geometries. The values obtained at high stresses
Figure 5.5  *Comparison of $G'_s$ and $G''_s$ of a 2.5 mM TAHP film formed at pH 5, measured using a stainless steel bicone geometry (blue) and a Pt-Ir DWR geometry (green).*

correspond to background contributions from the bulk phases and the instrument inertia (the raw phase at high stresses is approximately 175°). Hence, in the case of the larger bicone geometry, these values are significantly higher.

Similar variation in interfacial rheological properties have been observed in experiments performed on two-component interfaces consisting of DNA complexed with varying concentrations of a cationic surfactant (DTAB) [193, 194]. In these studies, a bicone geometry was used to show that the interfacial rheology of the DNA-surfactant complexes varied from linear, to plastic, to brittle as surfactant concentration was increased, and that this change could be directly linked to a change in the relaxation dynamics of the monolayers. Brewster Angle Microscopy images also showed that, in the brittle regime, the film could be fractured using a glass pipette, resulting in film ruptures similar in appearance to those shown in Figure 5.6. Rather than being due to a change in the dynamics of the system, the switchable interfacial rheology of the TAHP films studied here is a direct consequence of the mesoscopic structure of the films, which we can directly visualise, as in Figure 4.4.
5.4 Temperature Response: The TAHP Interface Dissolves When Heated

Temperature response is an attractive property for functional materials to have. It can be used to trigger a change in the system using a stimulus that is comparatively simple to apply. It has already been noted during the scattering experiments that TAHP-stabilised emulsions coalesce when heated. In this section I will study the regime in which this temperature response occurs. I find that when heated, TAHP-coated pendant drops change shape continuously with temperature. The film is seen to thin steadily, rather than discontinuously, as the system is heated. It will be found that the rheological moduli of the film decrease steadily with temperature, rather than dropping rapidly at a single characteristic temperature. These observations are used to infer that rather than being due to a discontinuous change in conformation at a characteristic temperature, the temperature response occurs due to dissolution of the TAHP into the fluid phases. I use confocal fluorescence microscopy and pendant drop shape analysis to link the appearance of the TAHP film to its rheological properties. I will show that TAHP-stabilised emulsions, when heated, coalesce. It will be found that the dissolution of the thick TAHP film from the droplet interface, the drop in the rheological moduli, and the heat-induced coalescence are all connected. This shows unambiguously that the TAHP stabilises the droplets by providing a steric barrier against coalescence.

5.4.1 Film Response to Heating

I begin by qualitatively studying the temperature response of the TAHP film using a pendant drop. This is shown in Fig. 5.6. I do this by showing how, when water is extracted from the pendant drop, the manner in which the pendant drop deforms under dilatational stress (applied by extracting water) depends on the temperature of the system. Here, the pendant drop was suspended from the needle at 25°C and the film was left to form for one hour, shown in Figure 5.6a. In the case of the measurement performed at 65°C the system was then heated, as shown in Figure 5.6b. The images show the droplet as the aqueous phase is withdrawn by the syringe. At 25°C the film is observed to rupture, tear, and detach from the droplet. At high (i.e., > 60°C) temperatures, withdrawal of the water results in a self-affine reduction in the droplet volume, showing the absence
of significant interfacial elasticity.

![Figure 5.6](image)

**Figure 5.6** Images of a TAHP-coated water droplet suspended from a needle in a dodecane/tetradecylamine bath at (a.) 25°C and (b.) 65°C. Photos of the droplet were taken as the water was extracted via the needle. [TDA] = 1 mM, pH 5, needle diameter = 1.83 mm.

The appearance of a pendant drop coated with a TAHP film is also shown in Fig. 5.7. This is presented alongside interfacial shear rheological measurements performed on a TAHP film at increasing temperature. At each temperature shown the drop was left to equilibrate for 30 minutes before imaging commenced. At low temperatures, the appearance of the pendant drop is similar to that observed in the previous chapter: a thick film is seen to coat the droplet, deforming the droplet such that it is no longer described by a force balance between buoyancy and surface tension (that is, by the Young-Laplace equation). As the film is heated from 38 to 48°C the amount of light transmitted by the film increases, and the surface roughness of the film can be clearly seen to decrease. Increasing the temperature to 57°C results in a dramatic change in the shape of the droplet, and only a partial coating of TAHP is present. The droplet profile is described well by the Young-Laplace equation in regions where the remaining solid TAHP is not present. Increasing the temperature to 66°C results in almost all of the TAHP being dissolved, and a good fit to the Y-L equation (fit error ≤ 1 µm). The water-dodecane surface tension of this drop is approximately 15 mN/m, significantly lower than the expected surface of a clear dodecane-water interface [80], showing
that surface active molecules are still present at the interface.

The temperature response of the TAHP film is dependent upon the concentration of TDA used and, hence, the thickness of the film. Interfacial shear rheological measurements of the film during heating at different TDA concentrations were performed, and are shown in Fig. 5.8. In the temperature range in which the rheological moduli of the film are within detection limits of the equipment, the film is an elastic solid. Increasing the temperature of the system leads to a decrease in the interfacial storage modulus of the film. There is a similar decrease in the interfacial loss modulus of the system. However, the values of $G_\prime$ and $G_\prime\prime$ are never observed to cross over until the raw phase between the force and displacement of the oscillation reaches $>170^\circ$, at which point instrument inertia dominates the measurement, making extraction of the rheological moduli challenging [187]. I refer to this as the ‘breaking’ temperature of the film. Given the negligible loss modulus of the film, I present only values for $G_\prime$ in Fig. 5.8.

Changing the fatty amine concentration varies the breaking temperature of the film. The elastic moduli are directly compared in Fig. 5.8. At $[\text{TDA}] = 2.5$ mM (Fig. 5.8 blue squares), the film can not be detected by the apparatus above $55^\circ$C. When TDA concentration is increased to $[\text{TDA}] = 6.5$ mM (Fig. 5.8 orange squares), the temperature at which the film cannot be detected is shifted above $65^\circ$C, which is above the accessible temperature range of the apparatus. This suggests that the temperature response of the system is due to dissolution of the TAHP in the fluid phases at higher temperature, rather than being due to a phase transition characterised by a single temperature. Light scattering experiments on the dodecane supernatant performed at high temperature ($65^\circ$C) showed no significant increase in scattering intensity that could be attributed to micelle formation, suggesting the TAHP is present in the dodecane as monomers.

### 5.4.2 Recovery of Film Strength After Cooling

A range of TAHP film morphologies can be observed by cooling the system, and are shown in Figure 5.9. The appearance of a droplet of aqueous hydrogen phosphate solution at pH 7, in a bath of dodecane containing 2 mM TDA, is shown as the system is cooled at approximately $0.5^\circ$C s$^{-1}$. At $43^\circ$C the droplet has no observable coating of TAHP, much like the drop at high temperature in Figure 5.7, and a good fit of the droplet profile to the Young-Laplace equation is obtained ($\gamma = 15$ mN/m).
As the system is cooled, clusters of solid TAHP can be seen to appear on the droplet interface. Cooling further causes the clusters to coarsen, eventually percolating and forming a lace-like structure, similar in morphology to the film formed in the crystallisation dishes at pH 8, shown in Fig. 4.4. There is a corresponding jump in the error of fit to approximately 5µm at 23 min, showing that the film significantly deforms the droplet. As the drop is cooled further, the interfacial film becomes visibly darker and completely coats the droplets. This phenomenon has been observed in droplets at a range of pH between 5 and 7. The temperature at which the film formed and coarsened in these measurements was found to increase with fatty amine concentration, in agreement with the observation that the film formation is solubility driven.
Figure 5.8  Interfacial shear storage modulus ($G'_s$) against (increasing) temperature for two different concentrations of TDA (blue: 2.5 mM; orange: 6.5 mM). Error bars are the standard error in 3 measurements. $T_{\text{break}}$ is denoted by the temperature at which the raw phase rose above 170° (estimated in the case of the 6.5 mM system).

The rheological behaviour of a TAHP film during cooling has also been observed (shown in Fig. 5.10). After being heated to 62°C (above the breaking temperature of the film formed at these conditions - $T_{\text{break}} \approx 55°C$), the system was then cooled to 25°C. The rheological moduli were measured for two hours, as the apparatus requires approximately 60 minutes for the temperature to equilibrate. As the system cools, a film is detected by the apparatus after approximately 5 minutes. The rheological moduli of the system then rapidly increase as more TAHP precipitates out of the dodecane and onto the interface. After approximately 60 minutes, once the temperature of the system has reached 25°C, the rheological moduli are seen to plateau.

Both the interfacial rheological measurements and the drop shape analysis measurements of the TAHP film during cooling, shown in Figs. 5.9 and 5.10 suggest that the TAHP film undergrows several growth stages: nucleation of crystallites, growth of the crystallites, percolation of the network. This is imaged directly using drop shape analysis, in which the growth of the crystals can be directly visualised, and the percolation of the network can be detected by a sharp increase in the error of the fit of the drop profile to the Young-Laplace equation.
The interfacial shear rheology measurements show that this growth can be detected as percolation and coarsening of the film, corresponding to an increase in the rheological moduli of the system. These processes happen continuously, over a broad range of temperatures, rather than at a single, characteristic temperature. This suggests that, rather than being due to a phase transition, such as that observed in temperature-responsive, fatty acid needle-stabilised foams [3], the temperature response in the TAHP system is driven by the increases solubility of the TAHP in the dodecane at high temperatures. I've discussed this analogous system in the Background of this thesis, Sec. 2.1.3.
5.4.3 Effect of Heating on Emulsion Stability

Direct imaging of the TAHP-stabilised emulsion during heating, both macroscopically and microscopically, is shown in Fig. 5.11. In the confocal micrographs in Fig. 5.11 an aliquot of TAHP-stabilised emulsion was dispersed into 5 ml of dodecane and imaged. In the photographs, a large amount of sample (droplet volume fraction $\approx 40\%$) was used in order to study the stability of the system to coalescence as the TAHP film was dissolved. To prepare the samples in the cuvettes, TAHP-stabilised emulsion droplets were pipetted into the glass cuvettes. The cuvettes were then immersed in a water bath for 30 minutes at the stated temperature.

Confocal micrographs in Fig. 5.11 show the interface thinning inhomogeneously as temperature is increased. The fluorescence signal from the interface, becomes significantly weaker as TAHP is dissolved into the dodecane. Typically, smaller droplets retain at least a partial covering of the interfacial film at higher temperatures. Needle-like crystals of TAHP and TDA-NBD can be clearly seen projecting from the droplet interface in the bottom-left of Figure 5.11 centre, at
The appearance of the TAHP-stabilised emulsion at 52°C is very similar in appearance to the sample at room temperature (not shown here due to similarity). Droplets were not inspected using microscopy to see if any coarsening had occurred, but clearly an emulsion is present in the cuvette. As the system is heated to 57°C, significant coalescence is seen to have occurred, with individual droplets large enough to be distinguishable by eye near the top of the cuvette. At 63°C, the emulsion has coalesced further, with the entire emulsion seen to coalesce upon being heated to 67°C. A milky white substance can still be seen surrounding the droplets, showing that TAHP is still present in the system, but that the residual TAHP is ineffective as an emulsifier.

![Figure 5.11](image)

**Figure 5.11**  

a.) TAHP-stabilized emulsion droplets heated to (left to right) 40, 50, and 60°C. Low concentrations of TDA-NBD are present in the water and fluoresce under the same frequency of light as the TDA-NBD present at the drop interface, though the signal from the water may be due to reflections. The right two micrographs have had the intensity doubled to make features in the image clearer.  

b.) TAHP-stabilized emulsions in quartz glass cuvettes imaged after the cuvettes have been immersed for 30 minutes at the stated temperature. [TDA] = 5 mM, aqueous phase is at pH 5. Image contrast has been enhanced for clarity.

The images in Fig. 5.11 show that film structure and emulsion stability are directly related. The dissolution of the TAHP causes the drop in film rheological moduli with increasing temperature. As the system is heated, the TAHP film dissolves into the dodecane, the film’s rheological moduli drop, and the TAHP-stabilised
emulsions coalesce. At high droplet volume fractions ($\phi_{\text{droplet}} \approx 30\%$), droplets have been observed to be stable above $50^\circ\text{C}$. This temperature is significantly higher than the temperature the second length scale was detected in the scattering experiments ($40^\circ\text{C}$), suggesting that the microscopic structure of the molecules within the TAHP has little influence upon the stability of the droplets against coalescence. Rather, as shown by the progressive coalescence of the emulsions in the vials in Fig. 5.11, the dissolution of the film removes the steric barrier to coalescence which the TAHP provides. It should be noted that the droplet concentration in the fluorescence micrographs in Figure 5.11 top, is significantly lower than in the cuvettes in the same figure, bottom, and so the droplets in the confocal micrographs are unstable at lower temperatures.

The point at which the rheological moduli of the film fall below the detection sensitivity of the interfacial rheology apparatus, combined with the direct fluorescence imaging of the droplet interfaces during heating, shows that it is the thinning of the film that causes the droplets to coalesce. Other workers have seen similar, temperature-responsive behaviour in foams stabilised by fatty acid needles, albeit arising from a slightly different cause [3]. The temperature-response in the fatty acid-stabilised systems is caused by the increase in temperature driving a phase transition from tubule to micelle conformation [3]. I’ve drawn this previously in Fig. 2.5. The temperature-responsive behaviour in the TAHP films occurs due to the dispersion of the TAHP in to the fluid phases, and is hence driven by the temperature-dependence of the equilibrium concentration of TAHP in the fluid phases. The acid soap-stabilised foams exhibited a marked drop in stability at a single temperature ($\sim 60^\circ\text{C}$) due to a change in the conformation of the fatty acids. By contrast, the coalescence temperature of TAHP-stabilised emulsions in the temperature range probed is dependent on TAHP-film thickness and the volume fraction of emulsion in the dodecane. Indeed, I have found that simply dispersing an aliquot of TAHP-stabilised droplets in a large volume of dodecane at room temperature induces their coalescence.

### 5.4.4 Emulsification by Extrusion

It has been shown that interfacially-assembled TAHP films form under a wide range of conditions, and that any bare oil-water interface present in the system rapidly acquires a very high interfacial elasticity due to TAHP formation. The
facility with which TAHP forms a film suggests that it is ideal for stabilising capsules fabricated via an extrusion mechanism. In this section I will show that, using the method developed for preparation of monodisperse capsules of Umbanhowar et al.\[9\], TAHP is extremely suitable for production of monodisperse capsules using microfluidic methods, whilst also possessing the high stability against coalescence of Pickering emulsions.

Figure 5.12 Photograph of the experimental set-up used to obtain the capsules shown in Fig. 5.13. Method taken from Ref. \[9\] et al. Constructed by David French, using the modifications proposed by Keith Bromley.

Water-in-oil capsules were made by injecting aqueous hydrogen phosphate solution into a co-flowing stream of 5 mM TDA dispersed in dodecane, as described elsewhere \[9\]. The equipment used in this experiment differs slightly from that described in Umbanhowar et al in that, rather than using a compressed nitrogen cylinder to drive fluid flow, a syringe pump with an electric motor was used to give greater control over the injection rate of the aqueous phase. 0.5 ml of aqueous solution was injected into the dodecane bath at a constant rate of 0.1 ml/minute through a glass needle with a tip width of 150 µm, which was placed 2 cm from the cup centre. The cup was rotated at approximately 1 Hz. The TAHP was fluorescently doped using NBD-Cl, as described in Sec. 4.2.2.
Water-in-oil capsules formed using the injection-in-coflowing-stream method are shown in Figure 5.13. The appearance of the interface of the capsules is very different from that of the emulsions. Individual plates or crystallites of material cannot be distinguished, and the interface appears significantly smoother. It was found that excessive cup rotation-rates during emulsification led to large cracks appearing at the droplet interface, which was attributed to droplet-droplet collisions during formation. Much like the emulsions, the capsules were found to be highly resistant to coalescence, remaining stable after significant shearing between two glass coverslips.

5.5 Conclusions

Rheological, emulsification, and temperature-response properties of the TAHP film have been studied. It has been shown that the tunable macroscopic structure of the TAHP film and its interfacial rheology are connected. When the TAHP film has a lace-like structure, it deforms plastically at large strains. When the TAHP film has a continuous, skin-like structure, the collective motions which allow for plastic deformation cannot happen, and so the film behaves like a classic brittle material.
Drop shape analysis and interfacial rheology have shown that the TAHP film is also temperature-responsive. When the system is heated, the film thins and its rheological moduli drop. Rather than happening at a single, characteristic temperature, it has been shown that this is due to dissolution of the TAHP into the dodecane. The temperature-response can therefore be tuned by varying the initial film thickness. The temperature-induced breaking of the film is reversible upon cooling, which leads to nucleation of the TAHP crystallites on to the oil-water interface.

Highly stable water-in-dodecane emulsions have been shown to be stabilised by TAHP, and the TAHP has been shown to be suitable for stabilisation of emulsions using a number of methods - both by shear, and by extrusion for the production of monodisperse capsules. Both the emulsion stability and the TAHP film exhibit identical pH dependence and temperature response, showing that the TAHP stabilises the emulsion by forming a steric barrier that hinders droplet coalescence.

Future work must better study potential applications of TAHP as a stabiliser. Of particular interest, both industrially and scientifically, would be developing water-in-oil capsules of tunable interfacial thickness and, hence, physical properties. Fine-tuning of the temperature response of the system could lead to potential applications in controlled release of active compounds.
Chapter 6

Emulsions with a Composite TAHP/Colloidal Particle Interface

In this chapter I will discuss the emulsions stabilised by a composite interface consisting of TAHP and colloidal particles made from polymethylmethacrylate (PMMA). I refer to these as ‘TAHP-PMMA’ or ‘composite’ interfaces. The particles used are relatively monodisperse ($\sigma_r \lesssim 0.10$) hydrophobic PMMA particles with poly-12-hydroxystearic acid (PHSA) polymer chains grafted on to their surface, which results in the particles having a very short-range repulsive pair potential in some non-polar solvents. I begin by re-visiting TAHP as an emulsion stabiliser and discussing some aspects relevant to the properties of the composite interfaces. I will show that TAHP shares several properties with Pickering emulsions (in particular, an interface that provides a steric barrier to coalescence, and the scaling of mean droplet diameter, $d_{43}$, as $d_{43} \sim [\text{TDA}]^{-1}$). I will show that this behaviour arises via two mechanisms. The first of these is the quantity of TAHP formed during formation, which is directly analogous to particle volume fraction in a Pickering emulsion. The second of these is, remarkably, the surface tension of the system. At the short time scales on which droplet break-up occurs, surface tension rather than interfacial elasticity governs droplet break-up in the TAHP-stabilised system. As long as there is sufficient emulsifier present, higher $[\text{TDA}]$ leads to lower surface tensions and, hence, smaller droplets.

I will then study the behaviour of water-in-oil emulsions stabilised by colloidal PMMA particles. These two systems are used as control groups for the study of

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1See Sec. 6.2 for a brief discussion of the synthesis and polydispersity of the particles.
an emulsion system stabilised by a composite interface. I study how the use of the two emulsifiers affects the interfacial structure, the droplet size distribution, and the stability of the emulsions in response to an external stimulus (i.e., heat). I will show that the drop size of the composite interface emulsion system is determined almost entirely by the fatty amine concentration. This allows me to vary particle volume fraction whilst keeping the droplet size constant. I will then apply TAHP as a molecular stopwatch that tunes particle uptake and arrangement at the droplet interface, whilst keeping droplet size constant. I will show that particle coverage of the droplet interface can be varied simply by increasing the amount of particles initially added to the system. It is found that, if a large amount of particles are added to system whilst the amount of surface area created during emulsification remains constant, droplets covered in self-affine aggregates of particles are formed. These aggregates consist of both TAHP and colloidal PMMA, and protrude from the droplets, giving them a hairy appearance. Finally the temperature response of the composite interface system will be studied. The dissolution of the TAHP via heating renders the interface fluid, allowing the particles to re-arrange and order.

6.1 Introduction

The structure and function of an emulsion, and the physics of its interface, are intimately related. The properties of the interface depend strongly on its constituents, which can include surfactants, proteins [188, 195], polysaccharides [196], lipids [197], and colloidal particles [43, 78]. These components can all stabilise emulsions in multiple ways, but all of them retard the rate at which emulsion droplets coalesce. Emulsions and the mechanisms by which they are stabilised have been reviewed to some extent in Sec. 2.2.

Beyond maintaining droplets in a non-equilibrium condition, there is great scientific and industrial interest in what an emulsifier can be used to do. The large surface area of an emulsion system makes them useful as reaction vessels [198]. The presence of a continuous phase through which an extra reagent can be flowed gives them applications in the synthesis of materials with unusual geometry [199, 200], and allows for the formation of thick-walled capsules that can then be used to protect and deliver useful compounds [201, 204]. The lengthscales and chemicals used in emulsion systems, combined with the relative ease with which functional components can be added, also make them suitable for producing
materials with biomimetic and bioengineering applications\[203, 207\].

Emulsion droplet interfaces consisting of multiple components, whilst more complicated, have long been of relevance due their presence in biological systems. The most familiar of these is milk, an oil-in-water emulsion whose interfacial membrane consists of tri- and di-glycerides, fatty acids, and proteins\[208, 209\]. Understanding the interactions between these stabilisers is critical for understanding emulsion stability during food processing\[210–212\]. An interesting case study of this is the effect of adding low molecular weight surfactant, such as Tween 20, to a protein-stabilised emulsion. Doing so leads to the destabilisation and coalescence of the droplets. This was shown by Mackie et al., using AFM and interfacial rheology, to be a purely interfacial phenomenon: at both the air-water and oil-water interface, adsorption of the surfactant to the protein-coated interface broke up the protein network, eventually displacing it\[213, 214\].

