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Relaxation Timescales in Densely Packed Adhesive Emulsions



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A thesis submitted for the degree of
Doctor of Philosophy
March, 2017

Declaration

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Acknowledgements/Preface

Several years ago, I came across an address delivered by Albert Einstein to the Physical Society of Berlin in 1918. In that speech Einstein mused on the different reasons that people are attracted to science. I won't summarize that great thinkers conclusions here, but since reading it I have often found myself reflecting on the sources of inspiration that started me on this journey.

To me science is the dedicated and disciplined study of change, of flux, of flow. The one constant is change! Throughout my PhD I have tried my best to view the scientific method as a practise of reverence directed towards impermanence, and the study of rheology acts as constant reminder of the change and flux that governs our reality. We will never know everything, there will always be change! Eager students for generations to come will always have new questions posed to them by learned professors, and visa versa. The PhD journey is a difficult but highly rewarding one and I consider myself lucky to have been gifted the opportunity to experience it. But it is not a journey that any student takes alone and this thesis would be incomplete without acknowledging the people who were with me along the way.

First and foremost I would like to extend my sincerest gratitude toward my supervisor, Professor Matthias Möbius. Matthias' keen eye and broad wisdom have always kept me focused on the task at hand. Without his patience and guidance I would have struggled to understand the nuances of experimental rheology required to complete this PhD. As well as that, his aphorisms have carried more weight than I think he realised. Throughout my PhD his advice, "Sometimes the Perfect is the enemy of the Good", has continuously echoed within my mind and without it I don't know if this project would have ever gotten off the ground. Thank you Matthias!

I also wish to thank all the members of the Foams and Complex Systems group. Professors Denis Weaire and Stefan Hutzler for providing uncountable amounts of insight and inspiration over the years. I would also like to thank all the students who have been a part of the group during my time here, you have all helped in different ways. Ho-Kei, Aaron, Steve, Michael, Cathal, Robert, Fritz, Jens, Ben and Steven, Thank you!

I would particularly like to mention David Whyte, with whom I've shared this journey since our undergraduate days in Theoretical Physics. David's programming fluency and eagerness to help has assisted me at countless points throughout my PhD. But more than that, he kept me sane during difficult experiments or tiring analysis by suggesting a quick cup of coffee over a game of cribbage. Thank you David!... I guess we'll never know who won more games. I would also like to thank all my friends, who are too numerous to list, but you all know who you are and you all helped in immeasurable ways. Thank you!

I want to sincerely thank family and particularly my parents. They've always supported my ambitions and never for a second doubted my ability to achieve whatever I set my mind to. Without their unwavering love and encouragement I wouldn't be the person I am today. Thank you Mam! Thank you Dad!

Last, but certainly not least, I want to thank my girlfriend Aoife. Aoife, a fellow scientist, has shared the struggles and triumphs that accompany the scientific pursuit with me over the past few years. without her love and support I don't know if I would have made it. Thank you Bibs, with all my heart!

Finally, I dedicate this entire body of work to all writers of past, present and writers yet to come, across all disciplines of human endeavour, without whom, I firmly believe, our species would have nothing.

Summary

We experimentally investigate the relaxation time, that is, the inverse rearrangement rate, of densely packed adhesive emulsions using two complementary methods. We use a recently introduced oscillatory technique known as strain rate frequency superposition to measure the relaxation time as both a function of strain rate and packing fraction. We use microscopic imaging to study droplet dynamics in the bulk of a flowing emulsion from which we can also infer the relaxation time, again both as a function of strain rate and packing fraction. In the Material and Methods chapter We describe the custom built apparatus we developed to study droplet dynamics.

Prior to our investigation of the relaxation time we measured the macroscopic rheology of adhesive emulsions using conventional techniques such as strain sweeps and flow curves. Using these techniques we obtained the yield stress, shear modulus and empirical Herschel-Bulkley parameters of our system and found them to be consistent with what has been reported in the literature.

We also measured the local strain rate in steady shear rheology using microscopic imaging and found that despite the use of sandpaper slip was present in our system. This caused us to call into question strain rates reported in the literature as it has long been assumed that sandpaper or roughened surfaces are sufficient to eradicate slip.

When we compared our measurements of the relaxation time from the two techniques we found different trends with regard to both strain rate and packing fraction. We proposed two possible reasons for this. One, as we do not know the behaviour of slip in oscillatory measurements or its dependence on packing fraction we suggested that a systematic investigation of slip may be used to resolve this discrepancy. We also suggested that yielding mechanisms may be different in

steady shear dynamics than oscillatory shear where there is a clear solid-like to liquid-like transition.

Our strain rate frequency superposition measurements uncovered a weak strain rate dependence of the shear modulus for adhesive emulsions which has not been reported in the literature. We hypothesize that this is a results of surfactant kinetics that exist in highly concentrated surfactant solutions, in our case, an adhesive emulsion.

Finally we also investigated the relevance of the deformation relaxation ansatz, which we discuss on the Introduction chapter, in describing the stress strain relationship of a flowing emulsion and found it to be valid over a wide range of strain rates. We use this result to calculate the elastic energy fluctuations in a flowing emulsion, via the non-equilibrium Stokes-Einstein relation, and found it to be consistent with what has been reported for two dimensional foams.

Soap Bubbles

From years of study and of contemplation
An old man brews a work of clarity,
A gay and convoluted dissertation
Discoursing on sweet wisdom playfully.

An eager student bent on storming heights
Has delved in archives and in libraries,
But adds the touch of genius when he writes
A first book full of deepest subtleties.

A boy, with bowl and straw, sits and blows,
Filling with breath the bubbles from the bowl.
Each praises like a hymn, and each one glows;
Into the filmy beads he blows his soul.

Old man, student, boy, all these three
Out of the Maya-foam of the universe
Create illusions. None is better or worse.
But in each of them the Light of Eternity
Sees its reflection, and burns more joyfully.

HERMANN HESSE

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Chapter 1

Introduction

*“The Way that can be spoken is
not the unvarying Way,
The name that can be named is
not the eternal name,
The nameless is the origin of
Heaven and Earth,
The named is the mother of
myriad things.”*

-Lao Tzu

In this Chapter we will begin by giving an overview of foams and emulsions and describing the laws that govern foams and emulsions. We then proceed by introducing rheology before finishing with some comments about the rheology of foams and emulsions.

1.1 An Introduction to Foams and Emulsions

Foams and emulsions are biphasic systems wherein a gas or liquid is dispersed within an immiscible fluid. Such is the case with gas bubbles or oil droplets suspended in a liquid, stabilised by surface active molecules ¹[1, 2, 3]. Examples of foams and emulsions are numerous and include coffee foam, which is sta-

¹While not used in this thesis water droplets can also be suspended in oil to create an emulsion

bilised by proteins and polysaccharides released when coffee is dissolved in boiling water[4, 5, 6], the head of a beer, again stabilised by proteins which are released during the fermentation process and Mayonnaise, a mixture of oil in vinegar stabilised by egg yolk[7, 8, 9, 10]. An image of shaving foam, another everyday example, can be seen in Figure 1.1 and a sunflower oil in water emulsion in Figure 1.2.

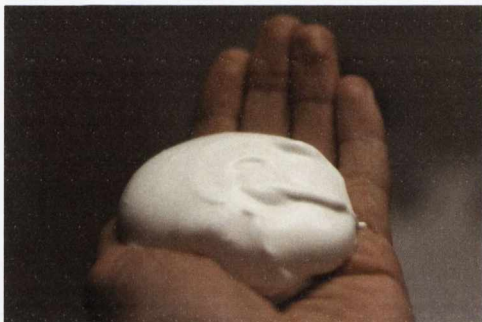


Figure 1.1: Gillette Foamy Regular

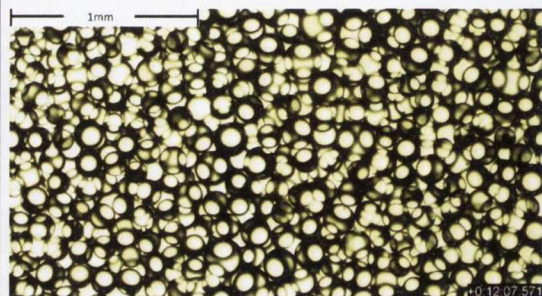


Figure 1.2: Sunflower oil in water emulsion

Physically, these systems are of great interest because of the extensive list of questions that arises from seemingly simple constituents [11]. What is the structure of these systems? How do these structures affect its mechanical properties? How do these structures change with time? And the question at the heart of this work, how do these structures change under the influence of external forces? In other words, how do they flow? This last question in particular appeals to the interest of material physicists as foams and emulsions exhibit both solid-like and liquid-like behaviour [12, 13]. This will be discussed in more detail below. Not only do these systems provide physicists, chemists and mathematicians with a wide variety of interesting problems, they also contribute greatly to technology. Aside from the culinary examples mentioned above we benefit from foams and emulsions in fire fighting, cosmetics, cleaning, mining and drug delivery[14, 15, 16, 17].