This work was also instructive as to the nature of the interactions between the different proteins that make up the film. \(\beta\)-lactoglobulin forms a gelled, strongly interacting, elastic film with a large interfacial elastic modulus. This leads to the surfactant adsorbing into defects in the protein network and forming self-affine clusters. Contrastingly, in the case of the more weakly interacting \(\beta\)-casein, the film has significantly lower surface rheological moduli, and the surfactant adsorbs in circular clusters, suggesting a domain shape governed by line tension rather than interfacial elasticity. Studies of droplets stabilised by these films show that the protein-specific interactions, and the effect they have on the interfacial rheology of the system, have important consequences for the break-up of droplets during processing\[185, 186, 215\].

Use of composite interfaces, and tuning the interactions between the components, can also radically increase emulsion functionality. Recent interest in this regard has arisen from applications in the pharmaceutical\[134\], food processing\[135, 216\], and minerals\[130\] industries. Of interest is the impact of interactions between charged colloidal particles and surfactants, most readily tuned by altering the charge state of the particle surface and the surfactants. This leads to a rather complicated range of behaviours\[217–219\]: chemically non-specific electrostatic interactions between the particles and the surfactant\[220, 221\], adsorption of the surfactants onto both the particles and the liquid-liquid interface\[222\], and alteration of the particle wettability\[58, 223\], which can even cause displacement of the particles from the interface\[224\]. In this chapter I will show that TAHP and colloidal PMMA stabilise by compatible means, and that balancing the ratio
of temperature-responsive (TAHP) and non-temperature-responsive (colloidal PMMA) stabiliser alters the interfacial structure of the droplet, both before and after heating.

Systems containing tunably-charged lipids and colloidal particles were studied by both Whitby and co-workers using emulsions \[130, 131, 225\], and by Maas \textit{et al} using interfacial rheology \[124\]. A range of effects were observed, though both found that adsorption of the charged lipids onto the particles led to the formation of aggregates with synergistic effects, measured in terms of increased rheological moduli and reduced droplet radii. Use of more chemically specific interactions between molecular and colloidal components can also be used to produce interesting systems: Cui \textit{et al} used surfactants that acted as cross-linkers between surface groups on nanoparticles, leading to rigid interfaces that stabilised non-spherical droplets \[125\]. In this chapter I will systematically investigate how the structure of a composite interface consisting of an interfacially assembled lipid (TAHP) and colloidal particles (sterically stabilised PMMA) govern the final state of a water-in-dodecane emulsion system.

In the previous two chapters, the properties of the interfacially assembled TAHP film have been studied. It has been shown that the film stabilises a temperature-responsive water-in-oil emulsion. Here I will study how the conditions under which the TAHP is assembled (i.e., the aqueous chemistry and the quantity of stabiliser) affects the properties of the resulting emulsion. Properties of interest here are droplet size and stability against coalescence. I will introduce a model Pickering emulsion system: hydrophobic PMMA particles that also stabilise water-in-oil emulsions. This system was chosen due to the extensive body of work performed on it, its simple surface chemistry in comparison with colloidal silica, and its recent use as a model emulsifier by other workers in the field \[226\]. I will then combine these two emulsifiers to form emulsions stabilised by a composite interface, and show that the two emulsification mechanisms can be used in tandem with one another. I will then tune the physical, rather than chemical, parameters of the composite interface system (that is, work at constant pH and phosphate concentration). By doing this I will show that the final structure of the TAHP/particle-stabilised emulsion and its interface can be tuned purely by varying the amount of particles added to the system. Tuning the pH of the system also yields some interesting effects, such as the synthesis of patchy droplets as the film formation rate is retarded.

I use light scattering and microscopy to study the droplet size, supernatant
contents, and state of aggregation of the emulsions. I then use confocal fluorescence microscopy to image the droplet interface. I show that the final droplet size is governed by the amount of TDA present in the system, and that the impact of varying particle volume fraction upon the drop size is negligible. This allows me to tune the density of particles at the droplet interface, without changing the size of the droplets, simply by varying the particle volume fraction. I will then use this fact to tune the area density of particles at the droplet interface, and show how, as I increase the amount of particles in the system, the interactions between the TAHP and the PMMA particles result in the formation of particle aggregates. These aggregates protrude from the droplet interface, giving a ‘hairy’ appearance. Finally, by using the temperature-responsive TAHP, and the non-temperature responsive PMMA particles, I will synthesise a droplet system with a dynamic interface. The temperature response will be found to exhibit tunability to only a limited degree, suggesting potential applications of the TAHP as a demulsifier.

6.2 Materials and Methods

The dodecane, water, and sodium phosphate salts are identical to those described Chapter 4 (details in Sec. 4.2.1). Emulsions were formed by shear using the Kinematica Polytron PT-3100 rotor-stator described in Sec. 3.1, operated at 15000 rpm ($\dot{\gamma} = 24000$ s$^{-1}$) for 1 minute, or at the stated shear rate if otherwise.

Emulsion Components

The dodecane in this section contains between 0.5 and 6.5 mM tetradecylamine and varying volume fractions of stERICally stabilised PMMA particles. The aqueous phase contains 100 mM phosphate ions. A schematic of the vial in which emulsions are formed, and the initial locations of the components prior to emulsification, is shown in Fig. 6.1.

The particles used in this work are colloidal polymethylmethacrylate (PMMA) particles. The particles were synthesised by dispersion polymerisation and characterised using dynamic light scattering by Andrew Schofield (University of Edinburgh). They include 7-nitrobenzo-2-oxa-1,3-diazol (NBD, a fluorophore) covalently bonded to the PMMA polymer backbone [227]. The particles are
sterically stabilised by covalently grafting poly-12-hydroxystearic acid (PHSA) chains onto the particle surface. This leads to a hard sphere-like particle pair potential when dispersed in an appropriate non-polar solvent \[228\]. In order to create fluorescent interfaces with a contrast in the fluorescence signals between the particles and the fluorescently tagged TDA, sterically stabilised PMMA particles dyed with DiIC\(_{18}\) (1,1'-Dioctadecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate) fluorescent dye were also used \[229\]. The DiIC\(_{18}\) is not covalently bonded to the particles, and so may potentially contaminate the sample. No stray fluorescence signal was observed in either of the phases, suggesting negligible diffusion of the DiIC\(_{18}\) out of the particles, and the results obtained using these particles were qualitatively identical to those obtained for the NBD-dyed-particle system. Nevertheless, the DiIC\(_{18}\)-dyed particles are only used here to make qualitative comparisons with the NBD-dyed particle system. As can be seen from the confocal micrographs shown later (see e.g., Figs. 6.14 and 6.15), the NBD-dyed particles have a fairly low polydispersity (\(\sigma_r \lesssim 0.10\)), whilst the DiIC\(_{18}\)-dyed particles are somewhat more polydisperse (see e.g., Fig. 6.22). An investigation of the effects of polydispersity is beyond the scope of this work, and the polydispersity of the dispersions has not been quantified. Visual inspection of the confocal micrographs in Figs. 6.14 and 6.15 shows the low polydispersity of the dispersions. A table summarising the PMMA particles used in this thesis is shown in Table 6.1.

To ensure that all particle dispersions had a similar sample history, and to enable
<table>
<thead>
<tr>
<th>Name</th>
<th>Radius (nm)</th>
<th>Dye</th>
<th>Dye covalently grafted?</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASM 183</td>
<td>500</td>
<td>NBD</td>
<td>Yes</td>
</tr>
<tr>
<td>ASM 385</td>
<td>726</td>
<td>NBD</td>
<td>Yes</td>
</tr>
<tr>
<td>ASM 356</td>
<td>990</td>
<td>NBD</td>
<td>Yes</td>
</tr>
<tr>
<td>ASM 391</td>
<td>760</td>
<td>DiIC$_{18}$</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 6.1  
Particle dispersions used in this work

direct comparison between different particle batches, all particle dispersions underwent the same washing procedure prior to use. All particle batches were dispersed for 12 hours in hexane and spun down in a centrifuge. The hexane supernatant was then removed, and the particles were re-dispersed in fresh hexane. This process is repeated 10 times, to ensure complete removal of any residual monomers remaining from the synthesis process [54]. The particles are then dried under vacuum overnight at 40°C. In order to make the particle dispersions used in the experiments, a dry mass of PMMA was then added to a known volume of dodecane. The particles were then dispersed extensively using an ultrasonic bath and a sample shaker in alternation for a week. This yielded particle dispersions of a volume fraction $\phi_p = 0.1$, which consisted predominantly of single particles, with only a small amount of residual doublets, triplets, and particle oligomers.

**Microscopy**

Light microscopy measurements were performed by transferring an aliquot of sample and some supernatant onto a ground glass cover slip and gently agitating the sample. Images were obtained using an Olympus BX50 upright microscope, using planfluorite-corrected objectives with 5×, 10×, and 50× magnification (NA = 0.15, 0.25, and 0.5 respectively), with a QImaging QICam Firewire CCD camera, which was operated at shutter speeds between 2 and 100 ms.

Confocal microscopy measurements were performed using the custom-built imaging chambers and confocal microscope described in Sec. 3.4. Confocal micrographs were obtained using both air and oil-immersion immersion objectives. Confocal micrographs at room temperature were obtained using an oil-immersion objective (40× magnification, NA = 1.3, plan-fluorite correction). At elevated temperature, confocal micrographs were obtained using 10×, 20×, and 40× magnification air-immersion objections (NA = 0.2, 0.4, and 0.6 respectively, all
Droplet Sizing

Droplet sizing was performed using a Beckmann-Coulter LS 13 320 single wavelength Laser Diffraction Particle Size Analyser. This apparatus uses light scattering to fit particle size distributions to the scattered intensity from a sparse sample, measured at angles between 0 and 35°, using the methods described in the ISO 13320 standard. It is suitable for sizing particles and droplets with a diameter between 0.4 and 2000 µm. To perform the measurement, samples are held in a metal cuvette with an anti-reflective film-coated glass window, and illuminated using a 5 mW 780 nm laser. The laser is of a sufficiently long wavelength such that the contribution to the scattering signal from NBD-fluorescence was negligible. To prevent sedimentation of the droplets, samples are agitated by a magnetic stirrer bar during the measurement. Scattering patterns were measured in 3 separate runs, each one minute long, to check for changes in the samples during the measurement due to coalescence or aggregation. The drop size distribution was fitted using the software provided with the particle sizer to the time-averaged scattering pattern after each run, and results shown here consist of the average over three runs.

Due to the sparing solubility of the TAHP in the dodecane, and the large volume of dodecane in which the emulsion is dispersed (10 µl emulsion in 10 ml of dodecane), the droplets were found to coalesce during the measurement. This was prevented by performing the measurements in dodecane which was saturated with TAHP. This was achieved by thoroughly dispersing 25 mg of TAHP in 250 ml dodecane using an ultrasonic bath at 60°C for two hours and then pouring the dodecane dispersion through filter paper, to remove any remaining large aggregates. TAHP-stabilised droplets were found to be stable when dispersed in the TAHP-saturated dodecane.

Two quantities obtained from sizing data are of interest in this chapter: the droplet diameter distribution, and the de Brouckere mean droplet diameter, $d_{43}$, which is referred to as the ‘average droplet diameter’ or ‘mean droplet diameter’ throughout this chapter. The de Brouckere mean diameter, $d_{43}$, of $N$ droplets of
diameter, \( d \), is defined as:

\[
d_{43} = \frac{\sum_{i} N d_{i}^{4}}{\sum_{i} N d_{i}^{3}}.
\]

The choice of exponents in Eq. 6.1 and, hence, the weighting of the mean is of some significance in emulsion science, and is discussed more extensively in Refs. [230, 231]. The de Brouckere mean, used here, weights the contributions from larger droplets more heavily. It is used here because the colloidal PMMA particles, which are an order of magnitude (or more) smaller than the droplets, contribute to the scattering pattern. By weighting the large objects in the dispersion more heavily in the calculation of the mean, the calculated value of the mean diameter will more closely represent the mean diameter of the droplets, whilst minimising the effect of the presence of the particles.

### 6.3 TAHP-Stabilised Emulsions

Before studying composite interfaces, it is necessary to map out the properties of TAHP-stabilised emulsions as a function of the parameters relevant to emulsification. In this section I vary pH, tetradecylamine concentration, [TDA], and shear rate, \( \dot{\gamma} \), during emulsification. I then study the effect that these parameters have upon droplet size and polydispersity. Some properties of TAHP-stabilised emulsions, including their interfacial structure and temperature response, have already been discussed in Chapter 4. Here I will compare their properties with a better-studied model Pickering emulsion system. Photography and light microscopy are used here to qualitatively study the emulsions. Static light scattering methods are used to study the droplet size quantitatively. Confocal fluorescence microscopy is used to study the interfacial structure of the emulsions.

#### 6.3.1 Effect of Varying pH

Here I discuss the effect of varying the pH of the aqueous phase upon the properties of the TAHP-stabilised emulsions (i.e., their size, appearance, and stability against coalescence). It has already been shown that increasing the pH (from 5 to 8) leads to slower kinetics of TAHP formation. The timescale on which
significant interfacial elasticities (i.e., \( G'_s \geq 50 \text{ mN/m} \)) are reached varies from under 1 second at pH 5, to the order of seconds at pH 7, up to several hours at pH 8. Between pH 7 and 8, the quantity of TAHP formed at the interface decreases by approximately 70%. The effect of varying the pH of the system is, therefore, rather complex. Both of these effects are likely to reduce the quantity of surface area stabilised against droplet coalescence.

The effect of increasing pH upon the efficacy of TAHP as an emulsifier is shown in Fig. 6.2. At pH 7, a TAHP-stabilised water-in-oil emulsion is highly stable against coalescence and contains individual droplets too small to be distinguished by eye. Qualitatively, the macroscopic appearance of the emulsions does not change between pH 7 and 7.6, and all of the water present in the system has been emulsified. At pH 7.8, the quantity of the emulsion stabilised can be seen to drop, and no stable emulsion is formed at pH 8.

![Figure 6.2](image1.png)

**Figure 6.2** Vials containing TAHP-stabilised water-in-oil emulsions at various (increasing, left-to-right, stated on vials) pH values. \( \dot{\gamma} = 24000 \text{ s}^{-1} \), \([\text{TDA}] = 2.5 \text{ mM}\).

Light micrographs of the TAHP-stabilised water droplets, as pH is increased from 7 to 7.8, are shown in Fig. 6.3. The droplets are generally spherical at all pH values, and can be seen to become significantly larger as pH is increased. The most significant increase in diameter is seen between pH 7.5 and 7.8. This is in good agreement with the observations made in the previous two chapters: between pH 7.5 and 8 the greatest change in film formation kinetics, final film strength, and film structure was observed.

The dependence of droplet size distribution upon pH at \([\text{TDA}] = 2.5 \text{ mM}\) is shown in Fig. 6.4. The size distribution for droplets stabilised at pH 5 is also shown
for comparison with the result at pH 7. At pH 7.2 and below, the droplets have a polydispersity of approximately 30%, and the average drop size increases by a factor of approximately 2 between pH 5 and 7.2. The most significant change in drop size occurs between pH 7.4 and 8, in agreement with the micrographs shown in Fig. 6.3. Above pH 7.4, the repeatability of the results obtained for this system is rather poor. The droplet size distributions are often multi-modal, and the rather large water droplets exhibit poor stability against coalescence. The trend in droplet size distributions show good agreement with the micrographs in Fig. 6.3, with the increase in drop size reflected in both data sets.

**Discussion of the Effect of pH Upon Droplet Size Distributions**

The behaviour of the TAHP-stabilised emulsions in response to changing pH can be understood solely in terms of the retardation of the formation kinetics of TAHP, and the change in the amount of TAHP formed, as pH is increased. Of these two, it is the retarded kinetics of TAHP formation that have the greatest
effect upon the emulsion. The significant change in drop size distribution between pH 5 and 7, in spite of the identical quantities of TAHP formed at these pH values, could occur due to either: retarded film formation kinetics, lower surface activity and, hence, higher surface tension at pH 7, or larger TAHP crystallites forming at higher pH, resulting in a thicker TAHP film and a lower surface area coverage (the last of these is suggested to be the case in the next section).

The absence of a stable emulsion at pH 8 shows that, above pH 7, it is the formation kinetics of the TAHP that governs the stability of the emulsion. As shown in Chapter 4, approximately 30% of the TDA added to the system under these conditions is expected to be present as TAHP. However, the lack of a stable emulsion at pH 8, combined with the observation in the previous chapter that it is the TAHP crystallites which provide a steric barrier to coalescence, suggest that the time scale at which the system coalesces is significantly faster than the time scale at which TAHP crystallites can form at this pH. This is not an effect of the reduced quantity of TAHP formed at this pH. Indeed, as I will show in the next section, the quantity of surface area stabilised by 1 mM of TDA at pH 5 is roughly equal to that stabilised by 2.5 mM TDA at pH 7. I will use the pH-dependence of the film’s formation kinetics later in this chapter (Sec. 6.5.3) to create patchy droplets, a topic which has been the subject of recent attention [232].
6.3.2 Effect of Varying Shear Rate

The dependence of drop size upon shear rate during emulsification is studied at three different primary amine concentrations in Fig. 6.5. Dependence upon both the concentration of tetradecylamine and the applied shear rate is observed. Both higher shear rates and higher amine concentrations lead to smaller final drop sizes. Studying the effect of varying shear rate is interesting as it allows the physical processes governing stabilisation by TAHP to be probed. The relative novelty of TAHP as an emulsifier means that none of the familiar rules governing Pickering emulsions or surfactant-stabilised emulsions will be of obvious relevance. Quantitatively controlling droplet size is of particular interest.

The relationship between mean droplet diameter \(d_{43}\), tetradecylamine concentration \([\text{TDA}]\), and shear rate during emulsification \(\dot{\gamma}\), is studied in Fig. 6.5. This shows the droplet size distributions and light micrographs of the emulsions. Three important trends can be observed. Firstly, at low fatty amine concentrations \([\text{TDA}] = 1 \text{ mM}\), very large droplets are stabilised by the TAHP, and the droplet radius is independent of the shear rate applied during emulsification. Secondly, at a single given shear rate, the size of the droplets decreases with increasing \([\text{TDA}]\). This trend occurs for all shear rates studied here. Thirdly, when there is more stabiliser in the system \([\text{TDA}] = 2.5 \text{ and } 5 \text{ mM}\), the \(d_{43}\) does exhibit a dependence on shear rate. This can be seen both qualitatively in the light micrographs (Fig. 6.5, bottom) and quantitatively in the mean droplet diameters (Fig. 6.5, top). At the highest shear rate studied \((32000 \text{ s}^{-1})\), emulsions for all \([\text{TDA}]\) appear to have reached a plateau value in the droplet size.

The shape of the droplets and the macroscopic structure of the emulsions studied here are practically independent of preparation conditions. At pH \(\leq 7.8\), and \([\text{TDA}] \geq 1 \text{ mM}\), the emulsion droplets are almost entirely spherical, and no significant aggregation of the droplets is seen to occur. By contrast, the PMMA particle-stabilised emulsions studied in the next section exhibit a wide variety of droplet shapes and extents of aggregation. This is reflected in the flow properties of the emulsions. Sedimented TAHP-stabilised emulsions hold weak peaks and flow when gently agitated, suggesting they have the mechanical properties of a very weak gel. This contrasts strongly with the properties of the aggregated Pickering emulsions studied in the next section, which require extensive agitation before they flow under gravity.
Figure 6.5  Top: The dependence of drop size with shear rate of a TAHP-stabilised emulsion at various TDA concentrations. Aqueous phase contains 100 mM phosphate at pH 5, oil phase is 4 ml dodecane containing the stated TDA concentration. Error bars correspond to droplet size polydispersities, which are approximately 30% for all measurements. Repeatability of the size measurements is significantly higher, on the order of ±10%. Bottom: Light micrographs of TAHP-stabilised emulsions at increasing shear rates. Aqueous phase at pH 5, [TDA] = 2.5 mM, shear rate stated in images

Discussion of Drop Size and the Origin of the Plateau

Two regimes of the relationship between [TDA], shear rate, and droplet size can be seen: a shear-limited regime at low shear rates, in which drop size decreases with increasing shear rate, and a [TDA]-limited regime at high shear rates, in which the drop size is dictated largely by the quantity of surface area that the primary amine can stabilise. Both of these trends can be understood as a result of the size of droplets created at a given shear rate and the amount of surface area that a given TDA concentration can stabilise. At the shear rates studied here,
the Reynolds number lies between 100 and 500. In this (non-turbulent) regime
droplet break-up occurs due to viscous stresses acting on the droplet surface (the
technical aspects of emulsification under these conditions have been discussed
in Sec. 3.1), and a number of semi-quantitative scaling relations that relate the
shear rate, drop size, and surface tension of the system can be written down.
Importantly, the maximum stable drop size in the shear zone of the rotor stator,
\(d_{\text{max}}\), is expected to scale with shear rate as \(d_{\text{max}} \sim \dot{\gamma}^{-1}\).

In the plateau region, \(d_{43}\) does not depend on \(\dot{\gamma}\). The plateau can thus be
interpreted as a consequence of the amount of surface area created during
emulsification exceeding the amount that can be stabilised at a given [TDA]. The
independence of \(d_{43}\) and \(\dot{\gamma}\) at [TDA] = 1 mM is a consequence of there always
being an excess of surface area formed during emulsification, even at the lowest
shear rates studied here. By contrast, at \(\dot{\gamma} \geq 24000\ \text{s}^{-1}\), a large excess of surface
area is created for all [TDA] studied here, with perhaps the exception of [TDA] =
5 mM. At sufficiently high shear rates, the system enters the ‘limited coalescence’
regime identified by Binks et al, in which partially coated droplets coalesce until
they have a sufficient covering of stabiliser to arrest further coalescence.