1.2 Structure of Foams and Emulsions

Creating an interface between a liquid and a gas, or between two immiscible liquids, requires energy [18]. This additional energy depends on the surface tension, σ , which is the energy cost per unit area to create an interface. As a result an interface will always attempt to minimise its area [19, 20]. More specifically, surface tension determines the shape of the interface created and the topological properties of the system. Generally the pressure difference across an interface is given by the Young-Laplace equation[21, 1, 2],

$$\Delta P = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1.1)$$

where ΔP is the pressure difference at the interface and R_1, R_2 are the two principal radii of curvature. Thus, for an undeformed, spherical bubble or droplet equation 1.1 becomes $\Delta P = \frac{2\sigma}{R}$. This tells us that the smaller the bubble or droplet the higher the Laplace pressure. This is what prevents bubbles and droplets from collapsing [22].

The curvature of the interface is subject to the amount of space the bubbles or droplets have in their immediate vicinity. If, for example, only a few bubbles are dispersed into a liquid bath they will not interfere with each other and thus remain spherical[23]. This kind of system is what is known as a bubbly liquid [2]. One of the primary properties governing foam and emulsion structure is the amount of space the bubbles or droplets are allowed to explore, or more specifically how densely the bubbles or droplets are packed together [24, 25], the measure of which is known as the packing fraction and is defined as,

$$\phi = \frac{\text{Volume of Dispersed Phase}}{\text{Total Volume of the System}} \quad (1.2)$$

The structure of the foam or emulsion depends on the value of this quantity [26]. For purely repulsive droplets when the packing fraction falls below a certain critical threshold, $\phi \approx 0.64$, the droplets are no longer sufficiently confined and the system loses its rigidity i.e it becomes a bubbly liquid. This threshold is known as

the wet limit, or the jamming point, and corresponds to the random close packing density for granular material[27, 28]. Above the jamming point the interaction between bubbles or droplets is approximately harmonic, although it depends on the number of contacts confining a given bubble, with a spring constant proportional to the surface tension[29, 30]. As one compresses the system further the continuous phase becomes excluded and the resulting structure is cellular [31]. This occurs as $\phi \rightarrow 1$ and is called the dry limit. In this limit the the interfaces come close enough that they form thin films and obey Plateau's laws [32]. Namely, the films intersect in three lines along the edges, which are liquid carrying channels known as Plateau borders[1]. Three Plateau Borders meet at 120° and four Plateau borders intersect at the vertices of each polyhedral bubble with an angle $\theta \approx 109^\circ$. A wet and a dry foam are shown for comparison in Figs 1.4 and 1.3.

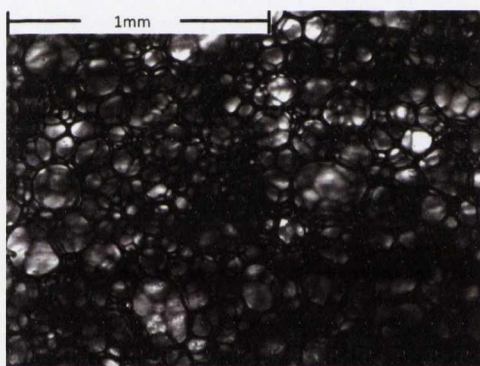


Figure 1.3: Dry Foam

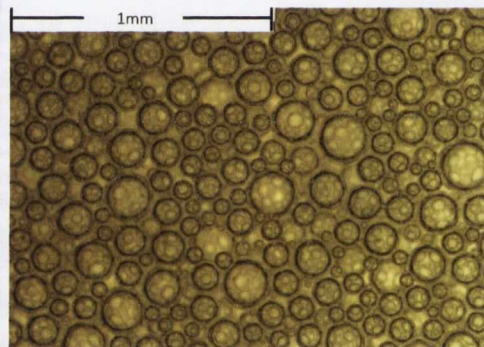


Figure 1.4: Wet foam

1.3 Stability of Foams and Emulsions

Consider the foam generated as you shake a bottle of carbonated water. This foam does not last for much longer than a second. This is because the distance between two interfaces diminishes rapidly as the liquid drains under gravity, the film becomes unstable and ruptures [33]. A stable foam requires the addition of surface active agents, or surfactants, to be present at the interface [34]. Surfactants are a class of molecules known as amphiphilic meaning that they have hydrophilic

heads (attracted to water) and hydrophobic tails (repelled by water). This chemical nature requires them to be present at the interface of a bubble or droplet provided they are below the critical micelle concentration (CMC) [35]. Above this value there are more surfactant molecules than surface for them to adsorb to. In this regime they cluster together to form spherical globules known as micelles, see Figure 1.5.

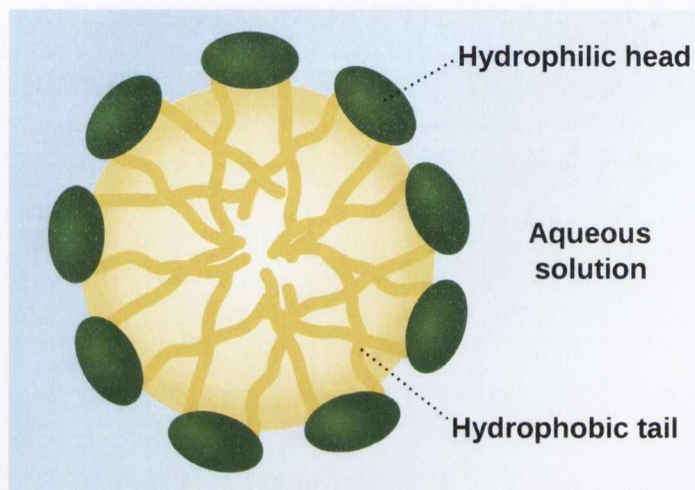


Figure 1.5: Micelle formed in a solution above the critical micelle concentration. The hydrophobic tails are contained within a sphere of hydrophilic heads. Image reproduced from wikipedia.org

In the presence of micelles there is an attractive force between droplets due to depletion interaction meaning that there can be solid-like behaviour below $\phi = 0.64$ [36]. Depending on the chemical nature of the molecule they will either carry a charge, in which case they are called ionic or cationic surfactant, or they do not carry a charge and are called anionic or non-ionic surfactants. In the case of ionic/cationic surfactants the system is stabilised by the electrostatic repulsion occurring at the interfaces. This interaction is governed by DLVO theory ² whereby if the surface charge density is sufficiently large the system can be considered kinetically stable (as opposed to thermodynamically stable) and the suspension will remain stable for large timescales. In the case of anionic surfactants steric effects induce a repulsion between interfaces. In both cases this repulsion is known as the disjoining pressure, but this alone will not prevent the structure from changing in

²Named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodoor Overbeek.

time [2, 37]. Below I will discuss some of the typical processes involved with foam and emulsion ageing.

1.3.1 Drainage or Creaming

As gravity acts on a foam or emulsion the continuous phase drains out of the system. The time scale governing this flow will depend on the viscosity of the fluid, the density difference between the two phases, the surface mobility of the interfaces and the thickness of the films, which is set by the packing fraction[38, 39]. In a foam the gaseous bubbles are considerably less dense than the liquid and thus will rise to the top very rapidly. In this sense the foam is said to drain. However, in an emulsion the density difference is typically less significant and this process is therefore measurably slower. For example, let us consider an emulsion comprised of water/glycerol and silicone oil ³and a foam consisting of air in water. If we take, from drainage theory, the characteristic timescale of drainage,

$$t_c = \frac{\eta Z}{2C_p \Delta \rho g R_V^2 (1 - \phi)} \quad (1.3)$$

Where Z is the number of contacts, η , the viscosity of the continuous phase, $\Delta \rho$, the density difference between the two phases, g acceleration due to gravity, ϕ , the fraction of the dispersed phase and C_p and R_V parameters depending on the geometry of the system. In our case, all other things being equal, only the viscosity and density difference play a role and we have, $t_c \propto \eta / \Delta \rho$. When we plug in the values for our two systems we find that the foam will drain 40 times faster than the emulsion, which could mean the difference between minutes and hours for experimental duration [2]. In emulsion literature the process of drainage is known as creaming[12, 40].