The limited coalescence phenomenon is familiar from Pickering emulsion systems.
The TAHP-stabilised emulsions also exhibit another trend not found in Pickering
emulsion systems: the dependence of droplet size on the quantity of stabiliser,
even at very low shear rates. It is also found that at \(\dot{\gamma} = 8000\ \text{s}^{-1}\), \(d_{43}\) reduces by
60% as [TDA] is increased. Interestingly, at [TDA] = 2.5 mM and 5 mM, there
is clearly an excess of stabiliser relative to the quantity of surface area created
(as shown by the decrease in \(d_{43}\) values at higher shear rates). The dependence
of \(d_{43}\) on [TDA] is observed at all shear rates studied here, even in the plateau
region. This behaviour emerges from the properties of the oil-water interface
during emulsification and droplet break-up. Two features of the TAHP film are
likely to play a role in describing droplet break-up at a given shear rate: the
interfacial tension and the interfacial elasticity. It is first important to note that,
although the final film formed by the TAHP is elastic, on the time scales probed
during emulsification surface tension is likely to play a role in governing droplet
break-up. French et al estimated dwell time of the droplets in the shear gap of
the rotor stator as \(37^{2}\)

\[
\tau_{\text{dwell}} \approx \frac{\delta_{\text{gap}}}{r_{\text{in}} \omega}.
\] (6.2)

\(^{2}\)This estimate, and others similar to it under various flow conditions, are discussed in Ref.

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For the Polytron rotor-stator employed in this section, gap width \( \delta_{\text{gap}} = 150 \, \mu \text{m} \) and internal stator radius \( r_{\text{in}} = 1.4 \, \text{mm} \). This corresponds to a dwell time \( \tau_{\text{dwell}} \) of the order 10-100 \( \mu \text{s} \) for shear rates between 10000 and 40000 \( \text{s}^{-1} \) (see Sec. 3.1 for technical details of the rotor-stators used here). At these timescales, surface tension is likely to play a much greater role in determining droplet structure than the rigid TAHP interface, which requires adsorption, counter-ion condensation, crystallite nucleation, and network percolation to occur before significant interfacial elasticities emerge. In the non-turbulent regime studied here, droplet radius is expected to scale as \( d_{\text{max}} \sim \gamma_{\text{ow}} \). In the case of purely fluid interfaces, the data in Fig. 6.5 suggest that increasing [TDA] from 2.5 to 5 mM results in \( \gamma_{\text{ow}} \) dropping by a factor of two-thirds. The presence of interfacial elasticity due to the presence of TAHP, if it forms on a relevant timescale, is likely to complicate break-up behaviour, and will exhibit dependence on dynamic surface tension, reaction kinetics, and interfacial yield stress [75, 77, 212]. The scaling of the drop size with [TDA] at constant shear rate is investigated in the next section, but at higher shear rates. This will show the importance of a second parameter: the amount of TAHP formed during emulsification. It will be argued that, interestingly, variation of both surface tension and the amount of TAHP formed are expected to lead to identical, rather simple scaling behaviour of \( d_{43} \sim [\text{TDA}]^{-1} \) at a single shear rate.

### 6.3.3 Effect of Varying TDA Concentration

Here the effect of varying fatty amine concentration ([TDA] \( \leq 5 \text{mM} \)) at pH 5 is studied. It has been shown that at pH 5 the film formation kinetics are at their most rapid. At pH 5, even at a flat interface with a relatively modest surface area, at least 90% of the TDA added to the system is converted into TAHP. In the previous section it was shown that varying TDA concentration allows the droplet size to be tuned trivially. Two regimes of dependence of \( d_{43} \) upon [TDA] were identified: one at low shear rates and the other at high shear rates. In this section I investigate the relationship between [TDA] and \( d_{43} \) quantitatively, and discuss the physical origin of both of these regimes. Here I work at a shear rate (\( \dot{\gamma} = 24000 \, \text{s}^{-1} \)), where \( d_{43} \) is independent of shear rate and droplet size is limited by the amount of TAHP formed.

Emulsions stabilised by varying concentrations of TDA are shown in Fig. 6.6. At [TDA] = 0.15 mM no stable emulsion is formed. The oil-water interface in this
system is somewhat ‘milky’ in appearance, suggesting the presence of colloidal TAHP, but the concentration is insufficient to stabilise an emulsion. At \([\text{TDA}] = 0.25\) and \(0.5\) mM a small quantity of emulsion is formed. The droplets in these emulsions are rather large (on the order of mm), and not suitable for further study. No excess water is seen at the bottom of the vials, suggesting the all, or most, of the water has been emulsified. At \([\text{TDA}] \geq 1\) mM, highly stable emulsions are formed. The stability of TAHP-stabilised emulsions against coalescence has only been qualitatively studied in this work, but my observations suggest they are highly stable. TAHP-stabilised emulsions have been observed, during the course of this project, not to significantly coarsen over the course of 3 years.

**Figure 6.6** Photographs of TAHP-stabilised emulsions at various tetradecylamine concentrations (increasing, left-to-right, stated on vials). \(\dot{\gamma} = 24000\) s\(^{-1}\), pH 5.

Light micrographs and droplet size distributions of the TAHP-stabilised emulsions, for a range of tetradecylamine concentrations, are shown in Fig. 6.7. At the lengthscales in the image here no roughness due to the TAHP crystallites at the oil-water interface can be seen. In general the water droplets are spherical, however some aspherical droplets can also be seen (e.g., in Fig. 6.3) suggesting a significant interfacial elasticity, in agreement with the interfacial rheology measurements made in previous sections. A negative shift in the drop size distributions can be seen as \([\text{TDA}]\) is increased. This difference in size is also seen in the light micrographs. Under the conditions studied here, the drop size distributions for the TAHP-stabilised system show excellent repeatability. This is illustrated in Fig. 6.7 inset, in which the drop size distributions from different batches of emulsions formed at 3 mM TDA are plotted, showing excellent agreement with one another. The TAHP-stabilised water droplets are rather monodisperse; the polydispersity was approximately 30% for all samples, independent of shear rate.
The scaling behaviour of droplet size with fatty amine concentration, measured at $\dot{\gamma} = 24000$ s$^{-1}$, is shown in Fig. 6.8. $d_{43}$ plotted against $[\text{TDA}]^{-1}$ is also shown, inset. This shows the same trend that was observed in the previous section: as $[\text{TDA}]$ increases, the droplet size decreases. Plotting $d_{43}$ against $[\text{TDA}]^{-1}$ shows that the two quantities are inversely proportional to one another.

The $d_{43} \sim \frac{1}{[\text{TDA}]}$ scaling is similar to the scaling in Pickering emulsions of $d_{43}$ with particle volume fraction, $\phi_p$, in the limited coalescence regime [233]. Using a simple geometrical argument, and assuming that initially a large excess of surface area (far greater than the amount that the particles could stabilise) Binks and Lumsdon argued that the characteristic radius of a Pickering emulsion droplet,
Figure 6.8  

Mean droplet diameter plotted against primary amine concentration ([TDA]) and the inverse ([TDA]−1, inset). \( \dot{\gamma} = 24000 \text{s}^{-1}, \text{pH} 5. \)

\( r_d \), in the limited coalescence regime is determined by a single length scale - the radius of the stabilising particles \( r_p \) \(^{146} \). This yielded the relation \( r_d \sim \frac{\phi_w r_p}{\phi_p} \), where \( \phi_w \) and \( \phi_p \) are volume fractions of dispersed phase and particles respectively. The origin of the \( d_{43} \sim [\text{TDA}]^{-1} \) scaling found here has a similar origin, and is suggestive of a fairly simple interpretation. In Pickering emulsions, the scaling behaviour emerges as a result of a single particle occupying a well-defined cross-sectional surface area. It is, furthermore, only observed when a large *excess* of surface area is created during emulsification. Likewise, for the TAHP-stabilised system studied in Fig. 6.8, I work at high shear rates where an excess of surface area created during emulsification. In this regime, where \( d_{43} \) and \( \dot{\gamma} \) are independent of one another, the final droplet size is dictated by amount of TAHP formed during emulsification. This suggests a single, characteristic lengthscale governing the size of the droplets at a given pH, possibly corresponding to an approximate thickness of the TAHP film.

The quantity of TAHP is one of just three parameters that are likely to govern the droplet size of the system. The TAHP-limited regime studied in Fig. 6.8 (which occurs at high shear rates) must also be distinguished from the surface tension-limited regime at low shear rates. A third parameter, the thickness of the interface, also plays a role in governing droplet size (though ostensibly this does not vary at constant pH). I will review all three of these parameters, and the scaling behaviour they give rise to, in the next section.
Origin of the $d_{43} \sim [TDA]^{-1}$ scaling

Fig. 6.5 shows the droplet size dropping whilst shear rate is kept constant for a wide range of shear values (between 8000 and 32000 s$^{-1}$). Two distinct regimes can be identified in the graph. The first of these is at low shear rates, where the droplet size depends on the shear rate even at constant [TDA]. The second of these is at high shear rates, where the droplet size is independent of shear rate, and is limited by [TDA] (and, hence, the amount of TAHP formed). The second of these effects has been investigated quantitatively in Fig. 6.8, and the scaling of $d_{43} \sim [TDA]^{-1}$ has been observed. A number of statements can now be made.

$d_{43}$ depends on [TDA] at all shear rates. At sufficiently high shear rates, $d_{43}$ will not be reduced by shearing the system harder. Finally, the shear rate at which $d_{43}$ becomes independent of shear rate depends on [TDA]. I will now discuss the origin of these three observations.

The TAHP-stabilised system is, in some senses, analogous to Pickering emulsions. In the case of Pickering emulsions, the scaling of $d_{43} \sim \phi_p^{-1}$ occurs when all the particles present in the system are taken up during emulsification. This has a simple interpretation: more particles can stabilise more surface area [46, 233]. The amount of surface area that a particle dispersion will stabilise at a constant particle volume fraction is thus related to a characteristic lengthscale: the particle radius. In the case of the TAHP-stabilised emulsions, three factors constrain the size of the droplets: the amount of TAHP formed, the size of the TAHP crystals, and the surface tension of the system during droplet break-up.

The first of these, the amount of TAHP formed, is roughly analogous to the particle volume fraction in a Pickering emulsion. If the droplets are coated by a film with a characteristic thickness, then varying the quantity of TAHP formed (by varying either the yield of the reaction or the quantity of TDA initially present in the system) will yield scaling of droplet size and $d_{43} \sim [TDA]^{-1}$. This region is observed when an excess of surface area is created during shear (i.e., in the region where $d_{43}$ is independent of shear rate). This is the region studied in Fig. 6.8.

The second of these, the thickness of the TAHP film, is roughly analogous to the particle radius in a Pickering emulsion. If the amount of TAHP formed remains constant, then changing the size of the crystallites (by, say, increasing the pH of the aqueous phase) will yield a thicker interface, and therefore reduce the amount of oil-water surface that the TAHP can coat. By analogy with a Pickering emulsion, one expects the droplet size to scale linearly with the crystallite size.
This effect is not studied quantitatively in this thesis (though it is hinted at by the differing drop sizes at pH 5 and 7 in Fig. 6.4) but is a promising subject for future work.

The third of these, the surface tension of the system, is an effect not observed in Pickering emulsions without alteration of the chemical constituents of the system. Adsorption of the tetradecylamine onto the oil-water interface during droplet break-up reduces the surface tension of the system. As noted previously, on long timescales this adsorption and the subsequent reaction with HPO$_4^{2-}$ yields elastic interfaces. However, on the short timescales relevant to droplet break-up, it serves only to reduce the surface tension of the system. In the case of there being an excess of stabiliser relative to the amount of surface area created (i.e., at low shear rates), the following argument shows that a dependence of $d_{43} \sim [\text{TDA}]^{-1}$ can be expected. The adsorption of the fatty amine onto the interface can be modelled as being either diffusive or, if the system is under flow, convective. Both situations predict the same behaviour from varying fatty amine concentration. The system studied here is driven at a rather high shear rate, though still in the laminar viscous flow regime, and so the adsorption is likely to be both diffusive and convective \[48, 75\]. In both of these regimes, the characteristic time scale of adsorption, $\tau_A$, scales as $\tau_A \sim [\text{TDA}]^{-1} \[48\]$. The Ward-Tordai relations in Eq. 3.8 predict that at short timescales the drop in surface tension, $\Delta \gamma$, over some characteristic timescale $\tau$ behaves $\Delta \gamma \sim [\text{TDA}]\tau^{1/2}$. All of the emulsions prepared in Fig. 6.8 were made at identical shear rates, meaning droplet break-up can be expected to occur on an identical timescale for all measurements. The surface tension of a droplet undergoing break-up in a rotor-stator on a timescale $\tau_{\text{dwell}}$ will therefore have a surface tension that decreases linearly with the quantity of TDA added to the system. The maximum stable droplet size at a given shear rate is governed by the critical capillary number

$$Ca_c = \frac{\eta \gamma r_c}{\gamma_{\text{ow}}}.$$  

(6.3)

Any droplet of radius greater than $r_c$ will be unstable, and break up due to viscous stresses acting on the droplet interface. Eq. 6.2 suggests that interfacial elasticity due to the TAHP film is unlikely to be significant on the timescale on which the droplets are formed, which, for the shear rates used here, is on the order of 25 µs. On the short time scales during which droplets are present within the shear gap, and prior to the onset of interfacial elasticity, this leads to the critical capillary number behaving as $Ca_c \sim \frac{1}{[\text{TDA}]}$. It is this effect that leads to the dependence of
the drop size upon [TDA] at low shear rates, where $d_{43}$ is still found to depend on $\dot{\gamma}$.

The first of these effects has been studied quantitatively for a single shear rate ($24000 \text{ s}^{-1}$) at pH 5, for a broad range of [TDA]. The third of these has been observed qualitatively at low shear rates (see e.g., Fig. 6.5). The second of these is the least-investigated, and further investigation of the pH-dependent behaviour of this system is certainly a promising avenue for future work. Fully mapping out droplet size as a function of the full parameter space of the system is, however, far beyond the scope of this thesis. As will be shown in the remainder of this chapter, it is also entirely unnecessary. It will be shown later that emulsions stabilised by both PMMA and TAHP in tandem have a droplet size that is determined almost entirely by the amount of TAHP formed, at least at high shear rates. The aim of this chapter is to probe the interactions between the stabilisers, to study competition between their adsorption rates, and to tune the interfacial structure; it will be found that the understanding of TAHP as an emulsifier obtained thus far is more than sufficient to achieve these aims.

6.4 PMMA-Stabilised Emulsions

In this section I will study the properties of water-in-oil Pickering emulsions. The emulsions were formed using the same methods employed in the rest of this work: by shear using a rotor-stator. The particles used as emulsifiers are hydrophobic, sterically stabilised PMMA particles. I will study the effects of particle volume fraction and the shear rate at which the system is emulsified upon the properties of the emulsions. Of particular interest is what happens when the quantity of surface area created far exceeds the quantity of surface area that the particles can stabilise (i.e., at high shear rates or low particle volume fractions). The aggregation of the emulsions at high shear will be studied, and explained in terms of the particle-bridging work developed by French and co-workers [47]. This section introduces the PMMA-stabilised emulsions as a control group for the next section, in which a composite interface is studied.
Specific Particle Surface Area

Emulsions stabilised by particles of three different radii \( r_p = 500, 726, \) and \( 990 \) nm will be studied. It is useful to be able to work at particle volume fractions that will occupy an approximately equal amount of surface area. The amount of surface area that the particles can occupy depends on the radius of particles being used, \( r_p \), the volume fraction of particles present in the system, \( \phi_p \), and the volume of the dispersed phase which is emulsified, \( V_d \). Particle volume fractions, \( \phi_p \), that stabilise equal amounts of surface area, \( S_{max} \), are thus given by the reciprocal length scale, \( \Phi_s \), where:

\[
\Phi_s = \frac{S_{max}}{V_s} = \frac{\pi r_p^2 N_p}{V_s} = \frac{\pi r_p^2 V_c \phi_p}{V_d V_p} = \frac{\pi r_p^2 \alpha \phi_p}{\frac{4}{3} \pi r_p^3} = \frac{3 \alpha \phi_p}{4 r_p}
\]  \( (6.4) \)

where \( V_c \) is the volume of continuous phase, \( N_p, V_p, r_p, \) and \( \phi_p \) are the number and volume of the particles are their radius and volume fraction (as a fraction of the non-polar phase), and \( \alpha \) is the volumetric ratio of oil and water (\( \alpha = 4 \) throughout this thesis). A table showing the approximate equivalent values of \( \Phi_s \) for the particle radii used in this chapter is shown in Table 6.2.

<table>
<thead>
<tr>
<th>( \Phi_s ) (( \text{mm}^{-1} ))</th>
<th>( \phi_p ) (( r = 500 )nm)</th>
<th>( \phi_p ) (( r = 726 )nm)</th>
<th>( \phi_p ) (( r = 990 )nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>0.00068</td>
<td>0.001</td>
<td>0.00136</td>
</tr>
<tr>
<td>28.9</td>
<td>0.0048</td>
<td>0.007</td>
<td>0.0095</td>
</tr>
<tr>
<td>151.5</td>
<td>0.025</td>
<td>0.037</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Table 6.2** Particle volume fractions \( (\phi_p) \) that stabilise identical quantities of emulsion surface area, compared between the radii of particles \( (r_p) \) used in this chapter.

\(^3\)Here I define this as the volume fraction of present initially in the continuous phase of the emulsion: \( \phi_p = \frac{V_p}{V_c} \)
6.4.1 Particle Preparation and the Validity of Eq 6.4

The final formula in Eq. 6.4 does not account for certain important factors. It assumes that the particles coat the droplet in a monolayer, and does not account for partial coverage of the droplets with particles. These assumptions will be validated in the next section using confocal microscopy, showing that the particles do indeed behave approximately as described by Eq. 6.4. It also does not account for particle packing ratio at the interface being less than one, and for the contact angle of the particles at the interface departing from 90°, or varying as a function of particle radius. The first two of these issues only introduce a numerical correction factor to Eq. 6.4, and does not affect the scaling (which is what is of principle concern here). The variation of particle contact angle with particle size is indeed a problem. Between batch variation in surface chemistry, along with varying densities of surface charge groups, due to the presence of dyes which are homogeneously distributed throughout the volume of the particles for instance, could affect this quantity. To control for this, the particles were washed prior to the study using identical methods, detailed in Sec. 6.2, to ensure a similar particle sample history.

6.4.2 Creating Aggregated Pickering Emulsions by Varying Shear Rate

Photographs and light micrographs of dodecane-in-water emulsions stabilised by a constant volume fraction ($\Phi_s = 28.9$ mm$^{-1}$, $r_p = 726$ nm) of PMMA particles are shown in Fig. 6.9. The aqueous phase contains 100 mM phosphate ions at pH 5. The only change from the previous section is the addition of the colloidal PMMA. The characteristics of the stabilised emulsion are strongly dependent upon the shear rate used to form the dispersed phase. At low shear rates ($\dot{\gamma} \leq 18000$ s$^{-1}$) the effect of increasing shear rate is to reduce the quantity of particles that remain in the dodecane, and to increase the quantity of water which is emulsified. Some particles can still be found in the supernatant, and can be seen in Fig. 6.9 attached to the glass vial.

As shear rate is increased further, to $\dot{\gamma} \geq 20000$ s$^{-1}$, the macroscopic appearance of the emulsions alters dramatically. The interface between the emulsion and the dodecane supernatant, which is flat at low shear rates, is seen to roughen. The emulsion, which sediments due to the higher density of the dispersed phase, is
found to occupy a greater fraction of the vial, even though the volume of water present in the system is constant. The flow properties of the emulsions also alter. At low shear rates an aliquot of emulsion, transferred to a glass microscope slide using a spatula, is found to flow when tilted (tilt angle $\approx 30^\circ$). By contrast, emulsions formed at higher shear rates hold peaks, suggesting the presence of a yield stress. Furthermore, in the case of the aggregated emulsions, individual droplets will not flow readily; rather, whole aggregates can be seen to move once the cover slip is tilted at a sufficiently high angle.

![Figure 6.9](image)

**Figure 6.9** Top: Water-in-oil Pickering emulsions stabilised by PMMA particles at increasing shear rates. $r_p = 726 \text{nm}$, $\Phi_s = 28.9 \text{ mm}^{-1}$. Bottom: Light micrographs of the emulsions formed $\dot{\gamma} = 14400 \text{ s}^{-1}$ and $24000 \text{ s}^{-1}$.

Light micrographs of the emulsions show a significant change in the microscopic characteristics of the emulsion. At low shear rates ($\dot{\gamma} = 14400 \text{ s}^{-1}$), the emulsion consists of individual droplets, with only a small fraction of the droplets seen to have aggregated. The majority of the droplets are aspherical. A significant fraction of the droplets are somewhat sphericylindrical in shape, with some droplets even exhibiting sharp corners. This is a direct consequence of the large interfacial stress of the jammed particle network. This arises due to the large capillary energy that attaches the particles to the interface, which far exceeds the free energy penalties due to curvature and increased oil-water surface area. At higher shear rates of $\dot{\gamma} = 24000 \text{ s}^{-1}$, the shape of the individual droplets is similar.
to that at low shear rates but the droplets are found to aggregate strongly. In order to image the emulsion formed at high shear rates ($\dot{\gamma} \geq 24000 \text{ s}^{-1}$) on the microscope the large aggregates were first broken using a spatula. The remaining, smaller aggregates were then imaged.

The change in the macroscopic appearance of the emulsions at higher shear rates is due to the aggregation of the droplets, and is a consequence of the particles in the system forming bridges between the droplets. Aggregated Pickering emulsions, formed by particle bridges, have been shown to form if more surface area is created by shear than can be occupied by particles [47]. This effect is rather fine-tuned, requiring that the particles be strongly bound to the interface, but still protrude sufficiently far from the interface such that they can be shared by two droplets. The conditions under which the sharing of particles between droplets can lead to droplet aggregation have been discussed in Sec. 2.2.1. Particle bridging is likely to be facilitated by the particles protruding a long way from the droplet interface, as would be expected from the rather hydrophobic PMMA particles used here [226]. The increase in apparent emulsion volume in Fig. 6.9 at $\dot{\gamma} \geq 24000 \text{ s}^{-1}$ is a consequence of the reduced packing of droplets due to the formation of multi-droplet aggregates with a fractal geometry. These can be seen by eye in Fig. 6.9 at $\dot{\gamma} = 32000 \text{ s}^{-1}$, where they cause the roughened appearance of the emulsion-dodecane interface. The PMMA-stabilised emulsions in Fig. 6.9 show a maximum in particle uptake at $\dot{\gamma} \approx 18000 \text{ s}^{-1}$ for $\Phi_s = 28.9 \text{ mm}^{-1}$. Applying higher shear rates to the system at this $\Phi_s$ only serves to create excess oil-water surface area, leading to particle bridging and droplet aggregation.

### 6.4.3 Varying Particle Volume Fraction at Constant Shear Rate

Rather than tuning the extent of droplet aggregation by varying the quantity of surface area created during emulsification, one can, equivalently, vary the amount of surface area that the particles can occupy, $\Phi_s$, whilst using a single shear rate. This varies the quantity of surface area which can be stabilised by the system whilst keeping the amount of excess surface area created during shear constant.

The effects of varying the particle volume fraction by over an order of magnitude, from $\Phi_s = 4.1 \text{ mm}^{-1}$ to $\Phi_s = 151.5 \text{ mm}^{-1}$, at constant shear rate ($\dot{\gamma} = 24000 \text{ s}^{-1}$), are shown in Fig. 6.10. This wide range of $\Phi_s$ has been chosen such that three
different regimes of Pickering emulsification can be identified, and to provide a suitable model system for further study with a composite interface emulsion. At very low particle volume fractions ($\Phi_s = 4.1 \text{ mm}^{-1}$ - Fig. 6.10, left) only a very small quantity of emulsion, consisting of very large droplets, has been stabilised. Excess water not incorporated into the emulsion can clearly be seen at the bottom of the vial, and the interface of the emulsion with the bulk oil is rather rough, implying the presence of aggregated droplets.

Increasing $\Phi_s$ to 28.9 mm\(^{-1}\) results in all of the water in the system being emulsified. The rough interface between the droplets at the non-aqueous supernatant suggests the presence of large droplet aggregates, which is confirmed by light microscopy (see Fig. 6.10, bottom-left). The droplets are rather polydisperse, with diameters ranging from 30 to several hundred $\mu$m, and a significant fraction of the droplets are aspherical. Increasing $\Phi_s$ further to 151.5 mm\(^{-1}\) results in further change in the appearance of the emulsion. The interface between the dodecane and the droplets is now flat, rather than rough, and the emulsion flows relatively easily when the vial is gently agitated and then tilted on its side. Microscopy images show that, at this much higher volume fraction, the droplets are significantly smaller and more spherical. Whilst some aggregates are present, suggesting that some droplet aggregation is inevitable in this system, the majority of the water is present as individual droplets. A far higher quantity of PMMA particles can also be seen in the dodecane supernatant at high $\Phi_s$.

The dependence of the emulsion properties upon $\Phi_s$, shown in Fig. 6.10, is a consequence of the greater quantity of surface area that the larger number of particles can occupy. As seen in Fig. 6.9, an increase in the quantity of surface area created during emulsification leads to the formation droplet aggregates. In Fig. 6.10, the shear rate (and, hence, the amount of surface area created) is kept constant, whilst the amount of surface area that the system can stabilise is increased. This is also reflected in the presence of a greater amount of residual particles in the dodecane supernatant, which can be attributed to insufficient surface area being created to accommodate all the particles present in the system.

The presence of residual droplet aggregates, even at very high $\Phi_s$, is somewhat surprising. These aggregates would be expected to be unstable whilst the system is being sheared. This suggests that they form after shearing, whilst the system is sedimenting. In the case of aggregates of droplets being created by particle bridging, the droplets aggregate due to collisions between droplets that are only
Figure 6.10  Photograph and light micrographs of water-in-dodecane Pickering emulsions stabilised by varying volume fractions of PMMA particles ($\Phi_s = (l-r) 4.1, 28.9, 151.5 \text{ mm}^{-1}$) at constant shear rate ($\dot{\gamma} = 24000 \text{ s}^{-1}$). Micrographs show emulsion formed at $\Phi_s = 28.9$ (left) and $151.5 \text{ mm}^{-1}$ (right).
partially-coated by particles. The shear dependence of the extent of aggregation in the system, along with the confocal micrographs shown later in Fig. 6.15, show that formation of particle bridges is the main cause of droplet aggregation in the system. The presence of a small quantity of aggregated droplets, even at very high $\Phi_s$, is seen in the micrographs on Fig. 6.10 and later in Fig. 6.11. This shows, whilst having an excess of particles inhibits bridging a great degree, the kinetics of droplet collisions are sufficiently rapid that the particle excesses here cannot prevent bridging entirely. This is likely a result of a fine balance between the timescale of particle adsorption and the timescale on which the particles are present in the shear gap. If the particles are sufficiently large they will not adsorb rapidly enough to completely inhibit particle bridges from forming [48].

**6.4.4 Effects of Changing Particle Radius**

The effect of changing particle volume fraction and shear rate during emulsification upon the properties of an emulsion have thus far been studied at a single particle radius. In the previous section it was shown that the creation of a large excess of surface area during emulsification leads to the creation of large, fractal droplet aggregates. I will now investigate the effects of changing the radius of the colloidal particles upon the extent to which the droplets aggregate. Varying the particle radius is interesting because the rate at which particles adsorb onto the oil-water interfaces depends on the particle size [234]. When comparing the results between emulsions stabilised by particles of differing radii, I work at particle volume fractions that stabilise equal amounts of surface area.

A shear rate sweep, first shown for $r_p = 726$ nm in Fig. 6.9 is shown in Fig. 6.11 for three different particle radii: 500, 726, and 990 nm. At a qualitative level, the emulsions look very similar regardless of particle size. At extremely high shear rates ($\dot{\gamma} = 32000$ s$^{-1}$), there is an apparent increase in emulsion volume, even though the quantity of water present in the system is constant at all shear rates for all $r_p$. As before, the rough appearance of the emulsion-oil interface in the vials is attributed to the formation of droplet aggregates. Probing the system with a spatula and imaging using bright field microscopy confirms this. Between shear rates of approximately 18000 and 21000 s$^{-1}$, whilst the emulsion-oil interface remains flat, increasing the shear rate also leads to the formation of (somewhat smaller) droplet aggregates, the presence of which was also confirmed by light microscopy.
The effect of changing particle radius at three different values of $\Phi_s$ has also been studied, as shown in Fig. 6.12. Qualitatively, the trends in emulsion appearance are the same for $r_p = 500$, 726, and 990 nm. At low $\Phi_s$ ($4.1 \text{ mm}^{-1}$) a very small quantity of droplets, with a large droplet radius, is formed. Increasing $\Phi_s$ results in a larger quantity of water being emulsified, with the emulsion consisting of aggregated droplets. Very high $\Phi_s$ results in a non-aggregated emulsion consisting predominantly of spherical droplets at very high $\Phi_s$, for all particle radii.

The micrographs of the emulsions formed at high-$\Phi_s$ in Fig. 6.12 show good agreement in drop size and shape. The micrographs show spherical, relatively monodisperse water droplets with a diameter of approximately 50 $\mu$m. The droplets are generally present as individual droplets, however some multi-droplet aggregates are also observed. The droplet aggregates formed at $\Phi_s \leq 28.9 \text{ mm}^{-1}$
Photographs and light micrographs of water-in-dodecane emulsions stabilised by PMMA particles of $r_p$ (l-r) 500, 726, and 990 nm, in an arrangement similar to that of Fig. 6.10. Each set of 3 vials shows $\phi_p$ increasing (l-r), with the value of $\phi_p$ covering an equal quantity of surface area for each value of $\Phi_s$. The values for $\phi_p$ are given in Table 6.2. Light micrographs show the high-$\phi_p$ sample for each $r_p$.

are unsuitable for sizing via light scattering. This is because multiple scattering events occur in the aggregates that make up the majority of the volume of the sample, making data difficult to interpret. The non-bridged emulsions formed at high $\Phi_s$, however, are suitable for quantitative analysis using light scattering methods. This allows the droplet size distributions at equivalent particle specific cross-sectional area, $\Phi_s$, to be compared. Droplet diameter distributions for the high $\Phi_s$ emulsions in Fig. 6.12 are shown in Fig. 6.13.

The droplet size distributions for $r_p = 500$, 726, and 990 nm show excellent agreement. All exhibit similar qualitative trends: a modal drop diameter of approximately 50 $\mu$m and a shoulder of larger droplets. The mean diameter, $d_{43}$, of all of the distributions lie within 10% each of each other ($d_{43, r = 500 \, \text{nm}} = 59.4 \, \mu\text{m}$, $d_{43, r = 726 \, \text{nm}} = 50.8 \, \mu\text{m}$, $d_{43, r = 990 \, \text{nm}} = 55.1 \, \mu\text{m}$). The effect of the slightly aggregated state of the emulsions upon the scattering data is not clear. The droplet size distributions observed are rather more polydisperse than visual inspection of the micrographs in Fig. 6.12 would suggest. Furthermore, whilst the scattering suggests the presence of a significant number of droplets with a diameter greater than 100 $\mu$m, few if any droplets of this size are observed in
the micrographs. This suggests that the origin of the shoulders in the drop size distributions in Fig. 6.13 is predominantly due to the remaining, larger, multi-droplet aggregates still present in the system.

### 6.4.5 Imaging Particle Bridges in Aggregated Emulsions Using Confocal Microscopy

Thus far photography and light microscopy have been used to show that, when an excess of surface area is created in the water-dodecane-PMMA particle system, droplet aggregates linked by particle bridges are formed. Confocal fluorescence microscopy is now used to compare the interfacial structures of the emulsions directly. The colloidal PMMA particles used here are synthesised with NBD covalently linked to the polymer backbone, which renders them fluorescent. The interfacial structure of the droplets can thus be investigated purely by studying the fluorescence signal from the particles. The appearance of the water droplets in dodecane (shown initially in Fig. 6.12) imaged using confocal fluorescence microscopy, is shown in Fig. 6.14. As in the previous chapter, composite images
Figure 6.14  Top Row: Individual confocal slices, Bottom row: Flattened z-stack consisting of multiple slices showing PMMA-stabilised droplets. \( \Phi_s = 151.5 \text{ mm}^{-1}, \ r_p = (l-r) \ 500, \ 726, \ \text{and} \ 990 \ \text{nm}. \)

consisting of multiple confocal micrographs taken along the z-axis are formed by summing the intensities of each slice, also shown in Fig. 6.14 bottom row.

Droplets are for all \( r_p \) are coated by a rather close-packed, jammed particle monolayer. As with the light micrographs, a range of both non-spherical and spherical droplet shapes can be seen, including some highly aspherical droplets (see e.g., Fig. 6.14 bottom-left), indicative of high interfacial rigidities. Some qualities of the monolayer appears to be independent of particle size and droplet shape: highly distorted shapes do not appear to require a multilayer to support higher stresses, and the particles appear to be immobilised, with little particle movement observed over the course of 10 minutes. The confocal micrographs of the emulsions with \( r_p = 500 \ \text{nm} \) show a greater population of non-spherical droplets for this particle size, but several spherical droplets can also be seen. The light micrographs, shown previously in Fig. 6.12 show that at \( r_p = 500 \ \text{nm} \) the majority of the droplets are spherical. The light micrographs, which have a lower magnification and therefore give a more representative picture of the droplet shapes present in the sample, suggest that the difference in the droplet shape between the samples is only slight. The larger number of non-spherical droplets
at $r_p = 500 \text{ nm}$ in Fig. 6.14 may be a consequence of sample ageing. The difference in particle size will also alter the rate of particle adsorption during emulsification, which may go on to affect the droplet shape. However, the difference between samples is rather small, and is not investigated further here.

**Confocal Micrographs of Bridged Particle Aggregates**

The light microscopy methods used so far are effective at studying the representative samples of the emulsions, such as showing the absence or presence of droplet aggregates and the droplet shapes, but provides limited information about the structure of the droplet interface. High-resolution confocal fluorescence microscopy has been applied here to study the interfacial structure of the droplets, allowing interfacial structure and dynamics to be captured, and to study particle bridging between the droplets.

The interfacial structure of Pickering emulsions, which have aggregated via particle bridging is shown in the 3D confocal fluorescence micrographs in Fig. 6.15. Images of the same region of the aggregate are shown in both images. Figs. 6.15ai and bi show confocal micrographs consisting of 99 combined confocal slices. The standard deviation of each pixel (across the 99 layers) is then calculated to yield an intensity value (the technical aspects of how these images are constructed are discussed in Sec. 3.4). For rather complex systems, such as this, in which curved interfaces, multiple droplets, and 3 different refractive indices are present, this yields clearer 3-dimensional images. This is discussed further in the microscopy section of the methods. Figs. 6.15a(ii and bii show images which consists of 3 confocal slices, the intensity values of which have been summed.

The droplet aggregates shown in Fig. 6.15 have a complex, fractal structure. The volume fraction of droplets within the structure is actually rather low, as can be seen in both the higher apparent emulsion volumes at high shear in the photographs in Fig. 6.9 and in the confocal micrographs in Fig. 6.15. The shared monolayer between the droplets on the right-hand side of the confocal micrograph on Figs. 6.15a(ii and bii is suggestive of the formation of particle bridging, but shadowing effects due to the particles, as well as lensing and scattering at the fluid-fluid and fluid-particle interface, means a fully index-matched model system (or, more convincingly still, Cryo-SEM, as used by French et al [47]) is required to fully study particle bridging and aggregate structure.
Figure 6.15  Confocal z- stacks of a Pickering emulsion formed at high shear ($\dot{\gamma} = 24000$ s$^{-1}$), showing particle bridges between droplets. a.) $r_p = 726$ nm, b.) $r_p = 990$ nm i.) Flattened z-stack confocal fluorescence micrograph consisting of 99 slices, voxel depth = 1 $\mu$m. ii.) Individual slice of the same image, in the region of where droplets are seen to be in contact.
6.5 Composite Emulsion Stabilisation

In previous sections the qualities of two emulsion system have been investigated: a TAHP-stabilised emulsion and a PMMA-stabilised emulsion. Three clear regimes of the PMMA stabilised emulsion were identified. At low particle volume fractions ($\Phi_s = 4.1$ mm$^{-1}$) there is sufficient particles to emulsify only a small amount of the water present in the system. At intermediate volume fractions ($\Phi_s = 28.9$ mm$^{-1}$) all of the water added to the system is emulsified, but there is insufficient particles present to create a Pickering emulsion consisting of individual droplets, and so the droplets aggregate, minimising bare oil-water surface by sharing particles. These aggregated emulsions tend to need extensive agitation before they flow when poured, and the aggregates can be rather large: up to several mm in diameter. At very high particle volume fractions ($\Phi_s = 151.5$ mm$^{-1}$) a large excess of particles is present in the system relative to the amount of surface area stabilised. This leads to the formation of a Pickering emulsion that flows when poured after only gentle agitation, and which consists mostly of spherical, single droplets with a droplet polydispersity of approximately 40%.

In this section a composite interface, consisting of colloidal PMMA particles and TAHP, is used to stabilise emulsions. It will be shown that the drop size is determined wholly by the quantity of the TAHP and the shear rate applied during emulsification. This will allow me to change the density of particles at the droplet interface simply by varying the particle volume fraction (which has a negligible effect on droplet size). This will then be used to tune the uptake of particles onto the interface, leading to the interface adopting a thick, ‘hairy’ structure with projecting tendril-like TAHP/particle aggregates at very high particle volume fractions. Finally I will show that, somewhat surprisingly and even at high $\Phi_s$, adding particles to the system yields only limited variation in temperature response, even when the emulsions have an apparently almost-complete coating of particles. I will briefly study the structure of the emulsions and their (dynamic) interfaces after heating has occurred, which will form the basis for the next chapter.

The emulsion now consists of a great many components, all of which have parameters that can be varied. I shall therefore stick to only a very narrow range of parameter space in this section. Everything presented in this section is based on the results obtained so far in this chapter. To allow for quantitative
comparisons between the Pickering emulsions studied in the previous section, identical specific surface areas of particles of $r = 500$ nm, $750$ nm, and $990$ nm will be used. In all but one section, a TDA concentration of $2.5$ mM will be used. The aqueous phase will always contain $100$ mM phosphate ions at pH $5$. In each section I will begin by discussing the composite emulsions stabilised by particles of a single radius ($r_p = 726$ nm), and then discuss the effects of varying particle radius. It will be shown that, at low particle volume fractions ($\Phi_s = 4.1$ and $28.9$ mm$^{-1}$), the interface consists largely of a single layer of particles dispersed homogeneously in the rigid TAHP film. At higher particle volume fractions ($\Phi_s = 151.5$ mm$^{-1}$), the TAHP and PMMA particles form large aggregates, which are present both in the bulk (having detached from the interface) and are found to project from the interface.

6.5.1 Composite Interface Emulsions: Varying $\Phi_s$ at fixed pH and [TDA]

I will begin by discussing the effect of varying particle volume fraction, $\Phi_s$, upon the properties of the TAHP/PMMA-coated interfaces. The macroscopic appearance of composite interface emulsions at increasing $\Phi_s$ is shown in Fig. 6.16. The emulsions in Fig. 6.16 are identical to those shown in Fig. 6.12, only with $2.5$ mM tetradecylamine added to the dodecane prior to mixing.

Macroscopically, at high $\Phi_s$ (151.5 mm$^{-1}$), the appearance of the composite interface emulsions in Fig. 6.16 is remarkably similar to that of the Pickering emulsions shown in Fig. 6.12. In both cases, stable water-in-oil emulsions are formed. The addition of tetradecylamine to the system results in a slight change in the macroscopic appearance of the emulsion at intermediate $\Phi_s$ (28.9 mm$^{-1}$), in that the interface between the emulsion and the dodecane supernatant is significantly flatter. This can be understood as a consequence of the TAHP stabilising a great amount of surface area, thus preventing bridge formation and, hence, droplet aggregation. A consequence of this is that the emulsion consists of non-aggregated, spherical droplets, as shown using light microscopy in Fig. 6.16. The most significant difference is at low $\Phi_s$, where the addition of the TAHP results in a stable emulsion being formed. By contrast, at the same $\Phi_s$, but in the absence of TAHP, only a very small quantity of emulsion was found to form. This demonstrates the compatibility of the TAHP and PMMA as emulsifiers: both stabilisers contribute to the stability of the emulsion. The images here do
not conclusively prove that particles are present at the interface, rather than one emulsifier excluding the other. The presence of the particle at the interface is confirmed by the use of confocal fluorescence microscopy later (see e.g., Figs. 6.22 and 6.23).

The appearance of the (dodecane) supernatant of the emulsions also exhibits a change in appearance with increasing particle volume fraction, as shown in the high-magnification light micrographs in Fig. 6.16 inset, whilst the light micrographs in Fig. 6.17 show that the aggregates form at all values of \( r_p \) studied.
here. At all values of $\Phi_s$, particles are seen to remain in the dodecane after emulsification, suggesting that there is competition between the two emulsifiers, and the quantity of particles seen in the supernatant increases with $\Phi_s$. The structure of the particles in the supernatant also radically changes as $\Phi_s$ is increased. At $\Phi_s = 4.1$ and $28.9 \, \text{mm}^{-1}$, the particles are dispersed as individual particles, with one or two doublets also visible. As $\Phi_s$ is increased to $151.5 \, \text{mm}^{-1}$, the particles can be seen to form large, multi-particle aggregates.

**Why do the TAHP-PMMA particle aggregates form?**

The mechanism for the formation of the TAHP-PMMA aggregates is not clear. In the oil, the particle pair-potential is predominantly repulsive. The presence of particle aggregates in the oil suggests that the aggregation is mediated by the TAHP. Furthermore, comparison with the emulsion supernatant in the absence of TAHP in Fig. 6.12 shows no such aggregates. This implies that the aggregates consist of both TAHP and PMMA particles. Given that the TAHP forms only at the interface, it also implies that the aggregates form via a mechanism of adsorption of the particles at the interface, followed by aggregation mediated by the TAHP crystallites and subsequent desorption. As will be seen later using confocal fluorescence microscopy (see e.g., Fig. 6.26), this has a radical effect on the appearance of the droplet interface, with many aggregates remaining attached to the interface, projecting from the droplet surface in self-affine tendrils. The question is also of some industrial relevance, and so warrants further study: the precipitation of insoluble components, and the aggregation it induces in colloidal particles, has important implications for food processing [235].

**Effect of $\Phi_s$ Upon Drop Size**

One important feature of composite interface systems is the extent to which the stabilisation mechanisms are antagonistic (i.e., their interactions reduce their individual efficacies as emulsifiers), synergistic (i.e., their interactions increase their individual efficacies as emulsifiers), or summative (i.e., their interactions are simply the sum of the two properties of the two stabilisers). In this section, I will observe the effect of varying particle volume fraction upon droplet size, whilst keeping all other variables constant. Emulsions in this section are emulsified at $\dot{\gamma} = 24000 \, \text{s}^{-1}$, with $[\text{TDA}] = 2.5 \, \text{mM}$. This shear rate is in the plateau region
shown in Fig. 6.5, where drop size is independent from shear rate. This suggests that addition of a large amount of extra emulsifier will lead to a reduction in drop size, provided that the interactions between the emulsifiers are either summative or synergistic. This will, however, be shown not to be the case, resulting in droplets whose size is dictated almost entirely by the TAHP.