1.3.2 Ripening or Coarsening

As apparent from Equation 1.1 smaller bubbles have higher Laplace pressure than their larger neighbours. Thus there is a pressure gradient causing the gas to diffuse

³As will be discussed in the Methods chapter this is the emulsion we use and why we chose it in this comparison

from smaller bubbles into their larger neighbours. Thus larger bubbles effectively consume the smaller ones. This process is known as coarsening, or Ostwald ripening for emulsions, and is inevitable. The rate of coarsening depends on gas solubility, liquid fraction and surfactant types [41, 42, 43]. Coarsening and ripening change the bubble size distribution with time which in turn affects the flow properties of foams and emulsions [44].

1.4 Rheology

Now that we have described the basic composition of foams and emulsion we will introduce the concepts used to describe the response of a system to shear. Rheology, from the Greek word *to flow*, is the study of the flow and deformation of a material and is the main focus of this study. Specifically, rheology investigates the response of a material to an applied stress [45]. Foams and emulsions can exhibit both solid-like and liquid-like behaviour. With this in mind we will briefly review the mechanics of ideal solids and fluids with the aim of merging the two approaches to describe the mechanical behaviour of foams and emulsions. First, let us explore what happens if we apply a linear shear stress, $\tau = \text{Force}/\text{Area}$, to an ideal elastic solid as shown in Figure 1.6. The resulting strain, defined as $\gamma = \frac{\Delta L}{h}$, responds linearly to the applied stress with a proportionality constant, G , known as the Shear Modulus. Namely,

$$\tau = G\gamma \quad (1.4)$$

This is essentially Hooke's law and applies to an ideal solid [46]. Let us next consider a simple fluid. Return to Figure 1.6 and visualise the cell as a fluid element. What happens when we apply a shear stress? Unlike a solid, a liquid flows with a constant strain rate which is defined by,

$$\dot{\gamma} = \frac{dL}{dt} \cdot \frac{1}{h} \quad (1.5)$$

where $\frac{dL}{dt}$ is the value of the velocity component in the direction of shear. When we impose a shear stress on the fluid element we find that for an ideal liquid,

$$\tau = \eta \dot{\gamma} \quad (1.6)$$

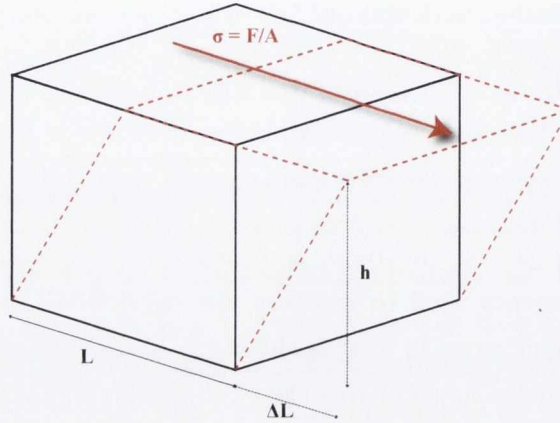


Figure 1.6: Linear Shear

Here the constant η is called the viscosity of the material and describes the materials resistance to flow. Honey, for example, has a high viscosity relative to water. A fluid that obeys the above Equation 1.6 is considered a Newtonian fluid. In Newtonian fluids η depends only on the temperature and not on the shear rate [47]. Foams and emulsions do not exhibit this simple relationship, instead $\eta = \eta(\dot{\gamma})$ and are termed non-Newtonian, or complex, fluids[46].

1.5 Viscoelasticity

Foams and emulsions exhibit both solid-like and liquid-like behaviour when undergoing deformation. For small strains, the bubbles or droplets deform resulting in an increased surface area. The surface tension acts as the restoring force. When the strain is removed the bubbles or droplets return to their original configuration, this corresponds to the solid-like, linear response regime[48]. However, at some critical strain, known as the yield strain, the bubbles or droplets deform to

such an extent that bubble or droplet rearrangements occur which induces plastic flow [49]. This point is the yield strain of the system and has a corresponding yield stress. Below the yield strain the bubbles or droplets respond elastically and return to their original configuration once the external strain is removed⁴[50]. An illustrative example of this property is shaving foam. The foam sits on your hand without flowing through your fingers but spreads smoothly on your face with ease, yet does not drip down your chin before you start shaving.

Because of their solid-like and liquid-like behaviour, foams and emulsions are in a rheological class of materials known as viscoelastic materials[46]. The response of viscoelastic materials can be probed through oscillatory rheology. To understand this consider applying a periodic strain to such a material,

$$\gamma = \gamma_0 \sin(\omega t) \quad (1.7)$$

In general, it will respond in the following manner

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (1.8)$$

The phase shift δ is crucial to the understanding of viscoelastic materials and, again, can be understood this by considering an ideally elastic and an ideally viscous system. For an elastic solid the response is immediate and thus $\delta = 0$. With a viscous fluid we have Newtonian behaviour,

$$\tau = \eta \dot{\gamma} = \eta \gamma_0 \omega \cos(\omega t) = \tau_0 \sin(\omega t + \frac{\pi}{2}) \quad (1.9)$$

So for a viscous fluids we have $\delta = \frac{\pi}{2}$. In general, for viscoelastic systems we get $0 < \delta < \frac{\pi}{2}$. The stress induced by a sinusoidally varying strain becomes

$$\tau = \tau_0 \sin(\omega t + \delta) = \tau_0 \cos \delta \sin(\omega t) + \tau_0 \sin \delta \cos(\omega t) \quad (1.10)$$

What this expression shows us is that we have two components of stress, one in phase and one out of phase by $\pi/2$ which we define as the storage, G' , and loss modulus, G'' , respectively,

⁴Provided coarsening and drainage are negligible.

$$G' = \frac{\tau_0}{\gamma_0} \cos \delta = G_0 \cos \delta \quad (1.11)$$

$$\Rightarrow G'' = G_0 \sin \delta \quad (1.12)$$

Thus G' is a measure of elastic energy stored within the system during shear and G'' a measure of the viscous dissipation during shear. The crossover point between the two indicates the transition between solid-like and liquid-like behaviour. The two moduli can be expressed in terms of a complex shear modulus,

$$G^* = G' + iG'' \quad (1.13)$$

Which is defined through:

$$\tau(\gamma) = G^* \gamma(t) \quad (1.14)$$

where $\gamma = \gamma_0 e^{i\omega t}$. To clarify this oscillatory technique we have included a plot of G' and G'' obtained from an emulsion with $\phi = 0.80$ with a strain ranging from 0.001 to 10 (Figure 1.7).

Before we close this section we want to highlight the fact that in this type of measurement the strain rate, $\dot{\gamma} = \gamma\omega \cos(\omega t)$, is not kept constant. For a constant strain rate oscillatory measurement one would have to vary the strain amplitude and the frequency such that $\gamma\omega = \text{constant}$. This type of measurement is known as strain rate frequency superposition and we discuss this further in Section 3.4.1.2.