Droplet size distributions for \( r_p = 726 \) nm for the emulsions shown in Fig. 6.16 are shown in Fig. 6.18 along with \( d_{43} \) values for all particle radii studied here (inset). Size distributions for droplets formed at \( \Phi_s = 151.5 \) mm\(^{-1} \) were not measured, as the aggregates, along with the thick, multilayer interface of the system, means the model describing the scattering from the droplets is no longer valid. The droplet size distributions also include a control experiment, in which a TAHP-stabilised emulsion without added particles was formed, for comparison. As can be seen, all three droplet size distributions in Fig. 6.18 show good agreement with one another, with little, if any, obvious systematic variation in drop size across a factor of 7 difference in \( \Phi_s \). As can be seen in Fig. 6.18 inset, the average droplet diameters all lie within ±20% of the mean \( d_{43} \) value for the systems studied (89.3 ±6.5 µm). This suggests that the size of the particles does, to some degree, affect the drop size distributions, which I investigate in the next section (see e.g., Fig. 6.20).

At the shear rates studied here (15000 rpm = 24000 s\(^{-1} \)), the quantity of particles added to the system has little, if any, observable systematic effect upon the size of the droplets. This is potentially indicative of three things: the droplet size being limited by the shear rate, the additional surface area that the extra particles can stabilise being negligible, or the additional particles not adding to the total amount of stabilised surface area. Performing the experiment in the plateau region means the first of these options can be discounted, as an excess of surface area is created during shear. The negligible change in droplet radius is therefore likely to be a mixture of the second two factors. The high-\( \Phi_s \), composite interface emulsions shown in Fig. 6.17 suggest that the amount of stabiliser added to the system is, indeed, significant. Whilst these emulsions are inappropriate for sizing using light scattering methods, visual inspection of the micrographs shows the droplets to be of roughly the same size as those formed at \( \Phi_s = 4.1 \) and 28.9 mm\(^{-1} \). The large amount of particle aggregates present in the supernatant after emulsification at high \( \Phi_s \) also says that the additional particles form aggregates that do not contribute to emulsion stability. The additional particles may also simply result in the interfaces of the droplets becoming thicker, forming interfacial
multilayers and protrusions from the droplet at high $\Phi_s$. This is, in fact, shown to the case in later sections (see e.g., Fig. 6.26). Regardless of the exact mechanism by which the droplet size remains unchanged with increasing $\Phi_s$, two important conclusions can be drawn from this section. Firstly, the two emulsifiers are compatible, if not necessarily synergistic. Secondly, the droplet size is determined not by $\Phi_s$, but by the tetradecylamine concentration. This is shown to be the case for multiple TDA concentrations in the next section. The effect of varying the size of the particles added to the system will also be studied.

**Effect of Particle Size**

It has been shown thus far that PMMA particles and TAHP stabilise water-in-oil emulsions using compatible mechanisms, and that the quantity of surface area stabilised at the shear rates and emulsifier concentrations studied here is determined by the fatty amine concentration alone. Throughout this chapter, varying the radius of the colloidal particles has also been of interest. This is done...
to probe the effect that particle size and particle adsorption kinetics have upon the TAHP as a stabiliser. The aim of this is to fabricate droplet interfaces with a range of particle radii for the study of particle dynamics at the interface (studied in the next chapter), and to test the range of parameter space over which the stabilisation mechanisms are compatible.

In this section the effect of varying PMMA particle radius, whilst keeping shear rate and [TDA] constant, is studied with particle sizing and light microscopy. This is done to test the extent to which the conclusions drawn from the experiments at \( r_p = 726 \text{ nm} \) (i.e., that drop size is predominantly determined by [TDA]) can be extended to all particle sizes used in this thesis. This is interesting because it will allow me to synthesise droplets with a tunable coating of particles for a range of particle sizes, whilst not having to alter any other parameters. Fig. 6.18 inset, shows that the particle radius does have a slight effect upon \( d_{43} \), and the extent of this effect must be measured. The effect of particle volume fraction and particle radius upon the interfacial structure is then studied in the section after this, in which it is investigated using confocal microscopy.

The effect of varying particle radius at equivalent values of \( \Phi_s \) upon the macroscopic appearance of the emulsions is shown in Fig. 6.19. Macroscopically, the effect of changing the particle radius upon the appearance of the emulsions is negligible, with all emulsions in Fig. 6.19 similar in appearance to those formed at \( r_p = 726 \text{ nm} \) (shown in Fig. 6.16). For all \( r_p \), a stable emulsion is formed even at very low \( \Phi_s \) due to the presence of the TAHP, whilst increasing \( \Phi_s \) only serves to change the colour of the emulsions due to the yellow NBD dye present in the particles. As with Fig. 6.16, the emulsion-dodecane interface is flat, suggesting the absence of large droplet aggregates.

Droplet size distributions and light micrographs of the droplets are shown for intermediate \( \Phi_s \) in Fig. 6.20. High-magnification light micrographs of the dodecane supernatant of the emulsions, showing excess particles not swept up during emulsification, are also shown (Fig. 6.20b, inset). Visual inspection of the light micrographs at low magnification (Fig. 6.20b) and high magnification (Fig. 6.20b, inset) show little change in the appearance of the emulsions, with the exception of the increasing size of the particles in the supernatant. The excess particles in the supernatant demonstrates that there is an excess of stabiliser relative to the amount of surface area created during emulsification, and shows that the stabilisers adsorb competitively onto the droplet interface. The droplet size distributions in Fig. 6.20a show size distributions for \( r_p = 500, 726, \text{ and } 990 \)
nm (green, purple, and orange lines respectively), and also in the absence of any added particles (black line). There does appear to be a slight systematic variation with particle radius, with $d_{43}$ increasing from 73 µm at $r_p = 500$ nm, up to 112 µm at $r_p = 990$ nm. This compares to $d_{43} = 99$ µm in the absence of particles, suggesting a shift of ±15% as particle radius is varied by ±33%.

The slight variation of the drop size with particle radius suggests that interactions between the TAHP and PMMA affect the emulsion properties to some extent. Smaller particles typically lead to a reduction in drop size, even though in theory the total amount of surface area that the system can stabilise remains constant. This suggests that the interaction is to some extent synergistic for low $r_p$ and antagonistic for high $r_p$. There are a number of possible mechanisms for this. Nucleation of the TAHP on the PMMA particles, shown to lead to particle aggregation in Fig. 6.16, will change the particle wettability and may result in a greater number of smaller particles detaching from the interface due to their lower capillary energy. The adsorption rate of the particles is known to be size-dependent [48, 231], which may affect aggregate formation. The trend could also simply be a result of the greater volume of particles for large $r_p$ giving rise to scattering not described by the model used here. The effect that can be attributed to varying particle radius is, however, rather small compared to the other parameters governing the behaviour of the system. The most important parameter governing droplet size is [TDA], which determines the drop size (at constant shear rate) almost entirely. This is shown in the next section.
Figure 6.20 Light micrographs and droplet size distributions for emulsions stabilised by 2.5 mM TDA and PMMA particles, showing the effect of particle radius. a.) Drop size distributions, including the drop size distribution for an emulsion with no added PMMA particles. b.) Light micrographs of the emulsions at increasing particle radius with (inset) high-magnification micrographs of the supernatant showing particles left over in the oil after emulsification.

Drop Size is Determined by the TAHP: The Effect of Varying [TDA]

It was shown in Figs. 6.5 and 6.8 that, for TAHP-stabilised emulsions formed at constant shear rate, drop size could be varied by changing [TDA]. This was attributed to a number of effects depending upon the shear rate, including the amount of TAHP formed and the lower surface tension of the oil-water interface raising the capillary number of the system and, hence, reducing the maximum stable drop size at a given shear rate. Given that, in the case of the TAHP-stabilised system, the droplet diameter was determined by shear rate and fatty amine concentration, it can be expected that this will also be the case for the composite interface stabilised emulsions. This is shown in Fig. 6.21.

Here, a low and intermediate particle volume fraction ($\Phi_s = 4.1$ and 28.9 mm$^{-1}$ respectively) are used in conjunction with a low and high fatty amine
concentration ([TDA] = 1.25 mM and 2.5 mM respectively), to determine which variable has the greatest impact upon drop size. The drop size distributions in Fig. 6.21 are in good agreement with that for the emulsions formed with no particles present, shown in Fig. 6.8 where \( d_{43} \) was found to be 150 µm and 100 µm at 1.5 and 2.5 mM TDA respectively, and with the previous experiment at 2.5 mM TDA in Fig. 6.18.

![Figure 6.21](image.png)

Figure 6.21  *Droplet size distribution histogram for the emulsions containing varying [TDA] and \( \Phi_s \). Light lines (left pair) have a high fatty amine concentration ([TDA] = 2.5 mM), whilst the dark lines (right pair) have a lower fatty amine concentration ([TDA] = 1.25 mM).*

As in the case of the composite interface emulsions with \( r_p = 726 \) nm in Fig. 6.18 at low and intermediate \( \Phi_s \) the drop size negligibly depends on the particle concentration. Instead, the tetradecylamine concentration determines the drop size almost entirely. As seen earlier (see Fig. 6.8), this is a combination of two separate factors: the capillary number of the system, along with the quantity of TAHP available for droplet stabilisation. At the high shear rates studied here, it is the quantity of TAHP that plays the biggest role. The additional PMMA particles added to the system, rather than acting to stabilise more surface area, end up present in the supernatant as TAHP-PMMA aggregates, or add to the thickness of the droplet interface. I will now investigate the effect that the additional particles have upon the structure of the droplet interface using confocal microscopy, and show unambiguously that adding particles does indeed result in thicker interfaces. Furthermore, I will show that the drop size being determined by the TDA concentration allows me to vary particle density at the interface whilst keeping droplet size constant, simply by varying the amount of particles I add to the system.

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6.5.2 Composite Interface Emulsions: \( \Phi_s \) and Interfacial Structure

It has been shown that colloidal particles and TAHP have emulsification mechanisms that are compatible with one another. At the shear rates studied here, the amount of surface area stabilised during emulsification is determined by the surface tension of the oil-water interface which, in turn, is determined wholly by the concentration of fatty amine in the system. A number of questions remain regarding the structure and dynamics of the droplet interface and competition between the adsorption of the two stabilisers. The extent to which the interfacial structure and, hence, temperature response can be tuned is also of interest. It has not yet been conclusively shown that the particles adsorb onto the droplet interface when significant quantities of TAHP are present. It has been hypothesised that, since (if there is enough stabiliser present) droplet size is largely independent of the amount of particles used, particle density at the droplet interface can be tuned simply by varying the amount of particles added to the system, whilst the droplet size will remain constant. Finally, the question of the dynamics of the interface at room temperature has so far been ignored. In previous chapters it was shown that the TAHP network was highly elastic, and that the crystallites at the droplet interface are stationary over the course of 30 minutes, allowing high quality fluorescence micrographs of the system to be obtained. In this section, it will also be shown that particles present at a TAHP-coated droplet interface do not move. Micrographs requiring 30 minutes of imaging time show no distortion due to particle motion, and time lapse images of the emulsion droplets show no motion of the particles over the course of 1 hour. That is, the elastic TAHP network in which the particles are embedded at the interface arrests thermal motion of the particles.

The Anatomy of a Composite Interface Droplet

In this section I investigate the interfacial structure of the composite interface emulsions shown in Figs. 6.19 using confocal fluorescence microscopy. I begin by using an interface in which the two components have dyes that can readily be separated on the confocal microscope. I use DiIC\(_{18}\)-dyed colloidal PMMA particles described in Table 6.1 and NBD-doped TAHP. The two components can clearly be distinguished in the confocal fluorescence micrographs in Fig. 6.22.
which shows a droplet stabilised by both PMMA and TAHP at $\Phi_s = 4.1 \text{ mm}^{-1}$. This is achieved by illuminating the system at 408 nm and 555 nm. When excited at 408 nm, fluorescence signals from both the TAHP and the DiIC$_{18}$-dyed particles can be seen. When excited at 555 nm, only the signal from the particles can be seen. This clearly shows that both the TAHP crystallites and the PMMA particles are present at the interface, even at very low $\Phi_s$.

For the rest of this section, in order to minimise sample contamination, no fluorescent dye was used to directly image the TAHP, and so only the colloidal PMMA particles are visible in the fluorescence micrographs. I use the NBD-dyed colloidal PMMA particles described in Table 6.1. Composite interface-stabilised droplets imaged using this method are shown in Fig. 6.23. The presence of the TAHP can be inferred from both the stability of the droplets even at negligible particle volume fractions, and from the confocal micrograph in Fig. 6.22.

**Interfacial Structure: Effect of $\Phi_s$**

The interfacial structure of the droplets exhibits a strong dependence on the amount of particles added to system. At low $\Phi_s$, the main contribution to droplet stability comes from the TAHP, and the droplet interface is only sparsely covered.
with particles. To clarify the location of the droplets both the fluorescence and transmission signals are shown at low \( \Phi_s \) in Fig. 6.23. Fluorescent particles can clearly be seen, both at the droplet interface and in the supernatant, confirming the uptake of particles to the interface even at very low particle volume fractions. As \( \Phi_s \) is increased, both particle coverage at the interface and the quantity of particles left over in the oil increase. At \( \Phi_s = 28.9 \text{ mm}^{-1} \), the droplet interfaces have a patchy appearance, with approximately half of the droplet interface coated with particles. The droplets are stationary for long time periods (at least one hour), and stable against coalescence, clearly showing that the remaining interface is occupied by the TAHP crystallites. As particle volume fraction is increased further, the emulsion interface acquires a radically different character. The droplets at high particle coverage (\( \Phi_s = 151.5 \text{ mm}^{-1} \)) are no longer coated in a monolayer of the particles. Rather, they now appear to be ‘hairy’, with large aggregates of TAHP and PMMA extending from the interface. These aggregates have a fractal geometry, and can extend as far as 10 \( \mu \text{m} \) from the droplet interface. The aggregates were also found in the bulk oil, as shown in the light micrographs of high-\( \Phi_s \) composite interface emulsions in Fig. 6.17. Given the interfacial formation mechanism of the TAHP, this implies that the aggregates first form at the interface, before detaching, possibly due to collisions during emulsification, or due to the aggregates breaking up due to shear flow.

The confocal micrographs in Fig. 6.23 show that interfacial structure and particle area density at the interface vary with \( \Phi_s \). The particle area density increases, even though the droplet size and, hence, free surface area for particle adsorption,
Figure 6.24  Confocal fluorescence micrograph of the supernatant of the composite interface particles at increasing $\Phi_s$ ($\Psi_s = (l-r) 4.1, 28.9, 151.5 \text{ mm}^{-1}$, $r_p = 726 \text{ nm}$). Image shows the bottom layer of the system, which is in contact with cover slip.

remains constant. This apparent contradiction can be resolved by considering both the increasing thickness of the interface caused by increasing $\Phi_s$ and the increasing quantity of particles present in the dodecane after emulsification, shown in the micrographs in Figs. 6.16 and 6.24.

**Interfacial Structure: Effect of Particle Size**

The appearance of the interface and supernatant of the emulsions shown in Fig. 6.19 has also been studied using two other particle radii: 500 and 990 nm. This was done in order to test how particle size, and therefore adsorption kinetics, affected particle uptake. The effect of varying particle radius upon the appearance of the hairy droplets at high $\Phi_s$, and the structure of the TAHP/PMMA particle aggregates left over in the supernatant, is also of interest.

Varying $\Phi_s$ between low and intermediate values ($4.1$ and $28.9 \text{ mm}^{-1}$) changes the area density of particles at the droplet interface. It has been shown previously that this does not significantly affect the size of the droplets. This suggests that both the interfacial thickness and the quantity of TAHP and PMMA which is displaced from the interface into the supernatant varies with $\Phi_s$. Confocal micrographs, with a side-on view of the droplets reconstructed from the individual slices, are shown for $r_p = 990 \text{ nm}$ in Fig. 6.25. The increase in area density of the particles can clearly be seen. The micrographs shown here, which are of sufficient quality that the 3D reconstructed image can be rotated by $90^\circ$ around the imaging plane.
to show the z-axis location of the particles (Fig. 6.25, aiii and biii). These images took over 20 minutes of continuous imaging to obtain, during which no motion of the particles was detected. This trend of particle area density increasing with $\Phi_s$ was also found for $r_p = 500$ and 990 nm, and will be re-visited later when the effects of heating the system to dissolve the TAHP are studied.

Confocal micrographs of the appearance of the droplets at all $r_p$, and high $\Phi_s$, are shown in Fig. 6.26. Large aggregates can be seen to protrude from the droplet interface at all values of $r_p$. A confocal micrograph of a system with $r_p = 990$ nm, $\Phi_s = 151.5$ mm$^{-1}$ is shown in Fig. 6.27 which also includes an enlarged area showing the fractal structure of the aggregates, which can clearly be seen to protrude from the interface.

Qualitatively, the appearance of the interface of the droplets is largely independent of $r_p$, within the range studied here. The area density of the particles as a function
of $\Phi_s$ is not studied quantitatively here, but a number of qualitative observations can be made, and these observations are valid for all particle radii studied here. When $\Phi_s$ is increased, the average particle area density on the droplet interface also increases. Increasing $\Phi_s$ also increases the quantity of particles left over in the supernatant. The coverage of drops formed at a single value of $\Phi_s$ is rather variable, though varying $\Phi_s$ across 1.5 orders of magnitude leads to the very obvious difference in interfacial structure shown in Figs. 6.23 and 6.25. Adding a very large excess of particles to the system, leads to the formation of thick, fractal interfaces, which have tendril-like aggregates of TAHP crystallites and PMMA particles both protruding from the droplet interface. These aggregates, which only appear at $\Phi_s \geq 28.9 \text{ mm}^{-1}$, are also found in the supernatant (see e.g., Fig. 6.24). The presence of the aggregates in the supernatant, combined with the interfacial mechanism by which the TAHP forms, suggests that these aggregates form via a mechanism of aggregation at the interface followed by detachment.
One possibility for future work is to study quantitatively the distributions of area particle densities at the interface, and how this varies with $r_p$. The ease with which high-quality confocal micrographs such as those in Fig. 6.25 can be obtained for this system make an exhaustive study possible, if not necessarily entertaining. One expects the characteristic time for a particle of radius $r_p$ to adsorb on to an interface during emulsification to decrease as $r_p$ decreases [48, 75]. This adsorption rate typically reaches a maximum at $r_p = 500 \text{ nm}$ [234]. The particle range studied here could therefore yield interesting results, and is clearly experimentally accessible. As both emulsifiers are clearly present at the interface, and the surface area created during emulsification is smaller than the amount that can be stabilised by the amount of emulsifiers present (as evidenced by the large amount of particles left over in the supernatant at all values of $\Phi_s$), it can be inferred that adsorption of particles and TAHP is competitive. Varying the particle radius ought to increase the rate at which the particles adsorb, and so tune the particle area density at the interface. An alternative method of doing this is to alter the pH of the aqueous phase, thus varying the rate at which the TAHP forms, and so the rate at which surface area is excluding from particle adsorption by the TAHP. This would, however, lead to variation in surface tension and so droplet size, and significantly alter the efficacy of the TAHP as an emulsifier. The impact of varying pH upon interfacial structure, and the importance of TAHP

Figure 6.27 Confocal fluorescence micrograph of $\Phi_s = 151.5 \text{ mm}^{-1}$, $r_p = 990 \text{ nm}$, with the area denoted, which contains a fluorescent aggregate, inset.
formation kinetics, are briefly discussed in the next section.

6.5.3 Tuning Particle Arrangement via pH

It has been shown throughout the previous two chapters that increasing the pH of the aqueous phase from 5 to 7 retards the kinetics of TAHP formation, and increasing pH from 7 to 8 both retards formation kinetics and reduces the quantity of TDA converted into TAHP. It is also expected that the colloidal PMMA particles included in the composite interface system will adsorb onto the dodecane-water interface at a rate that depends on the particle radius. In this section I use these tunable formation kinetics to apply the TAHP as a molecular stopwatch for particle adsorption and arrangement at the droplet interface.

To investigate the balance of TAHP formation and particle adsorption kinetics, the effect of changing the pH of the aqueous phase was studied. Two different $\Phi_s$ values were used. This was done in order to check that the droplet patches appeared due to pH variation, rather than being $\Phi_s$-specific. In this experiment, $\Phi_s = 30 \text{ mm}^{-1}$ and $60 \text{ mm}^{-1}$ of PMMA particles of $r_p = 500 \text{ nm}$ and a concentration of 2.5 mM TDA were used, and the pH of aqueous phase was varied before the emulsions were mixed. As in previous sections, to avoid contamination, the only fluorescent dye present in the system is the NBD. The dye is covalently bonded with the polymer PMMA matrix that makes up the colloidal particles, and so only the particles are visible in the micrograph.

Composite interface emulsions formed at increasing (top-to-bottom) pH are shown in Fig. 6.28. The particle distribution varies from mixed at pH 5, to ‘patchy’ at pH 7, in which the interface appears to consist of (bright) particle-rich and (dark) TAHP-rich domains. At pH 8 the droplet interfaces are completely covered with particles, suggesting the presence of only very small quantities of TAHP at the oil-water interface. At both low (Fig. 6.28 left) and high (Fig. 6.28 right) $\Phi_s$, the same trends are observed: evenly distributed particles at pH 5, separation into domains at pH 7, and total coating of the droplets with particles at pH 8. The particles were not observed to move during imaging, showing that they are embedded in an elastic TAHP-network at low pH, or in a jammed particle monolayer at pH 8. The size of the droplets also appears to change, with the droplet size increasing significantly at pH 8.

The emergence of the particle-rich domains at pH 5, and the total coating of
Figure 6.28  Confocal fluorescence micrographs of water-in-oil emulsions stabilised by a composite TAHP-PMMA particle interface. The white (fluorescent) objects are the PMMA particles - the TAHP is not visible in the images. The particles are stationary on a timescale of 1 hour, suggesting complete, or near-complete, interfacial coverage of TAHP crystallites. The pH is increased from 5 (top row), to 8 (bottom row). $\Phi_s = 30 \text{ mm}^{-1}$ (left column) or 60 mm$^{-1}$ (right column).