1.6 The Steady Shear Rheology of Foams and Emulsions

In the previous section we discussed the response of a foam to oscillatory strain. Now we will look at the behaviour during steady flow, $\dot{\gamma} = \text{constant}$. This behaviour is termed viscoplastic due to the continuous irreversible droplet rearrangements that occur during flow[51]. The most rudimentary expression for the response of non-Newtonian fluids was introduced in 1916 by Eugene C. Bingham. It simply states that the shear stress experienced by a yield stress material undergoing continuous shear is equal to the yield stress of the system plus an essentially

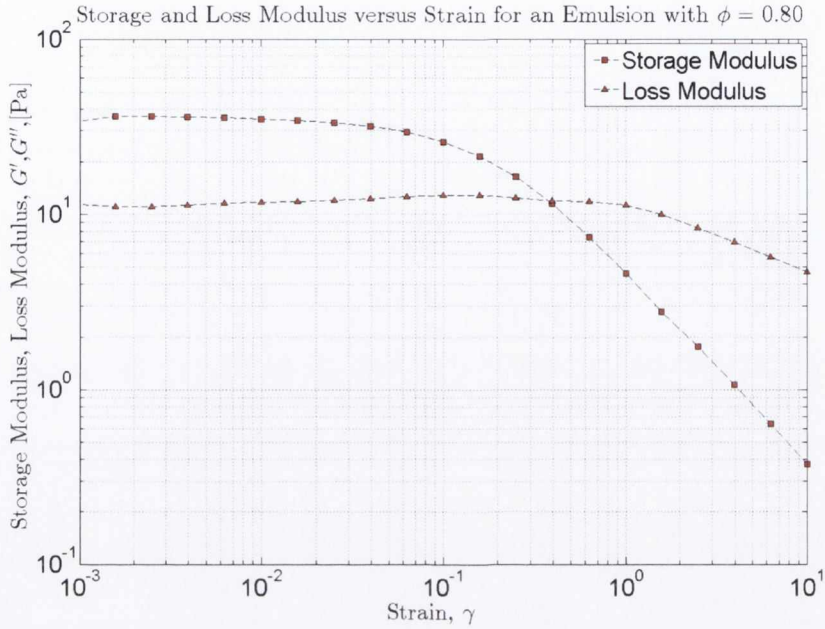


Figure 1.7: G' and G'' obtained by varying the strain, $\gamma = \gamma_0 \sin(\omega t)$, imposed on an emulsion with $\phi = 0.80$ with a γ_0 ranging from 0.001 to 10.

Newtonian response [52],

$$\tau = \tau_y + \kappa \dot{\gamma} \quad (1.15)$$

where τ_y is the yield stress, i.e the minimum stress required to produce plastic flow and κ is effectively the bulk viscosity of the material. However in 1926 two chemical engineers, W. H. Herschel and R. Bulkley, empirically extended this expression for rubber showing an non-linear scaling of stress with the strain rate for certain classes of complex fluids [53],

$$\tau = \tau_y + \kappa \dot{\gamma}^n \quad (1.16)$$

here κ can no longer be considered to a viscosity as it no longer has the appropriate units, instead it is simply referred to as the consistency. This expression has been well observed in foams and emulsions with the power law index, n , found within the range of $0.2 < n < 0.7$ [54]. This is known as the Herschel-Bulkley equation

and is often expressed as $\tau_v(\dot{\gamma}) = \kappa(\dot{\gamma})^n$ where $\tau_v = \tau - \tau_y$, is known as the *viscous stress*. The effective viscosity, $\kappa = \frac{\tau_v}{\dot{\gamma}} \propto \dot{\gamma}^{n-1}$, can describe a shear thinning fluid ($n < 1$) or a shear thickening fluid ($n > 1$)[55]. Foams and emulsions are shear thinning fluids, meaning the viscosity decreases with strain rate [13]. A typical stress versus strain rate plot, otherwise known as a flow curve, for a foam along with a fit to the Herschel-Bulkley equation is shown in Figure 1.8(A). Notice that the measured stress in the foam is orders of magnitude higher than the stress of the pure surfactant solution at the same strain rate.

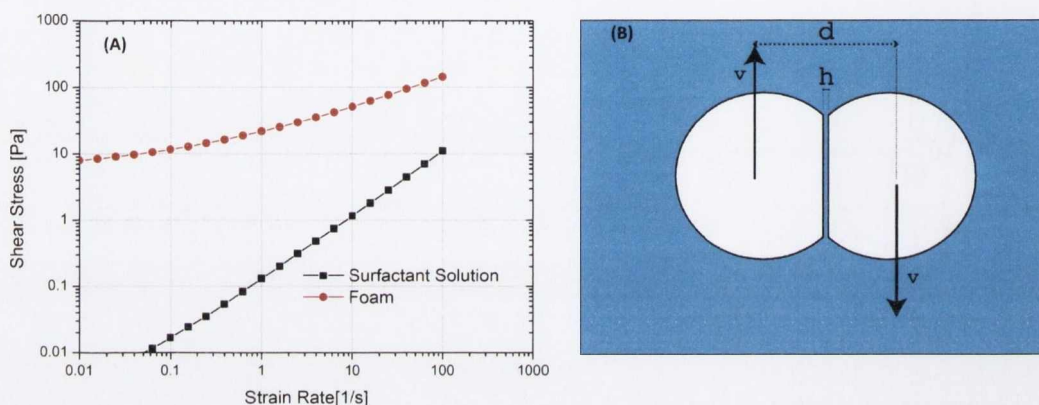


Figure 1.8: (A) Stress of a wet foam compared to the shear stress of a surfactant solution as a function of strain rate. (B) Schematic diagram of two bubbles sliding past each other to illustrate the effective strain rate.

1.7 Flow at the Bubble or Droplet Scale

Now that we have described the basic elements of foams and emulsions as well as their rheology we will proceed to discuss the behaviour on the bubble, or droplet, scale. We begin with the question, why are foams and emulsions so viscous? Recall the plot presented above in Figure 1.8(A) and the order of magnitude between the stress experienced by a surfactant solution and that experienced by a foam. Consider now, for the sake of simplicity, two bubbles sliding past each other with a relative velocity ΔV as depicted in Figure 1.8(B). The strain rate of the system is given by $\dot{\gamma} = \frac{\Delta V}{d}$. Where d is the bubble diameter. However the flow is localised

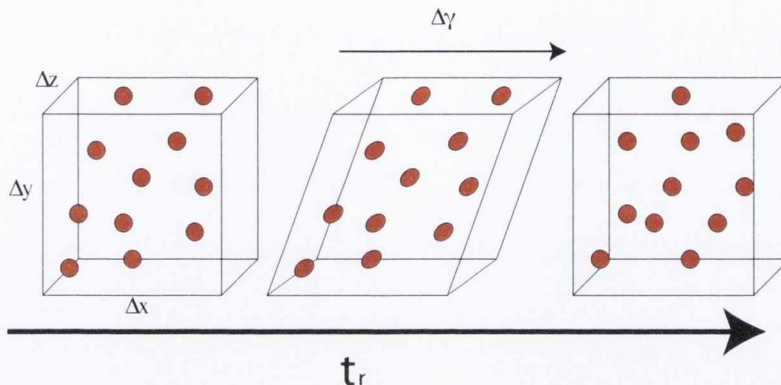


Figure 1.9: Schematic representation of the relaxation time model for Newtonian fluids. Fluid element $\Delta x \Delta y \Delta z$ undergoes small strain steps, $\Delta \gamma$, then relaxes fully by dissipating the elastic energy generated.

in the thin liquid film between the two bubbles. This leads us to define an effective strain rate $\dot{\gamma}_{eff} = \frac{\Delta V}{h}$, where h is the film thickness. Thus the effective strain rate of the liquid inside a sheared foam is roughly:

$$\dot{\gamma}_{eff} \approx \frac{d}{h} \dot{\gamma} \quad (1.17)$$

For bubbles of the order of $1mm$ and $h \approx 10^{-7}m$ we have $\dot{\gamma}_{eff} = 10^4 \dot{\gamma}$. This explains the difference in magnitude of the measured stresses for a foam (or an emulsion) and its surfactant solution. Note, however, that this simple picture does not explain other elements of foam and emulsion rheology such as shear-thinning behaviour or the presence of a yield stress.