The patchy domains occur due to the retardation of the film formation kinetics at pH 7. Even though the quantity of TAHP formed at pH 5 and 7 is identical, the formation of the TAHP network occurs much more slowly, leading to the PMMA particles aggregating into domains at the interface. At pH 8, no dark (and, hence, TAHP-coated) domains are observed on the droplet interface. This
is in agreement with the pH-dependence of TAHP-stabilised emulsion stability discussed in Section 6.4 at pH 8, the quantity of TAHP formed on the time scale of emulsification (1 minute) is negligible, and so the major constituent of the interfaces is the PMMA particles. This reduction in the amount of stabiliser present in the system also leads to the increase in droplet size. A number of other effects might also be expected to occur: in particular the particle density at the interface is expected to increase as TAHP formation kinetics are retarded. This does appear to occur, at least qualitatively, in Fig. 6.28, but the variation of the drop size with pH makes this effect rather difficult to study quantitatively.

6.6 Temperature Response

In this chapter, two emulsifiers have been used to create an emulsion: one of these emulsifiers exhibits temperature response (the TAHP), whilst the other does not (the PMMA particles). A photograph directly showing the difference in temperature response of the two stabilisers is shown in Fig. 6.29, which acts as a control experiment for this section. Fig. 6.29 shows TAHP-stabilised emulsion and a PMMA-stabilised emulsion before (Fig. 6.29a) and after (Fig. 6.29b) the emulsions were placed in a water bath at 75°C for 20 minutes. Heating the TAHP-stabilised emulsion causes the droplets to coalesce, whilst the PMMA-stabilised emulsion is unchanged after heating.

In previous chapters I have shown that the temperature response of the TAHP film is due to the temperature-dependence of the solubility of TAHP in the dodecane. Heating the droplets results in the TAHP crystallites that coat the interface dissolving into the dodecane. This also corresponds to a drop in the rheological moduli of the TAHP film, to levels below the detection limits of the DWR geometry, shown previously in Fig. 5.7. It has been shown in Figs. 6.23 and 6.25 that particle uptake can be trivially tuned, whilst keeping droplet radius constant, simply by adding more particles to the system. This is because the droplet radius in this system is governed entirely by the amount of TDA used. By combining the two emulsifiers, I will have emulsions that are coated by both a temperature-responsive and a non-temperature-responsive emulsifier.

In this section I will study the effect of varying the area coverage of the (temperature responsive) TAHP and the (non-temperature-responsive) PMMA particles, on the behaviour of the system when it is heated. The effect of heating
the system will be to dissolve the TAHP, resulting in a monolayer of mobile particles that coat the droplet interface. It must be emphasised that the particles do not move at the interface until the TAHP has been dissolved. The effect of the presence of particles on the emulsion stability is found to be remarkably limited, with composite interface emulsions undergoing significant coalescence even at very high $\Phi_s$. This suggests potential applications for TAHP in Pickering emulsion destabilisation. The arrangement of the particles once they are free to rearrange is also striking: upon dissolution of the TAHP the particle monolayer orders, adopting arrangements at the spherical interface governed by repulsive, electrostatic interactions. These ordered particle arrangements are briefly studied here, and will provide the basis of the next chapter, in which I will study them quantitatively.

### 6.6.1 Macroscopic Stability After Heating

The effect of varying $\Phi_s$ on the macroscopic behaviour of the emulsions when they are heated is shown in Fig. 6.30. Here, composite interface-stabilised emulsions are shown at increasing $\Phi_s$ (l-r, 0 - 151.5 mm$^{-1}$) both before (Fig. 6.30, left) and after (Fig. 6.30, right) being placed in a water bath at 75°C for 30 minutes. All of the emulsions show significant coarsening. In the case of the emulsions
containing particles, this can be seen most clearly by observing the underside of the vials (Fig. 6.30 bottom). Large, mm-size droplets can be seen in the emulsions at all $\Phi_s$, even when there is a large excess of particles in the system relative to the amount of surface area initially stabilised, such as at $\Phi_s = 151 \text{mm}^{-1}$. The presence of the particles does appear to arrest coalescence to some degree, with the TAHP-stabilised emulsion containing no droplets at all after heating, whereas the TAHP-PMMA interface system still appears to have some, larger droplets after heating.

The effect of heating upon the interfacial structure of dense emulsions, and how that relates to the macroscopically observed change in stability against coalescence in Fig. 6.30 was studied using confocal fluorescence microscopy. Observing dense emulsions of the high-$\Phi_s$ system, after heating, using light microscopy is challenging. The quality of the micrographs obtained prior to heating show a high level of detail, with PMMA particles clearly predominantly present at the interface, as shown in Fig. 6.27. Heating the system leads to a large drop in the quality of the micrographs. Scattering of light from the large quantity of the interface in the system (the fluids, the PMMA particles, and the TAHP all have mismatched refractive indices) means only the bottom 15 $\mu$m of the system can be observed. The fluorescence signal from the emulsions after
heating (Fig. 6.31 centre) is rather noisy, but some observations can be made from the data obtained. Most obviously, the quantity of the particles which have sedimented to the cover slip is vastly greater after the system has been heated, which is also a major cause of the more rapid extinction of the light intensity with depth. This suggests that the droplets shed particles from their interfaces during TAHP dissolution. Two populations of droplets can also be seen: very small droplets (dark regions in the fluorescence signal, Fig. 6.31) and very large ones (bright regions in the transmission signal, Fig. 6.31). Some of the smaller droplets are clearly in contact with the larger ones, suggesting some degree of stability against coalescence.

Surprisingly, the addition of a large quantity of particles to a TAHP-stabilised emulsion does not lead to greatly increased stability against heat-induced coalescence. Even at $\Phi_s = 151.5 \text{ mm}^{-1}$, in which the overwhelming majority of the droplet interface is coated with particles (see e.g., Fig. 6.27), the emulsions in Fig. 6.30 coarsen significantly when heated. The increase in the amount of particles seen at the bottom of the vial after heating also suggests that dissolution of the TAHP, and the coalescence events that this leads to, results in the droplet interface actually shedding particles during heating. This is not wholly surprising, given that the aggregates which protrude from the droplet interface at high $\Phi_s$ are held together by TAHP. The observed coalescence of the emulsions at all $\Phi_s$, though arrested to some degree as more particles are added to the system, suggests that TAHP could find potential applications in the destabilisation of...
Figure 6.32  Ejection of material from the interface of a crumpling droplet. The object has been denoted by an arrow in the images. The system has been heated to 65°C, leading to evaporation of the water and crumpling of the interface.

Pickering emulsions.

6.6.2 Studying Sparse Samples

Studying dense droplet dispersions using confocal microscopy allows the interfacial structure of the droplets after heating to be examined. However, the micrographs obtained after heating from the dense emulsions are of a rather low quality. Studying samples which contain only a very few (≤ 100) droplets in a large volume (5 ml) of dodecane allows for the interfacial structure of the composite interface emulsions to be studied both before and after TAHP dissolution. This leads to a number of interesting observations, including displacement of material from the interface, crumpling of the droplets due to dissolution of the water, and ordering of the particles at the interface once the TAHP has been dissolved.

The effect of heating a high $\Phi_s$ (151.5 mm$^{-1}$) composite interface droplet is shown in Fig. 6.32. As the system is heated, the droplet (which was initially spherical) was seen to shrink and buckle, adopting a non-spherical shape over time. It should be noted that, due to the significantly different volumes of droplets studied, the crumpling of droplets is not observed in the dense emulsion system in Fig. 6.31 in which the droplets can still be seen to be spherical after heating. Furthermore, as no droplets are in contact with one another, no coalescence is observed to occur. It is, however, instructive as to a number of processes that occur at the interface during heating. A large number of PMMA particles can be seen near the droplet. This suggests that the particles detach from the interface during heating if the interface consists of multi-layer aggregates of TAHP and PMMA. The four frames,
separated in time by 0.5 seconds, show either a droplet, or a TAHP-PMMA particle aggregate, being ejected from the interface, suggesting that heating, at least in part, contributes to the interface shedding colloidal particles.

The shedding of particles induced by heating could also explain the coalescence of the composite interface emulsions at high $\Phi_s$. As has been seen in micrographs of the emulsion supernatant at high $\Phi_s$, TAHP-PMMA particle aggregates are found after emulsification. Given that TAHP must be formed at the interface, this suggests that the aggregates detach from the oil-water interface. It could be that, when the system is heated, dissolution of TAHP encourages detachment of more aggregates from the droplet interface, resulting the creation of bare oil-water interface and inducing coalescence.

**Why do the droplets still coalesce, even at high $\Phi_s$?**

The buckling of the droplet is somewhat surprising given the instability of the emulsion in Fig. 6.31 to coalescence. The high interfacial rigidity of the system in Fig. 6.32 indicated by the buckling, might be expected to yield droplets that are highly stable against coalescence. However, this is not the case. There are a number of possible explanations for this. The crumpled droplet in Fig. 6.32 shows a droplet that has already been at the stated temperature for 15 minutes. It could be that coalescence takes place on much shorter time scales, and that the exposure of bare oil-water interface due to TAHP-dissolution is sufficient to induce coalescence, even at high $\Phi_s$. In that case, the droplet appearance in Fig. 6.32 is unique to sparse emulsion samples, as a droplet in a dense sample would coalesce long before evaporation of the water led to a sufficient reduction in droplet volume to result in the interfacial layer of particles becoming rigid. This suggests that dissolution of the TAHP plays a role in inducing coalescence.

**Heating Samples at Low $\Phi_s$**

Heating sparse droplet dispersions with a small amount of particles at the interface ($\Phi_s = 4.1$ and $28.9 \text{ mm}^{-1}$) leads to striking results. They will be discussed briefly here, and investigated more fully in the next chapter. Whereas the droplets with high $\Phi_s$ retain a near-complete, jammed, monolayer coating of particles, as seen in Fig. 6.32, droplets with only a sparse coating of particles are found to have rather dynamic interfaces. The typical appearance of a droplet
formed at $\Phi_s = 151.5 \text{ mm}^{-1}$, $r_p = 726 \text{ nm}$, after being heated to 60°C is shown in Fig. 6.33. Both the bottom and the top of the droplet are shown. The bottom of the droplet consists of two domains of particles: a static, disordered domain, in the centre of the droplet, and a dynamic, ordered domain, located closer to the droplet equator. The static domain exists due to contact between the droplet and the cover slip, which inhibits particle movement. The droplet is thus prevented from wetting the cover slip by the particle monolayer. In the ordered domain, the particles are seen to move, and are present in an ordered lattice. Moving the focal plane to the top of the droplet removes the effect of the cover slip, and the centre of the image shows ordered, dynamic particles (see Fig. 6.33). Imaging the top of the droplet does, however, introduce a number of image distortions due to refractive index mismatches in the system. The spherical droplet acts as a down-convertor lens, shrinking the top of the droplet, as reported in Ref. [236].

A diffuse halo, surrounding the particle, can also be seen due to light scattering from the particles.

The tunable particle coverage achieved by varying $\Phi_s$ is also reflected in the particle density after the TAHP has been dissolved. The top and bottom of a droplet, heated to 60°C, emulsified with $\Phi_s = 4.1 \text{ mm}^{-1}$, is shown in Fig. 6.34. The transmission PMT signal is also shown (Fig. 6.34), to show the location of the droplet. A number of differences can be seen at low $\Phi_s$. Most obviously, the low
density of particles results in greater inter-particle spacing. Whilst the particles appear to be separated by a characteristic distance, the extent of ordering seems to be far weaker than in Fig. 6.33, with far fewer clusters with 5-, 6-, and 7-fold rotational symmetry observed. The reduced coating of particles also results in the droplet wetting the cover slip, shown in Fig. 6.34, left, resulting in the formation of a circle of fluorescent particles at the three-phase contact line.

After heating (and, hence, dissolution of the TAHP), the particles at the sparsely coated composite interfaces are dynamic. The quality of the confocal micrographs make the system highly amenable to particle tracking, in this case implemented using trackpy, the Python implementation of the Crocker-Grier particle tracking algorithm. This is only briefly mentioned here, and discussed in more detail both in the Methods section (Sec. 3.6) and in the next chapter. Particle tracking has been implemented on the particles at the bottom of the droplet in Fig. 6.35, in which the trajectories of the individual particles have been shown. The particles in the centre of the droplet, which are in contact with the glass cover slip, do not move. The particles closer to the droplet equator, which are free to move, are seen to undergo both highly correlated motion, which is due to the flow of the surrounding fluid phases, and uncorrelated motion, which is thermal in origin.

Just as the area particle fraction can be tuned by varying $\Phi_s$ (shown in Figs. 6.33 and 6.34), the results shown so far for $r_p = 726$ nm are also relevant for the full range of particle radii studied in this chapter. Dynamic, ordered interfaces, consisting of both individual particles and aggregated particles clusters, for $r_p = 500, 726$, and $990$ nm have been observed, and are shown in Fig. 6.36. This shows
Figure 6.35  Timelapse confocal fluorescence micrographs of the particles on the bottom of a droplet, after the system was heated to 65°C. Particle tracking, with trajectories shown from oldest (blue) to most recent (green), shows the particles in contact with the cover slip are stationary, whilst those higher up the droplet are dynamic.

Figure 6.36  Confocal fluorescence microscope showing the top of a composite interface emulsion droplet after the system has been heated to 60°C. Droplets are coated with particles at increasing (l-r) $r_p = 500, 726, 990$ nm. All droplets were emulsified at $\Phi_s = 28.9 \text{ mm}^{-1}$.

the droplets after the system has been heated to 60°C, and demonstrates that ordered lattices appear for all particle radii studied here. The effect of clusters upon the lattice structure, clearly seen in the micrographs in Fig. 6.36, will be studied in the next chapter.

Upon heating, the TAHP interface dissolves which, as shown in the interfacial rheology experiments, leads to negligible interfacial rheological moduli. This leads to the colloidal PMMA particles at the oil-water interface becoming mobile, and ordering via long-range interactions. In the next chapter this system will be investigated quantitatively, using the information gathered in this chapter to tune the electrostatic interactions between the particles (which is the origin of their order) and the particle surface coverage. Dilute emulsions will be studied
to ensure that all TAHP present at the interface is removed by heating. Index-matched emulsions will be studied in order to remove the effect of the particles trapped by the glass cover slip upon the the ordering of the lattice. This allows me to study an undistorted image of the top of the droplet.

6.7 Conclusions and Future Work

Water-in-oil emulsions stabilised by a novel composite interface, consisting of an interfacially assembled lipid (TAHP) and colloidal PMMA particles, have been studied. The colloidal particles act as model Pickering emulsifiers that yield water-in-oil emulsions that are highly stable against coalescence. The interfacially assembled TAHP has behaviour that can be tuned using a number of variables: phosphate concentration, fatty amine concentration, pH, and temperature. It exhibits many of the properties intermediate to those of a Pickering emulsifier and a molecular emulsifier. It stabilises via a steric mechanism and forms an elastic layer. It also exhibits a number of rather unique features. At sufficiently large tetradecylamine concentration, TAHP-stabilised emulsions have a droplet size inversely proportional to the quantity of stabiliser used. This phenomenon has two origins, depending on the shear rate applied to the system during emulsification. At high shear rates, when a large excess of surface area is created, it is a consequence of the film having a characteristic thickness and the droplets undergoing limited coalescence. At low shear rates the reduction in drop size is due, surprisingly, to the lower surface tension of the system as tetradecylamine concentration is raised. The stabilisation mechanisms of TAHP and PMMA are also compatible with one another; the addition of colloidal particles to the system prior to emulsification produces droplets with composite interfaces that contain both TAHP and colloidal PMMA. The PMMA particles are embedded in the highly elastic TAHP network, and so do not diffuse at the interface. Droplets stabilised by the composite interface have a size dictated largely by the TDA concentration used. The particle density at the interface can therefore be readily controlled, whilst keeping drop size constant, simply by varying the quantity of particles added to the system prior to emulsification.

The two emulsification mechanisms are also, to some degree, antagonistic. This is observed in the temperature response of the system. Heating an emulsion stabilised by a TAHP-PMMA composite interface results in the coalescence of the system. The particles in the composite interfaces, even at very high \( \Phi \), only
Figure 6.37 A confocal fluorescence micrograph PMMA-TAHP-stabilised emulsion after heating to 65°C. $\phi_p = 0.005$, [$TDA$] = 2.5 mM, $r_p = 750$ nm. The bright points visible in the image are the fluorescently dyed PMMA particles.

serve to arrest coalescence to a very limited degree. Studying composite interfaces with only a sparse coating of particles leads to a visually striking result once the system is heated and the TAHP has been dissolved off: the particles order via long-range repulsive interactions. The system can thus be used to probe the properties of colloidal particle monolayers at a range of area particle densities as yet unexplored, as will be done in the next chapter.

The compatibility of the TAHP with Pickering emulsifiers, along with the number of variables that can be altered to tune the behaviour of the TAHP, opens up a number of mechanisms by which TAHP could be used to enhance the functionality of a simple Pickering emulsion. One variable that has been investigated to only a limited extent in this chapter is shear rate. The question of whether the emulsifiers work together in the presence of an excess of surface area has not been investigated fully. It has briefly been showed that particle patterning at the interface can be tuned by varying the kinetics of TAHP formation via pH. Further probing of kinetic aspects of the system, such as by further varying particle size by using nanoparticles, could lead to the large-scale synthesis of patchy droplets. Only a single particle type was used: varying the surface chemistry of the particles by
using e.g., silica particles may also lead to a number of interesting results. The exact mechanism by which instability to coalescence is induced by the TAHP must also be further explored; further investigation in this area could yield a potential application for TAHP in destabilisation of Pickering emulsions, which could find applications in enhanced oil recovery.
Chapter 7

Freezing on a Sphere: PMMA Particles on a Droplet Interface

In this section I discuss the behaviour of colloidal PMMA particles trapped at the surface of an emulsion droplet. Using the method discussed in the previous chapter, water droplets in dodecane coated with both colloidal PMMA particles and TAHP are created via emulsification. I use the mechanisms discussed in the previous chapter to tune the surface coverage of the PMMA, allowing me to produce very large quantities of droplets with a tunable coverage of particles. It was shown in the previous chapter that re-dispersing these emulsion droplets in dodecane and heating the system led to the dissolution of the TAHP, and the mobilisation and ordering of the particles. In this chapter, I disperse a very small number of droplets (100 or fewer) in a relatively large (5 ml) volume of dodecane. Heating the sparse emulsion system to 44°C ensures full dissolution of the TAHP, and yields ordered spherical lattices of particles. In this chapter I will refine the system by matching the refractive indices of the fluids. This allows me to study the crystalline structure of the particles on the top half of the droplet. I will present the first, to my knowledge, study of freezing of colloidal particles at the surface of a sphere, and show that this system is suitable for the further investigation of processes confined to curved interfaces, such as the dynamics of the crystals and the behaviour of the particles on sparsely coated, curved interfaces.
7.1 Introduction

Colloidal particles on curved surfaces behave differently from those on flat ones. For systems where the particles are separated by rather small distances, consideration of the topology of the surface and the number of particles present on it is enough to describe the static arrangement of the particles completely. By varying the density of the particles at the interface $\phi_a$, a range of behaviours emerge which require consideration of more than topology and lattice defects \cite{236, 237}. This introduction focuses on the experimental work that has been performed in this area; the technical and theoretical aspects of the structure of lattices on a spherical surface have been discussed in Sec. \ref{sec:2.3.4}. In this introduction I review some of the aspects of these systems that have already been studied, and identify three promising areas for future study: the ordering of the lattice at increasing $\phi_a$, the study of the dynamics of the spherical lattice, and the effect of form factor defects (particle dimers, trimers, and oligomers) in disrupting the defect structure of the spherical lattice.

Recent work on the problem of repulsive particles at curved surfaces has focussed on studying colloidal particles at a spherical oil-water interface \cite{7, 236}. Much of this work focussed on the static defect structure of particles on a spherical lattice, motivated to a great degree by theoretical work at the turn of this century \cite{6, 72, 73}. Of particular interest is not the structure of the lattice, but the arrangement of the defects in the lattice, whose presence is a topological necessity. These were initially studied using Pickering emulsions. Droplets coated with a sufficiently dense monolayer of particles form an ordered lattice. Bausch and co-workers used light microscopy to study an approximately density-matched system of 1 $\mu$m-diameter polystyrene microspheres at the interface of water droplets, surrounded by a mixture of toluene and chlorobenzene \cite{66, 238}. A great many of the properties of ordered monolayers at curved interfaces could be extracted from this work: the structure of grain boundaries, the diffusion of defects and grain boundaries through the lattice, and the spring constant of the lattices. Qualitative agreement between theory and experiment, that the number of defects grows linearly with the size of the system, was also found.

More recently, the case of dense particle monolayers confined to surfaces of arbitrary curvature has been studied using theoretical \cite{7, 239} and experimental \cite{7, 10} methods. The experimental technique was rather involved; glycerol drops coated with sterically-stabilised PMMA particles, surrounded by a CHB-
dodecane oil phase, were confined between glass cover slips, one of which could be moved using a micro-manipulator. The cover slip was used to alter the droplet geometry, and the system was then imaged using a fast confocal microscope to obtain particle locations in three spatial dimensions. Finally the system was simultaneously manipulated during imaging using optical tweezers to introduce particles onto the oil-water interface to study defect formation and the dynamics of structural relaxation after the addition of a single particle to the lattice [7]. The work recovered a great many of the results predicted by theoretical work for spherical lattices, as well as finding new ones. The defect structure of a much broader range of topologies was studied, and varying the Gaussian curvature of the interface led to the emergence of pleat-shaped defects on capillary bridges [7].

All of the studies mentioned thus far have looked exclusively at densely packed monolayers consisting of monodisperse particle dispersions. In some cases the particles are not adsorbed onto the droplet interface, but rather bound to it by electrostatic effects [7, 10, 49]. These systems of ‘curved colloidal crystals’ [7, 73, 238] are extremely well-suited for probing the effect of topology upon lattice structures, but a description of the behaviour of colloidal particles at an interface must incorporate more than just the effects of the shape of the system (the theory describing some of the interactions between colloidal particles has been reviewed in Sec. 2.3). Tuning the topology of the system, for instance, also has a profound effect upon the capillary interactions between the particles, provided that they are adsorbed onto the fluid-fluid interface. Ershov et al. used glass microscope slides with patterned hydrophobic regions to control the shapes of the droplets onto which particles adsorbed [11]. A comparison of the results obtained in Refs. [10] and [11] is instructive as to the different physics governing the systems (shown in Fig. 7.1). In the system used by Irvine et al., the particles are not adsorbed onto the oil-water interface, but rather bound to it by an image charge in the aqueous phase. The dipolar interaction between the particles leads to (mostly) hexagonal lattices of particles. Contrastingly, the particles in the work of Ershov et al. are adsorbed onto the interface, and interact at long ranges via capillary interactions caused by the distortion of the non-spherical interface by the particles. This interaction has a quadrupolar symmetry, and so leads to the formation of square crystals.

The previous example illustrates just one aspect of the wealth of behaviour associated with colloidal systems at an interface. There remains a great deal of scope to further investigate the effect of changing the shape of the interface upon
the effects already well-studied for planar surfaces. The 2-dimensional melting transition for instance, which is well-studied for flat interfaces \([240,241]\), remains effectively untouched for curved surfaces. Knowledge of the dynamics of these curved crystals, including the phonon modes of a lattice on a sphere \([242,243]\), and the effects of charge screening and thermal noise \([244–246]\), is rather lacking.

There are a number of reasons to think that studying such phenomena on a curved, rather than a flat, geometry will be interesting. Most important is the role of defects. Spherical crystalline systems exhibit model disorder in an otherwise perfect lattice, providing a fascinating arena in which to study the effect of disorder upon the physics of the system. A system that allows for fine control of the particle density at the interface, whilst also allowing for temperature and viscosity effects to be varied, is necessary to tackle such problems. In the previous chapter such a system was developed. In this chapter I will refine the system by matching the refractive indices of the solvents and ensuring full dissolution of the interfacial TAHP. A major advantage of this system over ones mentioned so far is that its components are non-volatile and non-hazardous, making it extremely suitable for probing a range of sub-phase viscosities and temperatures for extremely long times. I will show that, as the particle area density \(\phi_a\) is increased at the surface of a sphere, the system moves from a disordered state, dominated by capillary interactions and thermal motion, to an ordered phase, bearing the classic defect and grain boundary structures observed by previous workers.
7.2 Materials and Methods

In order to image the lattice structure on the droplet at tunable particle densities, a number of refinements to the system presented at the end of the last chapter are required. Three main goals were identified: ensuring the TAHP was fully dissolved, minimising distortion of the image due to refractive index mismatch between the fluids, and imaging the top of the droplet such that static particles in contact with the cover slip were not in view.

7.2.1 Preparing Emulsions with Dynamic Interfaces: Dissolving the TAHP

It is important to note that, in emulsions stabilised by a composite TAHP/colloidal PMMA interface, the PMMA particles are prevented from moving by the elastic TAHP network in which they are embedded. In typical TAHP/PMMA-stabilised systems, in which a relatively large sample of emulsion (i.e., order 10 \( \mu l \)) is transferred to an imaging chamber using a spatula, no particle motion will be observed, even if the sample is left for several days in 1 ml dodecane. The aim of this chapter, however, is to study the dynamics of PMMA particles at the droplet interface.

In order for interfacial dynamics to be studied in the system, it is necessary to dissolve the TAHP. This allows the particles to move at the interface and, ultimately, order. This is achieved by using very small volumes of emulsion (i.e., minimising the quantity of TAHP in the system) and heating the system to 44°C (i.e., increasing the saturation concentration of TAHP in the dodecane). The final step of heating the emulsion is then followed by leaving the system to equilibrate for 2 hours, which ensures full dissolution of the TAHP, as well as a large reduction in motion of the particles caused by sub-phase flows. Fig. 7.2 shows a comparison between a dense (Fig. 7.2a) and a sparse (Fig. 7.2b) emulsion at room temperature, as well as showing the appearance of a sparse emulsion after it has been held at 44°C for 2 hours (Fig. 7.2c).

Dense emulsions, shown in Fig. 7.2b, consist of roughly 10 \( \mu l \) of emulsion droplets transferred into 1 ml dodecane. The particles in these samples do not move over the course of an hour, as they are embedded in an elastic TAHP network. Sparse emulsions, shown in Figs. 7.2b and c., consist of approximately 100 nl of droplets...
Figure 7.2 Confocal fluorescence micrographs of TAHP/PMMA interface-stabilised emulsions under various conditions. a.) A dense emulsion (approximately 10 µl of emulsion in 1ml dodecane) at room temperature. No motion is detected in the system after 1 hour. b.) A sparse emulsion (approximately 100 nl emulsion in 5 ml dodecane) at ambient temperature and c.) A sparse emulsion 2 hours after being heated to 44°C. Notice in a.) the absence of interfacial dynamics, b.) the complex re-arrangements in the interfacial structure as the TAHP is dissolved, and c.) the rigid lattice in which the particles undergo thermal motion about an equilibrium position.
in 5 ml of dodecane. Such systems exhibit very complicated behaviour when initially placed in the dodecane due to the dissolution of the TAHP. It is beyond the scope of the current work to study the behaviour of the particles during TAHP dissolution any further. The first 10 minutes of the TAHP dissolution process (which occurs due to the concentration of TAHP coating the droplets being less than the saturation concentration of TAHP in the volume of dodecane used) are shown in Fig. 7.2b. This corresponds a concentration of approximately 125 mM of TAHP, compared to a saturation concentration at room temperature on the order of µM. The system is then gently heated to 44°C to ensure full dissolution of the TAHP. The system was then left for 2 hours before imaging to allow the TAHP to dissolve and the particles on the interface to equilibrate. Convective motion of the particles at the interface was also found to be greatly reduced after this time. This yielded droplets with particles arranged in a lattice consisting predominantly of monomers, with a small number of particle doublets and triplets. The doublets and triplets did not break apart upon heating to 65°C. This suggests that the aggregates are present not due to residual TAHP, but rather are artefacts of the particle drying and droplet synthesis method.

### 7.2.2 Preparation of Index-Matched Water-in-Oil Emulsions with a Composite Interface

Matching the refractive indices of the system allows an undistorted image of the particle lattice at the top of the droplet to be obtained, and removes any effects upon the lattice due to the partial wetting of the coverslip by the droplet. Refractive index matching of the fluids was achieved by adding glycerol ($n = 1.4748$) to an aqueous solution of 254 mM ($n_w = 1.338$) of phosphate at pH 5. A mixture of 42% v/v phosphate solution yielded water-glycerol mixtures with a refractive index $n_{\text{dodecane}} = n_{\text{water-glycerol}} \pm 0.0003$ and a phosphate concentration of 100 ±5 mM and pH 5.1 ±0.1. The pK$_a$ of glycerol is 14.15, and so hydrolysis of the OH groups present in the glycerol does not significantly affect the pH of the aqueous phase or the interfacial behaviour of the TAHP. Refractive indices of the fluid phases were measured each time a new batch was prepared using an Abbe refractometer. Emulsions were then prepared using 4 ml 2.5 mM TDA and PMMA particles in dodecane, and 1 ml water-glycerol containing 100mM phosphate. Emulsions were then sheared at $\dot{\gamma} = 32000 \text{ s}^{-1} = 20000 \text{ rpm}$ using

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1This corresponds to about 50 droplets.
Photographs of dodecane-water/glycerol mixtures after shearing at $32000 \text{ s}^{-1}$. The water/glycerol mixture has a refractive index which matches the dodecane, and contains 100 mM phosphate. The dodecane in the left vial contains 5 mM TDA.

the Polytron rotor stator described previously.

Photographs of index-matched, dodecane-water/glycerol are shown in Fig. 7.3. Directly after mixing, prior to phase separation of the fluids, the vial containing no TDA was transparent. This is due to reduced scattering from the index-matched droplet interface. The cause of the white appearance of the emulsion in the vial containing TDA is due to light scattering from the TAHP crystals alone, which are not index matched to the surrounding solvents.

**Image Acquisition**

Use of elevated temperatures in this section prohibits the use of oil-immersion objectives. As such, the confocal micrographs presented in this section were acquired using a 40× magnification, air-immersion objective (NA = 0.6, plan-fluorite corrected), attached to the Zeiss LSM T-PMP/LSM700 confocal laser scanning inverted microscope described previously (see Sec. 4.2.6). Excitation of fluorophores in the colloidal PMMA particles was achieved using a 488 nm wavelength 10 mW laser.
Solvent Preparation

In preliminary experiments, inconsistent charging of the particles and solubility behaviour of the TAHP was observed. As discussed in Fig. 4.7, stock dodecane obtained directly from suppliers often has polar impurities. This leads to lower measured values of surface tension than those quoted in the literature. Given the low dielectric constant of dodecane ($\epsilon_r = 2.0$), electrostatic forces are 40 times stronger than for the equivalent quantity of charge in water, meaning that even a small amount of charged impurities in a solvent can yield unexpected electrostatic effects. Obtaining the literature values for liquid-liquid surface tensions requires that polar impurities be filtered out of the non-polar solvents (in this case, dodecane). Filtration is achieved by pouring the dodecane (ReagentPlus-grade, $\geq 99\%$ purity, Sigma-Aldrich) through a sequence of three funnels, each containing a round of fluted filter paper that holds the Aluminium Oxide powder (58Å pore size, 150 mesh, weakly acidic, Sigma-Aldrich) as shown in Fig. 7.4a. A comparison of the surface tensions before and after filtration is shown in Fig. 7.4b. The measured surface tension after filtration is approximately 51 mN/m, which compares well with the value of 53.2 mN/m reported by Zeppieri et al, suggesting the presence of only trace quantities of polar impurities in the dodecane.
The viscosity of the aqueous phase was measured using a TA DHR-2 stress-controlled rheometer and a stainless steel 2°, 6 cm diameter cone-plate geometry operated in controlled stress mode. Temperature dependence of viscosity was measured by performing a temperature ramp of 1°C min⁻¹ using a Peltier plate attachment and measuring viscosity continuously. The densities of the index-matched solvents were measured after mixing using an Anton Paar DMA 4500 Oscillating U-Tube Density Meter. The index-matching of the solvents made drop shape analysis methods unsuitable for surface tensions measurements. Instead, the maximum drop volume method was used to estimate the surface tension (the technical aspects of this are discussed in Sec. 3.2.3 of the Methods section). The viscosity, density, and surface tension (against dodecane) of the index-matched water-glycerol mixture is shown in Table 7.1.

<table>
<thead>
<tr>
<th>Viscosity (mPa s)</th>
<th>Density (g cm⁻³)</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.17 ±0.22</td>
<td>1.158 ±0.003</td>
<td>29 ±4</td>
</tr>
</tbody>
</table>

Table 7.1  Viscosity, density, and surface tension of water-glycerol mixtures containing 100mM phosphate with refractive index $n_{\text{mixture}} = 1.421$, measured at 43.8°C. Errors correspond to between-batch standard deviations.

The presence of the glycerol leads to a change in all three quantities. The viscosity of the water-glycerol mixture is approximately 8 times greater than that of water ($\eta_{\text{water}} = 0.89$ mPa s). This has the effect of slowing the motion of the particles, allowing the system to be imaged at rather low frame rates. The density increase of the water-glycerol mixture also reduces the rate of sedimentation of the particles at the interface, as the densities of the particles and the droplets are only slightly mis-matched ($\rho_{\text{particles}} = 1.18$ g cm⁻³). The reduction in surface tension and the increase in the density difference of the fluid phases will cause increased deformation of the droplets due to their increased effective weight. The largest droplets studied here have a diameter of 100 µm. Given this and the values in Table 7.1 the upper bound of the Bond number and lower bound for the capillary length of the system are $4 \times 10^{-4}$ and 2.5 mm respectively (definitions of these two quantities are given in Sec 3.2.1). The distortion of the droplets due to buoyancy is therefore negligible, and it is appropriate to model the top of the droplets as a spherical cap. The absence of deviations from a spherical cap geometry was also confirmed by taking a high z-resolution confocal z-stack, and measuring the aspect ratio of the droplet after applying the correction factor discussed in section 3.4.
Figure 7.5  Confocal micrograph, consisting of multiple slices, of a water/glycerol droplet, containing 100mM phosphate at pH 5, in dodecane at 43.8°C. Image was taken 4 hours after sample had been dispersed in dodecane, and the system has been heated to 43.8°C. Bright circles in the image are the fluorescently tagged PMMA particles. The image took approximately 1 minute to obtain, and so some motion of the particles is observed. Left: The bottom of the droplet, in contact with a hydrophobised glass cover slip. Right: The top of the droplet.

7.2.3 Sample Imaging and Particle Ordering

The appearance of an emulsion drop, coated with PMMA particles which are trapped at the dodecane-water/glycerol interface, is shown in Fig. 7.5. Lensing of the image in the top half of the droplet, such as that observed in Ref. [236] is not seen here due to matching refractive indices of the aqueous and non-aqueous solvent. The only fluorescence signal in the image comes from the PMMA particles. Both the bottom (Fig. 7.5a) and the top (Fig. 7.5b) of the droplet are shown. The darkening of the fluorescence signal towards the top half of the equator of the droplet is due to shadowing by the (non-index matched) PMMA particles. The entire image was taken using 80 individual slices. Each slice had an imaging time of 0.7 seconds. Some blurring of the particles due to motion during can be seen, particularly towards the equator of the droplet. The highly correlated nature of the motion shows that this is due to sub-phase flow. The image was taken 4 hours after the system was dispersed in filtered dodecane and heated to 43.8°C, allowing the system to equilibrate.

The particle distributions on the top and bottom halves of the droplet in Fig. 7.5
are different. In the lower hemisphere, the particles have been displaced from the centre of the droplet by partial wetting of the (hydrophobic) cover slip by the droplet, leaving a small circular void at the interface. Particles near this void are pinned in position by frictional interactions with the cover slip. The particles at the bottom half of the droplet consist disproportionately of multi-particle aggregates. This is due to sedimentation or the more massive particle aggregates; the density of the particles ($\rho_p = 1.18 \text{ g cm}^{-3}$) exceeds the densities of both the non-polar ($\rho_{\text{dodecane}} = 0.749 \text{ g / cm}^{-3}$) and polar ($\rho_{\text{water-glycerol mix}} = 1.16 \text{ g / cm}^{-3}$) phases. These aggregates are observed in the system even after the original particle dispersions from which the samples are made have been placed in an ultrasonic bath for 8 hours a day for several weeks, and are an artefact of the washing, drying, and re-dispersal process by which the particle dispersions are prepared.

The particle lattices consist predominantly of single particles. A small quantity of particle dimers can be seen as well, such as in the bottom-right hand corner of Fig. 7.5b. These dimers, which I refer to here as ‘form factor defects’ affect the local ordering of the system to some extent, though the distortions die off rather rapidly. The particle tracking algorithm can track these dimers effectively, and they contribute towards to total areal particle density. The scope of this chapter is, however, limited to studying the effect of increasing areal particle density upon global lattice structure, rather local distortions due to defects. As such, I exclude them from the analysis of the structure here, and simply calculate their centre of mass position as the location of that lattice point. This process is illustrated in Fig. 7.6.
7.2.4 Particle Identification and Assignation of 3D Particle Locations

Particle tracking used a full 3D image of the system, such as that shown in Fig. 7.5, is not feasible as the image takes approximately 1 minute to obtain. Even in the rather viscous water-glycerol mixture, the particle positions shift sufficiently in this time that particle trajectories are impossible to reconstruct. Furthermore, refractive index mismatches between the medium in which the microscope objective is contained (air) and the system means that particles cannot be identified at the droplet equator. Therefore, rather than implementing full 3-dimensional particle tracking, the 3-dimensional positions of the particles are measured by forming a composite image consisting of only 1-3 confocal slices, and assuming that the particles lie on the spherical droplet interface. This leads to an acquisition time between 0.25s and 2s per frame, depending on the desired focal depth and size of the droplet. The droplet presented in this work typically consist of two confocal slices. The total imaging time of such a micrograph is approximately 1 second for imaging, and a further 0.5 seconds for the focal axis to return to the origin.

Particle tracking was then performed on the composite image using trackpy [107], a Python implementation of the widely-used Crocker-Grier particle tracking algorithm [108]. Some of the technical aspects of the Crocker-Grier most relevant to this work have been outlined in Sec. 3.6.

7.2.5 Assigning 3-Dimensional Particle Coordinates

The particles in this work are tracked on a flat focal plane, yet they are confined to a spherical surfaces. This means that as particles move away from the apex of the droplet, a systematic error is introduced into their location. This error increases with distance from the apex of the droplet. To correct for this, the depth (z-axis) co-ordinate of the particle can be calculated from the droplet geometry. Due to the small size (diameter \( \leq 100 \mu m \)) and relatively high surface tension of the system, the top-half of the droplets can be treated as a spherical cap, even if the

\[ \Delta = 2R \sin \left( \frac{\sin^{-1}(x/R)}{2} \right) \]

\[ \Delta = 0 \] at the circle apex, and \[ \Delta = R(\sqrt{2} - 1) \] at the equator.

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\( ^2 \)On a circle, radius R, the difference in x-coordinate of two points on a circle (the distance measured on a confocal slice) and the chord length between the two points (their actual separation), \( \Delta = 2R \sin \left( \frac{\sin^{-1}(x/R)}{2} \right) \). \( \Delta = 0 \) at the circle apex, and \( \Delta = R(\sqrt{2} - 1) \) at the equator.
Figure 7.7  Diagram showing formation of a composite images. Individual confocal slices were taken (each slice took 500ms to obtain in the image shown here), and then the final image (bottom) is formed by summing the brightness values in each slice. Additional time is required for the vertical displacement of the objective to return to the origin, and so the maximum frame rate for a 3-slice image of a droplet this size is approximately 1 frame per 2.5 seconds.
droplet wets the coverslip. The radius of the droplets and the location of their
centre is measured by taking a single z-stack with a high z-resolution (typically
\( \delta z = 500 \text{ nm} \)) and finding the widest point in the image. The centre and radius
of the droplet is then found by fitting an ellipse to the slice at which the droplet
is widest. Given the particle coordinates \((x, y)\), the location of the centre of the
droplet \((x_0, y_0)\), and radius of the droplet \(R\), the z-coordinate of each particle is
given as:

\[
z = \sqrt{R^2 - (x - x_0)^2 - (y - y_0)^2}
\]

(7.1)

Distances between two points on the sphere are calculated not as the Euclidean
distance, but as the great circle distance, \(\sigma\). The great circle distance between a
pair of particles on the surface of a droplet with radius \(R\) is calculated as:

\[
\sigma = 2R \sin^{-1} \left( \frac{\sqrt{(\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2}}{2R} \right)
\]

(7.2)

Separations of the particles are then represented either in terms of the great circle-
distance between the particles, or re-scaled by the droplet radius and expressed
in terms of their angular separation.

### 7.2.6 Measuring Order: Radial Distribution Function

In order to study the effects of particle packing upon the structure of the spherical
lattice, a measure of the extent of order present in the system is required. A
suitable measure of this, which allows for comparison with the case of a flat
system, is the radial distribution function (or ‘pair correlation function’) \(g(\sigma)\).
This is defined as \([62, 241]\):

\[
g(\sigma) = \left\langle \delta(\sigma') \delta(\sigma - \sigma') \right\rangle = \frac{1}{C} \left\langle \sum_{m}^{N} \sum_{n \neq m}^{N} \delta(\sigma_m) \delta(\sigma_n - \sigma) \right\rangle
\]

(7.3)

where the \( \langle ... \rangle \) symbol denotes time-averaging. This is achieved practically
by calculating all the inter-particle distances for every possible pair of particle
cordinates and binning them. When properly normalised by the constant \(C\),
\(g(\sigma)\) gives the probability of finding a particle a distance \(\sigma\) away from another

---

3Recall that arc length \(\sigma = R\theta\), where \(\theta\) is the angle separating two points. The length of a
chord between the two points \(C = 2R \sin \frac{\theta}{2}\), and \(C\) is given simply by the Euclidean distance
between the two points measured in Cartesian coordinates \(C = \sqrt{(\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2}\)
particle, and the extent to which this exceeds (or is less than) that in a system with no spatial correlations (i.e., an ideal gas). The area over which \( g(\sigma) \) is calculated will increase with \( \sigma \). This is accounted for by binning both the model data and the measured data in bins of equal spacings, yielding the correct normalisation. The choice of \( \sigma \) as the distance metric, rather than Euclidean distance, is necessary to calculate correlations at long distances correctly. This is particularly important when studying the extent to which spatial correlations decay with distance. Before presenting any results, I will here go through some of the technical aspects of calculating \( g(\sigma) \) from the data shown in Fig. 7.7.

**Calculation of the Normalisation Constant, \( C \)**

For this system, the normalisation constant \( C \) is the radial distribution function of an ideal gas confined to the surface of a sphere. \( C \) was found numerically, by creating a set of randomly, uniformly distributed points on the surface of a spherical cap, with the same areal particle density as the measured data. Sampling this over 1000 randomly generated particle configurations was sufficient to obtain low-noise in the distributions.