The underlying the origin of Herschel-Bulkley type behaviour in foams and emulsions is still an active area of research with several competing models[56, 57, 58]. The main question is how the non-linear Herschel-Bulkley behaviour arises from dynamics on the bubble or droplet level. The energy required to shear a foam is dissipated in the thin films during bubble rearrangements [54]. Continuous rearrangements lead to erratic motion of the droplets in all directions with respect to

the mean flow [59]. This results in so called shear induced diffusion with a characteristic diffusion constant. The diffusion constant is determined by the timescale of rearrangements, which is strain rate dependent[59, 60]. Thus the diffusion constant is a measure of the rate of dissipative droplet rearrangements. To understand this more clearly let's return to a Newtonian fluid, or more specifically a thermal fluid. Consider dissipation within an element $\Delta x \Delta y \Delta z$ of a fluid as depicted in Figure 1.9. The work done to maintain flow is given by,

$$\frac{dW}{dt} = F \Delta v = (\tau \Delta x \Delta y)(\dot{\gamma} \Delta z). \quad (1.18)$$

Thus, the dissipation rate per unit volume, $\dot{\epsilon}$ is given by,

$$\dot{\epsilon} = \tau \dot{\gamma} \quad (1.19)$$

which, upon using equation 1.6 yields,

$$\dot{\epsilon} = \eta \dot{\gamma}^2 \quad (1.20)$$

What determines the value of η ? This can be estimated by visualising the flow, not as a smooth motion with a fixed strain rate, but as a sequence of microscopic strains on short time scales i.e. of the order of the mean collision time between molecules, that is, the relaxation time. On short timescales, $t_r \propto 10^{-12}s$ at room temperature, the fluid behaves solid-like[3]. That is, $\tau = G\gamma$. By integrating the force on the top face of the fluid element with respect to the displacement $dx = \gamma \delta z$ we get,

$$\epsilon \Delta x \Delta y \Delta z = \int_0^\gamma \tau(\gamma') \Delta x \Delta y d(\gamma \Delta z) = \int_0^\gamma G \gamma \Delta x \Delta y d(\gamma \Delta z). \quad (1.21)$$

Thus,

$$\epsilon = \frac{1}{2} G \gamma^2. \quad (1.22)$$

The fluid has been taken out of thermal equilibrium, and after a fixed time, t_r , this elastic energy is dissipated and the system has returned to equilibrium. Now returning to equation 1.20 and expressing the dissipation rate as $\dot{\epsilon} = \frac{\epsilon}{t_r}$ and the strain rate as $\dot{\gamma} \approx \frac{\gamma}{t_r}$, where t_r is the time taken for the energy to dissipate, the

relaxation time, we find:

$$\eta = \frac{1}{2}Gt_r. \quad (1.23)$$

For a Newtonian fluid, $G \approx \frac{k_b T}{a^3} \approx 10^9 Pa$, where a is the molecule diameter, and plugging in the relaxation time we find $\eta \approx 10^{-3} Pa$ which is a value typical for small molecule liquids such as water and ethanol [61].

We would now like to amend this picture so as to describe the microscopic relaxation of foams and dense emulsions. Foams and emulsions are athermal systems, meaning that $k_b T$ is not sufficient to rearrange the bubbles or droplets. If, instead of thinking about temperature induced collisions, we think of shear induced rearrangements, then provided the time scales of coarsening and drainage are negligible, we can re-imagine this picture. In this case we may interpret the relaxation time as the typical inverse rearrangement rate of the bubbles or droplets [3]. Thus if we measure the diffusion constant of a foam or emulsion we can directly measure the typical time between dissipative rearrangements. Our estimate for the viscosity now looks like,

$$\eta_{foam} = \frac{1}{2}Gt_r(\dot{\gamma}), \quad (1.24)$$

where G can be obtained via the oscillatory technique described in Section 1.5. This relation is known as the deformation-relaxation ansatz [3]. We can also use the Stokes-Einstein relation to describe this process.

Based on this ansatz, we can also comment on the Stokes-Einstein Relation. For a thermal liquid the equilibrium Stokes-Einstein equation states,

$$\eta(T)D(T) = \frac{k_b T}{6\pi r}, \quad (1.25)$$

where T is the temperature of the system and r the particle radius. We pose the question, is there a non-equilibrium Stokes-Einstein relation that applies to foams and emulsions where instead of a thermal energy driving the dynamics there is a constant strain rate, which keeps the system in a steady state? The diffusion constant is a measure of the inverse dissipative rearrangement rate, that

is, $D \propto \frac{1}{t_r}$. So, if the relaxation ansatz holds (Equation 1.23, the non-equilibrium Stokes-Einstein relation for foams and emulsions gives,

$$\eta(\dot{\gamma})D(\dot{\gamma})\langle d \rangle \propto E_{el}. \quad (1.26)$$

Where, E_{el} is an energy scale obtained from fluctuations in the elastic energy of the system and d the bubble diameter[62, 59].

Before closing this section we will briefly discuss how one would measure the diffusion constant. In a system containing random displacements, such as thermal collisions or shear induced rearrangements. If we consider displacements in one dimension, Fick's law applies,

$$\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2}. \quad (1.27)$$

Where N is the population density at point x and D is the constant of proportionality, that is, the diffusion constant. We evoke the boundary condition that no particles diffuse out of the sample, that is,

$$\frac{\partial N}{\partial t} = 0, \quad (1.28)$$

Thus to find the mean value of the square displacement, we use the definition of the variance,

$$\langle x^2 \rangle = \int_0^\infty N(x, t) x^2 dx. \quad (1.29)$$

Using Equation 1.27 and integrating twice by parts we have,

$$\frac{\partial}{\partial t} \langle x^2 \rangle = D \int_0^\infty x^2 \frac{\partial^2 N}{\partial x^2} dx = \left[x^2 \frac{\partial N}{\partial x} \right]_0^\infty - [2xN]_0^\infty + 2 \int_0^\infty N dx. \quad (1.30)$$

Allowing the first two terms to vanish so that integrating with respect to time and using $\langle x^2 \rangle = 0$ at $t = 0$ we get,

$$\langle x^2 \rangle = 2Dt \quad (1.31)$$

If we expand Equation 1.30 to more dimensions we can see this Equation 1.30

becomes,

$$\langle r^2 \rangle = 2dDt. \quad (1.32)$$

Where d is the number of dimensions in which diffusion is taking place.

1.8 Rheological Geometries

In the preceding section we described the response of systems to shear and strain whilst remaining vague about the geometry in which this behaviour can occur. We will conclude this chapter by outlining the main geometries used in rheology as they will be referenced at various points throughout this thesis.

1.8.1 2D Geometries

Due to the opaque nature of foams many experiments have been done on 2-dimensional systems [63, 59]. This typically requires one of three geometries all shown in Figure 1.10. Firstly there is what is known as the Bragg raft, Figure 1.10(A), where a layer of bubbles or droplets simply float on a liquid pool [63]. This arrangement is named after W. L. Bragg who used this set up to study the grain boundaries in crystals [1]. Following this there is the confined Bragg raft wherein a plate compresses the bubbles or droplets from above but they are still freely floating on a liquid pool beneath, Figure 1.10(B). Finally there is the oft used Hele-Shaw cell wherein bubbles or droplets are compressed above and below by solid plates, Figure 1.10(C) [64].

These configurations merely hold the sample in a monolayer. In addition to this there are two methods for imposing shear, Figure 1.11. The most simple case is that of linear shear, shown in Figure 1.11(A), where either one or both walls are shearing. A closed cell that provides circular shear is the Couette geometry, Figure 1.11(B), again here one or both boundaries can be mobile.

2D geometries enable simultaneous measurements of foam rheology and individual bubble trajectories. However they do have one drawback, bubble drag on the boundary which is not experienced by bubbles within a 3D foam [59].

1.8.2 3D Geometries

In 3D, the rheology of foams and emulsions is often probed as depicted in Figure 1.12. The parallel shear cell, Figure 1.12(A), has two variants. There is the parallel plate geometry where two flat plates confine the sample with the top plate providing shear. In this geometry the strain rate goes as,

$$\dot{\gamma}(r) = \frac{\omega r}{H}, \quad (1.33)$$

where r is the distance from the centre, ω the rotational velocity and H the height of the gap. In this geometry the strain rate increases with radius. In cases where it is important to keep a constant strain rate there is also the cone-plate geometry in which the top plate, instead of being flat, is a cone. This keeps the strain rate linear through the gap as the height of the gap changes with the distance from the centre allowing the ratio in Equation 1.33. In Figure 1.12(B) we show the Couette geometry used for 3D systems. In this geometry it is typically the inner wall that provides the shear.

1.9 Conclusion

Now that we have introduced the basic concepts of foams physics and rheology we can thoroughly outline our objectives. While experiments and simulations have been conducted in 2D foams, 3D systems do not have the problem of drag with the boundaries. As such, we measure the macroscopic rheology and microscopic droplet dynamics of a 3D emulsion. We intend to relate the functional form of the flow curve, that is, the Herschel-Bulkley relation, to the microscopic dynamics. A transparent emulsion with seeded fluorescent tracer particles is placed into a rheometer that can both control and measure the stress and strain in the sample. The tracer particles are used to probe the dynamics on the droplet level. The following are the questions this thesis attempts to address:

1. How does the diffusion constant, and hence the microscopic relaxation time, change with strain rate for a given packing fraction?

2. How does the diffusion constant, and hence microscopic relaxation time, change with packing fraction for a given strain rate?
3. How does the relaxation time measured from microscope dynamics compare with the relaxation time measured macroscopically via oscillatory measurement?
4. Can the microscopic relaxation time be related to the viscosity via the deformation-relaxation ansatz as expressed in Equation 1.24?
5. Does the flow transition that has been found to occur in 2D simulations (See Figure 2.9 Section 2.2 in Literature Chapter) exist in 3D systems [60]?

1.10 Structure of the Thesis

In Chapter 2 we explore the body of work that has already been conducted on foams and emulsions, paying particular attention to the numerical and experimental studies on bubble dynamics in flowing foams and emulsions. In Chapter 3 we discuss the materials and method implemented to answer the questions listed in 1.9. We spend some time describing the optical configuration that we designed and built to be used in conjunction with a rheometer which allowed us to measure droplet dynamics in a flowing emulsion. In Chapter 4 we describe the rheological characterisation of our emulsion and compare our results with the established trends that we outline in Chapter 2. In Chapter 5 we discuss the main results of our thesis which is the strain rate and packing fraction dependence of the relaxation time. We compare the results from our two methods and discuss our findings. At the end of Chapter 5 we enquire as to the validity of the deformation relaxation ansatz (Equation 1.24) in describing the stress strain rate relation in flowing emulsions. In Chapter 6 we summarise the results presented in Chapters 4 and 5 and conclude with suggestions of additional experiments that would expand this work.

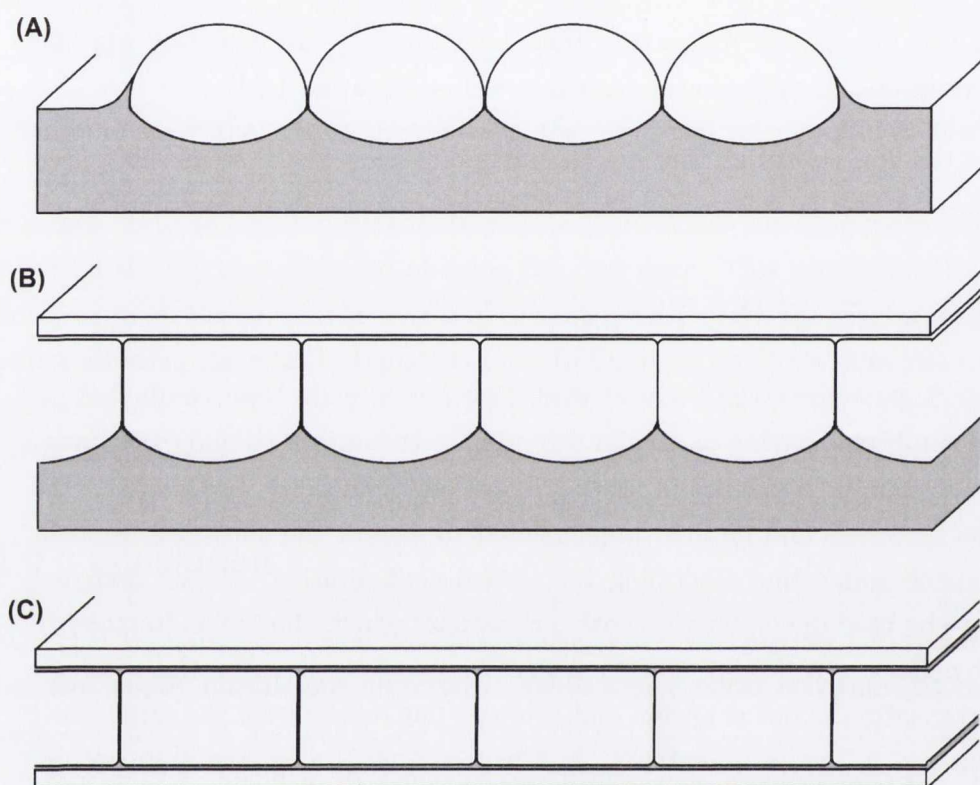


Figure 1.10: 2 Dimensional geometries used to study bubble trajectories in a flowing foam. (A) Bragg raft whereby the bubbles are suspended on a liquid surface [63]. (B) Bubbles suspended on a liquid pool but confined from above by a glass plate [59]. (C) Hele-Shaw cell wherein bubbles are confined from above and below by glass plates [64].

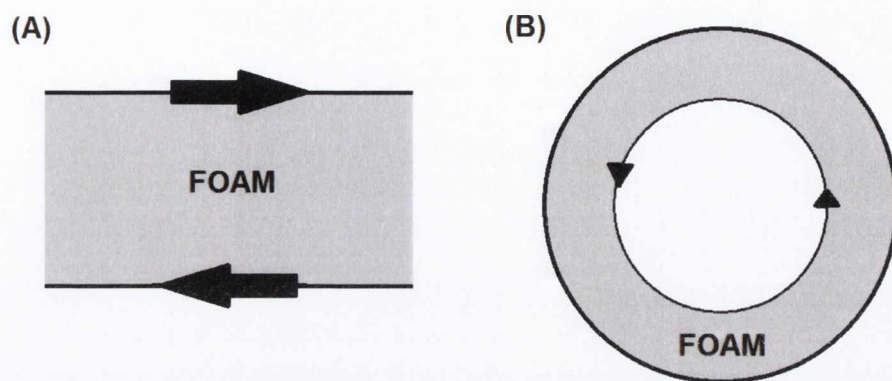


Figure 1.11: 2 Dimensional geometries

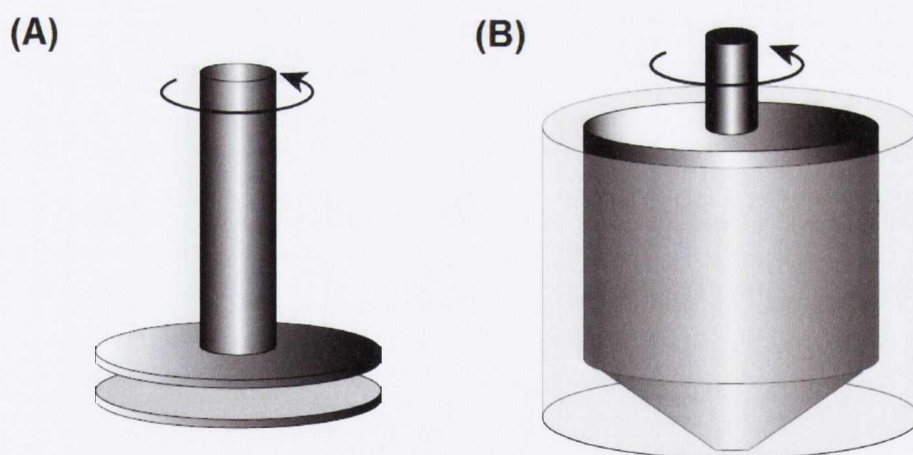


Figure 1.12: 3 Dimensional geometries

Chapter 2

Literature

“Across the millennia, an author is speaking clearly and silently inside your head, directly to you. Writing is perhaps the greatest of human inventions, binding together people who never knew each other, citizens of distant epochs.”

-Carl Sagan

In this chapter we will discuss the experiments, simulations and theory that have been developed over the last few decades in the field of foam and emulsion rheology. We will begin with the established macroscopic rheology before mentioning some of the more recent advances in the field. Then we will look at what work has been done to probe dynamics on the scale of bubbles and droplets.

2.1 Macroscopic Rheology

In this section we will begin by discussing the investigation of the elastic properties of foams and emulsions. Then we will introduce the work done on the response of these systems undergoing steady flow.