Creating a set of uniformly distributed points on the surface of a sphere requires more consideration than might be expected. It is not sufficient to simply generate points which are uniformly distributed in the spherical coordinates (polar angle \( \phi \) and azimuthal angle \( \theta \) - these are defined in Appendix 2). This is because the surface area element of a unit sphere \( dS = \sin \phi \, d\theta \, d\phi \) is a function of the polar angle \( \phi \).

In this work, \( g(\sigma) \) is calculated on a spherical cap, the radius of which is equal to the radius of the focal plane of the image, \( r_{foc} \). The generation of uniformly distributed points on the surface where \( \phi \in [0, \phi(r_{foc})] \) is achieved by calculating [247]:

\[
\begin{align*}
\theta &= 2\pi u \quad u \in [0, 1] \\
\phi &= \cos^{-1} (2v - 1) \quad v \in [v_{min}, 1] \\
v_{min} &= \frac{1}{2}(1 + \cos \phi(r_{foc}))
\end{align*}
\]

More intuitively, the surface area element is a circle which gets bigger as we move towards the equator. Distributing points uniformly in \( \phi \) and \( \theta \) makes the total number of points in each area element constant, which leads to the points bunching towards the poles of the sphere. A number of mechanisms exist to account for this; an excellent summary of these can be found in Ref. [247].

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Figure 7.8  
A comparison of the distribution of 123 particles on a spherical cap of a 38.3 µm-radius droplet for an ideal gas (left) and for PMMA particles (right). The outline of the droplet on which the particles sit has been drawn in both images (blue line).

where $u$ and $v$ are uniformly distributed random numbers. A comparison of the distribution of the points in the emulsion system, and for the case of an ideal gas, has been shown in Fig. 7.8. The computed data (Fig. 7.8) is compared with data obtained for a 38.3 µm-radius droplet. The upper 16% of the sphere was imaged, corresponding to a range of polar angle $\phi \in [0^\circ, 43^\circ]$.

Range over which $g(\sigma)$ is calculated

The pair correlation function studied here is treated as a bulk property of the system. As such, it is important to account for edge effects caused by the system only being imaged over a fraction of the sphere ($\approx 20\%$ of the surface). It is important that the radius over which $g(\sigma)$ is calculated for a given particle does not fall outside of the cone that contains the focal plane. This leads to faster-than-expected decays in correlation. To achieve this, $g(\sigma)$ is calculated only for particles in the upper-third of the focal plane, such that all particles lie within $\frac{\phi_{foc}}{3}$. Particles that lie outside of this cone do not have $g(\sigma)$ calculated for them, but they contribute towards the calculation of $g(\sigma)$ for all particles lying within the cone. This way $g(\sigma)$ can be calculated over an angular separation of $\frac{2}{3} \phi(r_{foc})$.

The sample of particles for which $g(\sigma)$ is calculated is a compromise between taking a homogeneous sample of the system, and maximising the range over which
the calculation of $g(\sigma)$ is valid. For the droplet in Fig. 7.8, 12 particles lay within $\frac{\phi_{foc}}{3}$, meaning that $g(\sigma)$ is calculated over a great circle distance $\sigma = R_{\text{drop}} \times \frac{2\phi_{foc}}{3}$. For a single frame, this yields rather large errors in $g(\sigma)$. To compensate for this time-averaging over multiple frames is applied. Video duration was chosen as a compromise between the time scale on which evaporation significantly altered the droplet geometry (this was on the order of 10 minutes, depending on droplet size), and data quality. Between 400 and 600 frames were typically used, though up 1000 images could be obtained for larger droplets. For the droplet shown in Fig. 7.8, 500 images of the droplet were taken (at a rate of 1.5 seconds per frame), which yielded high-quality radial distribution functions. Imaging over relatively long time scales also ensures a homogeneous sample of the crystal is taken. Motion of the sub-phases perturb the sample, especially for low $\phi_a$. Between frames, this motion is negligible, but it is rather significant on the timescales over which 500 frames are taken (approximately 12 minutes), meaning a large range of the configuration space available to the particles is observed.
7.3 Results and Discussion: Emergence of Order at Increasing $\phi_a$

Droplets with 3 different particle densities were studied, $\phi_a = 0.07, 0.16$ and 0.25, to investigate the effect of $\phi_p$ upon the lattice structure. Multiple droplets at similar $\phi_a$ (typically $\pm 0.005$) were observed, in order to look at the effect of particle dimers and trimers upon structure. I begin by looking at droplets with $\phi_a = 0.25$, and then study the effect of reducing $\phi_a$ upon the structure.

The appearance of two droplets at $\phi_a \approx 0.25$, along with their radial distribution functions, is shown in Fig. 7.10. Locally, structures with 5-, 6-, and 7-fold rotational symmetry can all be seen. These defect structures have been marked explicitly on the lattice in Fig. 7.9. The pentagonal and heptagonal structures tend to involve a particle oligomer, suggesting that their presence within the topological defects is energetically favourable. The radial distribution functions for both droplets agree with each other extremely well. Both exhibit a strong, narrow peak in $g(\sigma)$ at a lattice spacing of approximately 2.7 $\mu$m, and the peaks are of identical magnitude for both samples. The higher order peaks, which represent spatial correlations between next-nearest (and further) neighbours, decay in magnitude with increasing distance. The amplitude of the peaks in $g(\sigma)$ falls off with increasing $\sigma$, but significant spatial correlations are still observed over 6 lattice spacings. Greater distances than this were not studied due to the limited area of the droplet that could be visualised. The second and third peaks are split into two sub-peaks. The two sub-peaks correspond to structural correlations arising from translations along different planes of the spherical ‘crystal’.

Both droplets have differing numbers of form factor defects. The droplet with $\phi = 0.254$ has six doublets, and one triplet in the focal plane of the image, whilst the droplet at $\phi = 0.247$ has 14 doublets and 5 triplets. In spite of the differing arrangement and structure of the form factor defects on both droplets, the long range structure of both lattices is almost identical. The defects clearly distort the structure locally, though the differing form factor defect arrangement and densities in the systems do not appear to destroy long-range order in the system.

Fig. 7.10 shows that the PMMA particles crystallise at sufficiently high $\phi_p$, and have a radial distribution function characteristic of the (mostly) hexagonal order in the system. The emergence of this order with increasing $\phi_a$ was also studied. Droplets at $\phi_a = 0.007, 0.156$, and 0.247 were observed. Radial distribution
Figure 7.10  Top: Radial distribution function for two droplets, $\phi_a = 0.247$ (green line) and 0.254 (purple line). Bottom: Confocal micrographs of the droplets, coated with fluorescence PMMA particles, $r_p = 726$ nm. The green line extends further as the droplet is larger, and so $g(\sigma)$ is truncated at a greater distance.
Figure 7.11  Radial distributions functions and droplet images at increasing (top-to-bottom) $\phi_a$. Axes identical in all graphs.
functions, along with images of the droplets, in Fig. 7.11.

At low \( \phi_a \) (\( \phi_a = 0.07 \)) the extent of spatial ordering in the system is significantly reduced. The particle density exhibits a broad, fluid-like peak at approximately 5\( \mu \)m. The spatial correlations in the system decay to negligible values over approximately 3 lattice spacings, showing that long-range and quasi-long-range order is absent from the system. None of the higher order peaks show the splitting characteristic of a hexagonal-like ordering of a thermal system. As \( \phi_a \) is increased (\( \phi_a = 0.156 \)) the appearance of the graph changes significantly. The characteristic spacing between nearest neighbours decreases to 3.7 \( \mu \)m, and the first peak in \( g(\sigma) \) is significantly higher and narrower. The peaks decay significantly more slowly with increasing distance, but all appear to be single peaks, showing that crystallisation has not occurred in the system at this particle density. As particle density is increased further to \( \phi_a = 0.247 \) the crystallisation observed in Fig. 7.10 is recovered. The second and third order peaks in \( g(\sigma) \) split, showing hexagonal ordering of the lattice over at least two lattice spacings.

The structural features observed in Figs. 7.10 and 7.11 are characteristic of a system undergoing an ordering phase transition with increasing \( \phi_a \). At the particle densities studied here, the interactions between the particles are predominantly repulsive and electrostatic in nature. As the particle density increases, these repulsive interactions lead to the system undergoing a phase transition from a disordered fluid at \( \phi = 0.07 \) to a lattice with a large degree of hexagonal, crystalline order at \( \phi_a = 0.25 \). At particle densities intermediate between these two values, the extent of spatial ordering can be seen to increase. It is known that in 2D systems at planar interface a hexatic phase exists at intermediate particle densities [240]. This hexatic phase is characterised by rotational order of the particles, but with spatial correlations that die off rather rapidly [63]. Structural defects, present by necessity on a sphere, are known to play a critical role in driving the transition from ordered, to hexatic, to fluid phases in 2-dimensional systems [248]. Full analysis of the defect structure and angular correlations present in the system is beyond the scope of the current work, but make exciting prospects for future study.
7.4 Conclusion

Crystallisation of a 2D spherical lattice with increasing particle density, $\phi_a$, has been studied using emulsion droplets coated with colloidal PMMA particles. Emulsion droplets stabilised using a composite TAHP-PMMA particle interface were prepared with tunable $\phi_a$, and the fluids in the emulsion were index-matched by adding glycerol to the aqueous phase. Heating the system led to the dissolution of the TAHP, and ordering of the particles via long-range, likely electrostatic, interactions. It has been shown that as $\phi_a$ is increased, the particle lattice undergoes a transition from a fluid-like state at $\phi_a = 0.07$, to an ordered one at $\phi_a = 0.25$. At intermediate $\phi_a$, the extent of spatial correlations observed is seen to increase, but no crystalline-like order was observed. This suggests the presence of an intermediate, likely hexatic, phase, though further study of angular correlations in the system is required to confirm this. The observations made here agree qualitatively with observations made for colloids at a planar interface. This suggests potential for future work in studying the effects of topological defects upon the ordering of the particles at high $\phi_a$.

The system has been shown to produce large quantities of droplets with fine-tuned particle coverages. It also contains no volatile compounds, making it suitable for study at elevated temperatures. This makes it amenable to further study of a wide range of physical phenomena. Previous chapters showed that particles with a range of radii could be used with this system. The system could be suitable for studying binary mixtures of spheres at the droplet interface, which are already known to yield interesting results at planar surfaces [240]. The dynamics of the lattice at high $\phi_a$, which has also attracted recent attention at planar interfaces [242, 243], is also suitable for investigation using this system.

The most interesting prospect for future work is an investigation into the behaviour of the defects in the lattice. Defects, present on triangulations of a sphere by topological necessity, are already known to play a critical role in phase transitions in 2-dimensional systems. Investigating already well-studied phenomena on a spherical lattice has the potential to study defects in a highly controlled way. The defect structure itself of static lattices also has a number of open questions. Whilst this has been studied extensively for the case of monodisperse particles, polydispersity introduces a range of effects of critical importance in colloidal systems. In this work, I have introduced defects of a new kind - multi-particle aggregates. The behaviour of these, and their impact of
upon the spherical lattices is potentially rather interesting. Fig. 7.10 shows that these tend to sit not in 6-fold coordinated regions, but at the centre of the lattice defects. Study of the effect of such defects upon the local lattice structure using Delaunay triangulation could yield a number of interesting results, informing future design of functional materials.
Chapter 8

Conclusion and Outlook

The films formed by tetradecylamine and hydrogen phosphate at the dodecane-water interface, and the emulsions they stabilise, have been studied. At pH 8 and below, charged tetradecylammonium cations adsorb onto the interface, and a layer of hydrogen phosphate counter-ions condense. Rather than producing a monolayer, this yields a thick, insoluble layer of tetradecylammonium hydrogen phosphate (TAHP). Confocal fluorescence microscopy shows that these films consist predominantly of aggregated crystallites, up to 100 µm in length. Small angle neutron scattering shows that these crystallites contain lamellar order. Fourier transform infrared spectroscopy measurements performed on dried TAHP show that it has a well-defined stoichiometry, consisting of two tetradecylammonium cations bound to a single hydrogen phosphate anion.

The TAHP films have a macroscopic structure that can be easily tuned by varying the pH of the aqueous phase. This, along with their large surface shear moduli, make them suitable model systems for studying interfacial rheology. At pH 7 and below, the TAHP forms a skin-like film. At pH 8, it forms a lace-like film. The rheology of the films and their structure have been directly related: the lace-like film deforms plastically, whilst the skin-like film deforms in a brittle manner. Interfacial rheology has also been used to relate the structure of the film to the stability of the temperature-responsive, water-in-oil emulsions that TAHP stabilises. When a TAHP film is heated the film thins, its rheological moduli drop, and the emulsions it stabilises coalesce. Confocal fluorescence micrographs of TAHP-stabilised droplets during heating show that this is due to dissolution of the TAHP into the bulk fluid phases.
Emulsions stabilised by a composite interface consisting of TAHP and colloidal PMMA particles have also been studied. Adjusting the tetradecylamine concentration varies the surface tension of the system at the very short timescales relevant to emulsification, allowing the average drop size to be easily tuned. This allows the TAHP to be used as a molecular stopwatch that tunes the extent of particle uptake to the droplet interface. The particle density at the droplet interface can thus be easily varied simply by varying the volume fraction of particles added to the system prior to emulsification. This suggests potential applications in the formulation of patchy droplets, containing patches of functionalised particles.

Finally, the temperature response of the TAHP has been used to synthesise an index-matched emulsion system. Dissolving the TAHP leads to the particles mobilising at the interface, and ordering over very long distances via dipolar electrostatic interactions. The phase behaviour of the particles as function of areal particle density has been investigated, with the particles shown to undergo a phase transition from a liquid, to a crystalline phase with increasing particle density.

This work opens up a number of exciting avenues for future work. The TAHP films are ideal for rheo-optic studies. Observing the plastic-to-brittle transition that the change in film structure causes would be of particular interest, and is well within the capabilities of existing equipment. The tunable temperature response of the TAHP-stabilised emulsions must be better understood and controlled, with potential applications in water treatment and the encapsulation and controlled released of agricultural chemicals. The potential use of pH as a stopwatch for the TAHP reaction could also be applied to the monodisperse capsules, to create capsules with a tunable interfacial thickness and, hence, tunable mechanical properties. Finally, the index-matched emulsion system has immense potential for the study of the physics of colloidal systems at curved interfaces. Further investigation, focussing on the behaviour of the defect structure during the melting and freezing transition, along with studying the lattice dynamics of the crystallised systems, would provide the opportunity to study the effect of topology on a number of physical phenomena.
Appendix A

Translation of ‘Remarques sur la diffusion des rayons X dans les smectiques A’

Crystalline Physics - Remarks upon the scattering of X-Rays in the Smectic A Phase

Alain Caillé, presented by André Guinier


The intensity \( I(q) \) scattered by a single crystal in the smectic A phase is studied for \( q \) in the region of the Bragg peak with wave vector \( |q_z| = 2\pi/d \). Different laws occur for different directions of the wave vector \( q \). The characteristic exponents are a function of the temperature.

Liquid crystals, in the smectic phase, are configured in equilibrium in equidistant lamellae, separated by distance \( d \), arranged perpendicular to the \( z \)-axis. The intensity of the scattered x-rays possesses maxima corresponding to the Bragg condition: \( |q_z| = 2\pi/d \), where \( q = k_r - k_i \); \( k_r \) and \( k_i \) are, respectively, the
reflected and incident wave vectors. We calculate the intensity scattered by the thermal fluctuations in displacement \( u(\mathbf{r}) \) by lamellae in the direction of the \( z \)-axis, which couple to dilations, \( \theta \), in the volume. We assume that \( \theta \) and \( \frac{\partial u}{\partial z} \) are small (harmonic approximation); for this case, the thermodynamic averages of the Fourier components \( U_q \), are found to be (1):

\[
\langle |U_q|^2 \rangle = \frac{k_B T}{Bq_z^2 + K_1 q_{\perp}^4}
\]

where:

\[
U_q = \int e^{i\mathbf{q} \cdot \mathbf{r}} u(\mathbf{r}) \, d^3 r \quad \text{and} \quad \bar{B} = B - \frac{C^2}{A} > 0
\]

\( A, B, \) and \( C \) represent isothermal rigidities, and \( K_1 \) is a Frank constant. We assume that the width of the Bragg peak, due to static defects in a perfectly ordered lamellar structure, is small compared to the enlargement due to thermal fluctuations. We consider the case of the x-rays being scattered by a single, infinite domain of surfaces defined by the equation

\[
z_n = nd + u_n(\mathbf{r}_{\perp})
\]

\( n \) is an integer and \( u_n(\mathbf{r}_{\perp}) \) is the displacement of the \( n \)th lamella in the \( z \)-direction at a point \( \mathbf{r}_{\perp} \) (in the plane of the lamellae). The intensity of x-rays scattered by this system at thermal equilibrium (expressed in electronic units) is:

\[
I = |f_0|^2 \sum_n \int d\mathbf{r}_{\perp} e^{iq_z nd} e^{iq_{\perp} \cdot \mathbf{r}_{\perp}} \langle e^{iq_z (u_n(r_{\perp}) - u_0(0))} \rangle
\]

where \( q_{\perp} \) is the vector component of \( \mathbf{q} \) perpendicular to the \( z \)-axis, and \( \langle ... \rangle \) represents a thermal average. \( f_0 \) is the atomic scattering factor for the system described in equation [A.3]. In the harmonic approximation, all linear combinations of \( u_n(\mathbf{r}_{\perp}) \) are random and Gaussian-distributed. Thus:

\[
\langle e^{iq_z (u_n(r_{\perp}) - u_0(0))} \rangle = \exp \left( -\frac{1}{2} q_z^2 \langle |u_n(r_{\perp} - u_0(0))|^2 \rangle \right)
\]

For large \( n \), we replace the summation over \( n \) with an integral over \( z \); the mean squared displacement thus becomes:

\[
\langle |u_n(\mathbf{r}_{\perp}) - u_0(0)|^2 \rangle = \frac{2}{(2\pi)^3} \int d^3 \mathbf{q} \left( 1 - e^{-|\mathbf{q}|} \right) \langle |U_q|^2 \rangle
\]
Using expression A.1 and expression A.6 for \( z \gg \frac{a^2}{\alpha} \) we obtain:

\[
G(r) = \langle e^{iq_z(u_n(r_\perp)-u_0(0))} \rangle = \exp(-2M) \exp\left(-XE_1\left(\frac{r_\perp^2}{4\alpha z}\right)\right) \left(2\frac{2a}{r_\perp}\right)^{2X}, \quad (A.7)
\]

where:

\[
\alpha = \left(\frac{K}{B}\right)^{\frac{1}{2}} \quad \text{and} \quad X = \frac{\pi k_B T}{2 K a^2 \alpha}.
\]

\( M \) plays the role of the Debye-Waller factor. It is linear in \( T \) and quadratic as a function of the wavenumber \( |q| \) :

\[
M = -q^2 \frac{k_B T \gamma}{2 \pi B \alpha}
\]

\( \gamma \) is the Euler constant (\( \gamma = 0.577... \)). \( E_1(x) \) is the exponential integral function

\[
E_1(x) = \int_{x}^{\infty} \frac{e^{-t}}{t} dt
\]

The correlation function \( G(r) \) is written:

\[
G(r) = 2e^{-M} \left(\frac{a^2}{\alpha z}\right)^{2}, \quad \rho \ll z, \quad (A.11a)
\]

\[
G(r) = 2e^{-2M} \left(\frac{2a}{\rho}\right)^{2X}, \quad \rho \gg z. \quad (A.11b)
\]

The diffuse intensity is obtained from equation A.7 for the two principal directions (\( z \) and \( x \)):

\[
I \sim \frac{1}{(q_z - \frac{2\pi}{d})^{2-X}}, \quad q_\perp = 0, \quad (A.12a)
\]

\[
I \sim \frac{1}{q_\perp^{2-2X}}, \quad q_z = 0. \quad (A.12b)
\]

The laws are very different from those found for scattering in a solid \(^2\), where \( X \) for single-phonon scattering would be zero. For liquid crystals (smectic A), \( X \) is of the order unity. It is also noted that the exponent of Eq. A.12 is different if we move along \( q_z \) or \( q_\perp \). The displacement \( u_n \) of the lamellae is more strongly correlated in the \( z \)-direction that in the place of the lamellae. This anisotropy leads to a maximum in intensity lying in the \( q_\perp \) direction. This phenomenon is observed in photographic X-ray diagrams \(^3\) for a smectic A oriented using a

\(^1a^2\) corresponds to the mean molecular area in the lamellae

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magnetic field. The parameter X depends linearly on α. On approaching the smectic-nematic transition temperature, \( T_{SN} \), and if the transition at \( T_{SN} \) is of the second order, we expect \( \bar{B} \to 0 \) and \( X \to \infty \). However, for large X, it is likely that the harmonic approximation is not appropriate. It is therefore interesting:

- to verify Eq. A.12 for \( T \) significantly lower than \( T_{SN} \), using measurements on single domain samples: existing studies (4) (McMillan) do not allow such a verification. A more detailed study is underway (5);
- to highlight deviations from harmonic laws for \( T \to T_{SN} \)

P. G. de Gennes and J. Jouffroy first drew these problems to my attention.

(4) W. L. McMillan, X-Ray scattering from liquid crystals.
(5). J. Joffroy, Private communication
Appendix B

Spherical Coordinate Convention

At least seven different conventions for the labelling of spherical coordinates exist throughout the literature. The convention I use in this thesis is shown in Fig. B.1. $\phi$ corresponds to the polar angle, measured from the +ve $z$-axis. $\theta$ corresponds to the azimuthal angle, measured anti-clockwise from the $x$-axis. $r$ is the radius of the sphere.

$\phi$ corresponds to the polar angle, measured from the +ve $z$-axis. $\theta$ corresponds to the azimuthal angle, measured anti-clockwise from the $x$-axis. $r$ is the radius of the sphere.

Figure B.1 Spherical coordinate conventions used in this text (particularly in Chapter 7), along with the coordinate transforms.