2.1.1 Elasticity and Yielding

It would be remiss not to begin a literature review on foam rheology without mentioning the theoretical and experimental work performed by H. M. Princen in his four canonical papers published in the mid-80's, *Rheology of Foams and Highly Concentrated Emulsions* [65, 66, 67, 50], the latter two of which were published with A. D. Kiss who did much of the experimental work. Princen begins this work by noting the absence of theoretical discussion of foams and emulsions. He fills this void by developing a model by treating bubbles as infinitely long cylinders, the first work on the theoretical foundations of foam and emulsion rheology. From this simple idea he proceeds to rigorously deduce the role of volume fraction, contact angle and film thickness of such systems to their mechanical properties, namely the yield stress and static shear modulus. The central findings of this model are the following expressions for yield stress, τ_y , and shear modulus, G_0 ,

$$\tau_y \propto \frac{\sigma}{R} \phi^{1/3} \tilde{F}_{max}(\phi), \quad (2.1)$$

$$G_0 \propto \frac{\sigma}{R} \phi^{1/3}, \quad (2.2)$$

where σ , is the surface tension, R the radius, ϕ the packing fraction and $\tilde{F}_{max}$ a function representing the dimensionless contribution of each droplet. What is important from this formulation is that the shear modulus and yield stress both scale with the Laplace pressure of the foam defined in Equation 1.1. This tells us that smaller bubbles produces a stiffer foam. From this model Princen also describes what he called a “Mode I to Mode II Transition” whereby, due to the constraints imposed by Plateau’s rules, a neighbour exchange takes place during shear. This process, depicted in Figure 2.1 was later named the T1 transition by Weaire and Rivier [68] and is still studied in 2 and 3-dimensional foam and emulsion rheology today [69].

After developing this model, Princen went on to perform a rigorous experimental investigation of the yield stress and static shear modulus of compressed 3D emulsions in a Couette geometry. The experiments verified the expressions derived for the yield stress and amended the expression for the static shear modulus by,

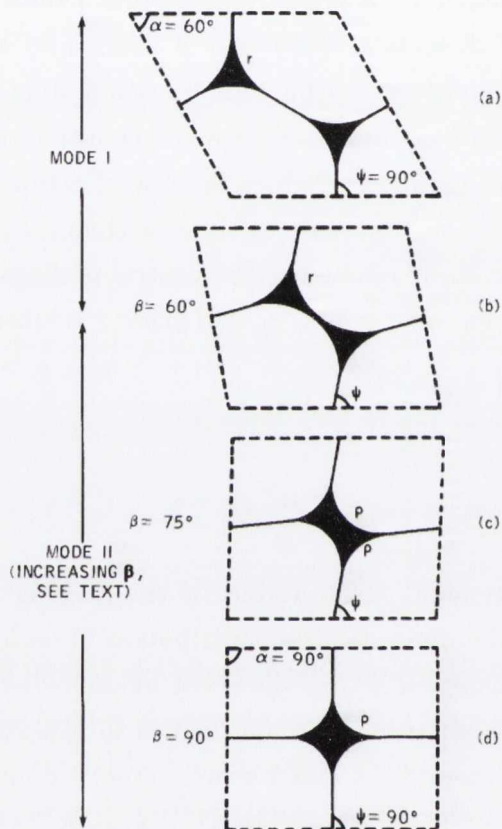


Figure 2.1: Figure taken from [68] depicting a neighbour transition which Princen named a "Mode I to Mode II Transition"

$$G_0 = \propto \frac{\sigma}{R} \phi^{1/3} (\phi - \phi_c), \quad (2.3)$$

where ϕ_c is the critical packing fraction, or the jamming point.

Fifteen years after Princen's papers, Saint-Jalmes and Durian conducted oscillatory measurements on polydisperse wet foams in roughened Couette and cone-plate geometries[70]. As well as clarifying the rheological equivalence of foams and emulsions they found that when the range of packing fraction, ϕ , was extended over the entire jammed region, $0.64 < \phi < 0.99$, Princen's relationships no longer held. Instead they found that $\tau_{yield} \propto (\phi - \phi_c)^2$ and $G_0 \propto \phi(\phi - \phi_c)$, the latter already having been found in simulations and experiments on emulsions conducted by Mason and Weitz two years previously [71]. They hypothesised that the discrepancy between these new findings and Princen's was the range of packing fraction chosen. Princen results were still found to be in good agreement at $\phi > 0.75$ suggesting that Princen's expressions are only valid in highly compressed systems. They also found that the yield strain was proportional to ϕ .

The question arising out of this work was does rescaling the shear modulus or the yield stress by the Laplace pressure from different foam and emulsion systems, measured in different geometries, scale onto one curve? This question was addressed in 2005 by Rouyer *et al.* [72]. In this work they conducted their own measurements of the yield stress using an inclined plane geometry, that is the system is sheared by gravity, and oscillatory measurements in a Couette geometry. The first finding of this work was that the yield stress was in agreement between the two methods and went as $(\phi - \phi_c)^2$, the same trend reported by Saint-Jalmes. However when they compared their yield stress, normalised by the Laplace pressure, with previous work, including Princen, Mason and Saint-Jalmes, a master curve was not found, see Figure 2.2(A).

However they then proceeded to normalise the yield stress by the static shear modulus and discovered that the majority of the data collapsed onto one curve and adhered to $\frac{(\phi - \phi_c)}{\phi}$ as shown in Figure 2.2(B). Any remaining inconsistencies were attributed to shear banding, i.e. localised shear strain, that they found to occur

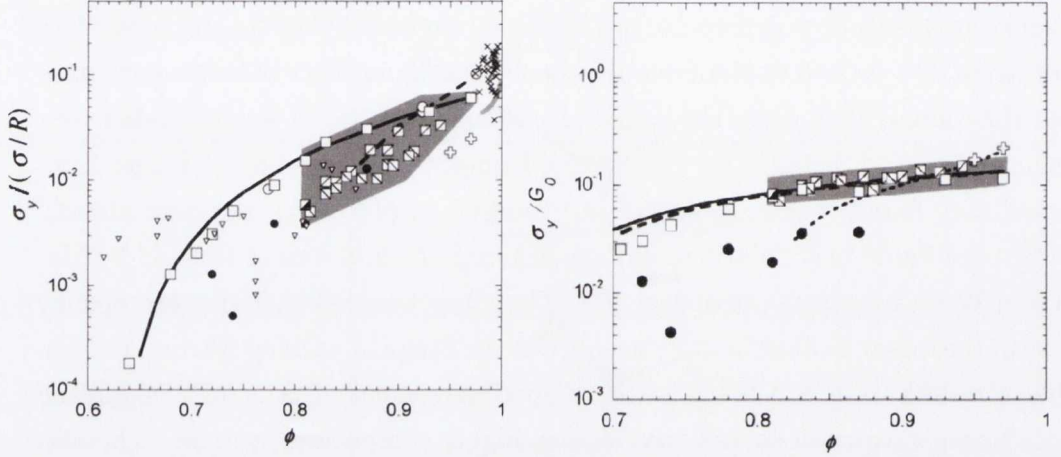


Figure 2.2: Figure taken from [72] (A) Yield Stress Normalised by the Laplace pressure, showing the inconsistencies of different group's measurements of the normalised yield stress on foams and emulsions: Princen and Kiss, steady shear, (dashed line) [66], Gardiner *et al.*, inferred from the rest angle of pendulum dropped into a foam [73], (continuous gray line), Saint-Jalmes and Durian, oscillatory, (continuous black line) [70], Wenzel *et al.*, steady shear, [74] (x), Yoshimura *et al.*, steady shear [75], (open circles) Calvert and Nezhati, steady shear [76], (inverted triangles), Khan *et al.* [77], stress relaxation technique, (open crosses), Mason *et al.* oscillatory (open squares) and steady shear (closed circles) experiments [78]. Present study: Gillette foam for oscillatory (square with downward stroke) and inclined plane methods (half-filled square), and TTAB foam (oscillatory) (square with upward stroke). The gray area is a guide to the eye highlighting the scatter of oscillatory measurements reported by different authors. (B) Yield stress normalized by elastic shear modulus vs. volume fraction. Rouyer *et al.* data are compared to previous results: Princen and Kiss [67] (dotted line), Saint-Jalmes and Durian [70] (oscillatory), (continuous black line), Khan *et al.* (open crosses), Mason *et al.*, oscillatory (open squares) and steady shear (closed circles) experiments [78]. Present study: Gillette foam for oscillatory (square with downward stroke) and inclined plane (half-filled square) measurements, TTAB foam, oscillatory, (square with upward stroke). The dashed line corresponds to the curve: $\tau_y / G_0 = 0.39(\phi - \phi_c) / \phi$. The gray area is a guide to the eye to highlight the consistency between oscillatory measurements.

in steady shear flow but not in the elastic regime during oscillatory shear.

Until this point all oscillatory experiments consisted in keeping either the strain amplitude or the frequency constant. In 2007 Wyss *et al.* devised a new oscillatory technique, strain rate frequency superposition (SRFS), whereby both the strain amplitude and the frequency varied in such a way as to maintain constant strain rate throughout the frequency(or strain) range [79]. In doing so they could macroscopically investigate the strain rate dependent rheology of soft materials. Following the introduction of this technique by Wyss into the field, Saint-Jalmes investigated the relaxation time as a function of strain rate for aqueous foams [80]. By conducting SRFS measurements on wet foams in roughened cone-plate and plate-plate geometries, for different strain rates, Saint-Jalmes *et al.* were able to determine the yielding frequency (inverse of the structural relaxation time) of a foam as function of strain rate. An example of the data produced by such a measurement is presented in Figure 2.3.

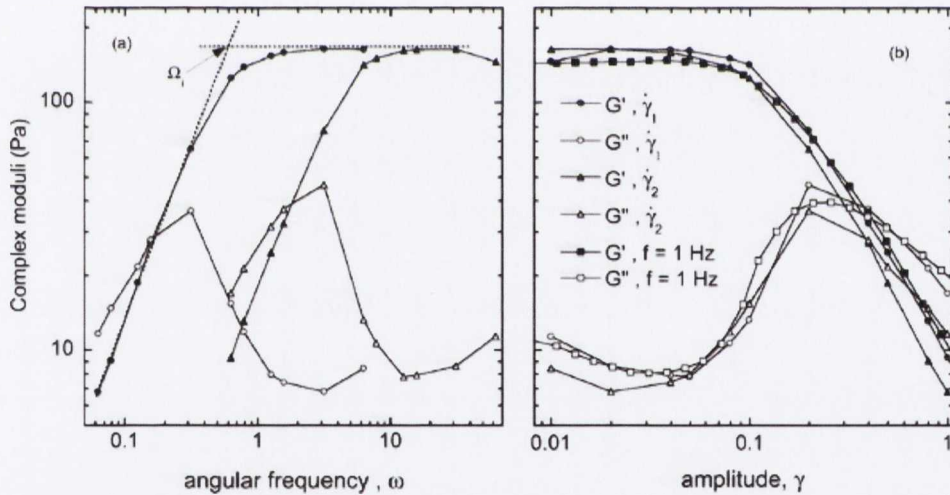


Figure 2.3: Figure taken from [80] (a) Strain rate frequency superposition measurements of a foam for two different strain rates, $\dot{\gamma} = 0.06s^{-1}$ (triangles) and $\dot{\gamma} = 0.6s^{-1}$ (circles). This data shows that the characteristic cross-over frequency is dependant on strain rate. (b) Strain sweeps for the two strain rate shown in (a) as well as one at constant frequency. The inclusion of this graph shows the relevance of SRFS measurements which reveal information about the foam which traditional rheology could not have obtained.

After investigating two decades of strain rate the following relationship between

the relaxation time and strain rate was found to be,

$$\frac{1}{t_r} = \frac{1}{t_0} + \frac{\dot{\gamma}^\beta}{\gamma_{yield}}, \quad (2.4)$$

where t_0 is the strain rate independent relaxation time set by coarsening time-scales of the foam. β was found to be slightly below 1. This relationship was found to be in agreement with that found by Durian in his experiments using diffusive wave spectroscopy which we will discuss below. By making this comparison with Durian's work Saint-Jalmes highlights the relevance of comparing macroscopic rheology with dynamics on the bubble or droplet scale, the objective of our work.

2.1.1.1 The Role of Surfactants in Foam and Emulsion Elasticity

In the early days of foam research little heed was paid to the nature of the surfactant. However as the field developed people began to realise that both the interfacial properties of the surfactant stabilised films as well as the surfactant concentration played a pivotal role in foam and emulsion rheology [81, 54]. What we want to pay particular attention to here is the effect of concentration. As mentioned in Section 1.3 when the concentration of surfactant increases above the critical micelle concentration depletion interaction can make an emulsion adhesive [82]. Datta *et al.* investigated the behaviour of adhesive emulsions relative to repulsive emulsions [36]. They found elastic behaviour well below the random close packing density. They also found that above ϕ_{RCP} the shear modulus was identical in both magnitude and functional form as that of the repulsive emulsion. They also conducted SRFS measurements and found in the adhesive case that the relaxation time had a sub-linear relationship with packing fraction, with β from equation 2.4 ranging from 0.8 to 1.

2.1.2 Steady Shear Rheology

Now we will discuss the work done on foams and emulsions that are in a continuous flow regime. Again we will begin this section with Princen. In the final of his

Rheology of Foams and Highly Concentrated Emulsions papers, along with Kiss, they investigated the shear viscosity, η_s , of a flowing emulsion. They proposed the following expression,

$$\eta_s = \frac{\tau_{yield}}{\dot{\gamma}} + C(\phi)\eta\left(\frac{\tau}{\eta R_{32}\dot{\gamma}}\right)^{1/3} \quad (2.5)$$

In their experiments the exponent was found to be $1/2$. They argue that this difference is due to the absence of the disjoining pressure in the model.

Denkov *et al.*, Tcholakova *et al.*, Politova *et al.* and Mitrinova *et al.* in a series of papers spanning almost a decade uncovered the role of surfactants in steady shear foam and emulsion rheology [57, 83, 54, 84, 85]. In 2005 Denkov *et al.* developed a model which was inspired by Princen's. Instead of infinitely long cylinders however, they modelled foams as monodisperse bubbles in a face-centred-cubic configuration [57]. They describe flow as motion of planes in the FCC structure. They use this idea to deduce the viscous friction within a flowing foam. Their model found that the type of surfactant plays a role in the steady shear rheology of foams and emulsions. In general, they argue, that surfactants can be divided into two categories depending on their interfacial properties. Immobile surfactants produce films with rigid interfaces resulting in Poiseuille flow between the interfaces. Mobile surfactants on the other hand have freely moving interfaces which allows for plug flow. Their experiments showed that depending on which category of surfactant was used dictated the Herschel Bulkley index (n in Equation 1.16). For rigid, immobile interfaces, $n \approx 0.3$, whereas surfactants producing mobile interfaces gave $n \approx 0.5$. Their model proved to be in excellent agreement with their experimental data. However it has as an assumption Laminar flow between bubble lanes, an assumption that is in contrast with findings elsewhere in the field which showed non-affine intermittent bubble trajectories [60].

Recently, Fall *et al.*, Møller *et al.* and Paredes *et al.* have experimentally explored the rheology of a foam both well below and well above the jamming transition, ϕ_{RCP} [86, 87, 88, 89]. In these investigations they conducted stress versus strain rate measurements of flowing emulsions in the range of $0.1 < \phi < 0.8$ confined within

roughened cone-plate and Couette geometries. Paredes *et al.* found that flow curves measured at different packing fractions could be rescaled onto a master curve. See Figure 2.4 for a plot showing the unscaled and scaled flow curves. Paredes was not the first person to find this scaling behaviour, Teitel and Olsson found this scaling behaviour on simulations on foams and Basu *et al.* found it in experiments on suspensions on soft micro-gel particles [90, 91]. What is worth noting from these results is that the scale factor of the stress axis, $\tau/|\Delta\phi|^{2.13\pm0.11}$, is consistent with the value found in Saint-Jalmes experiments on yield stress, that is, $\tau_{yield} = (\phi - \phi_c)^2$. Moreover, they show that the ratio of the two scaling components correspond to the Herschel-Bulkley exponent (Equation 1.16). They propose a model of heterogeneous dynamics suggesting that in a flowing foam there are stagnant regions of particles and flowing regions dispersed within and that the ratio of the two regions varies with time. Using this idea Paredes *et al.* derived an expression for viscosity as a function of the fraction of stagnant regions.

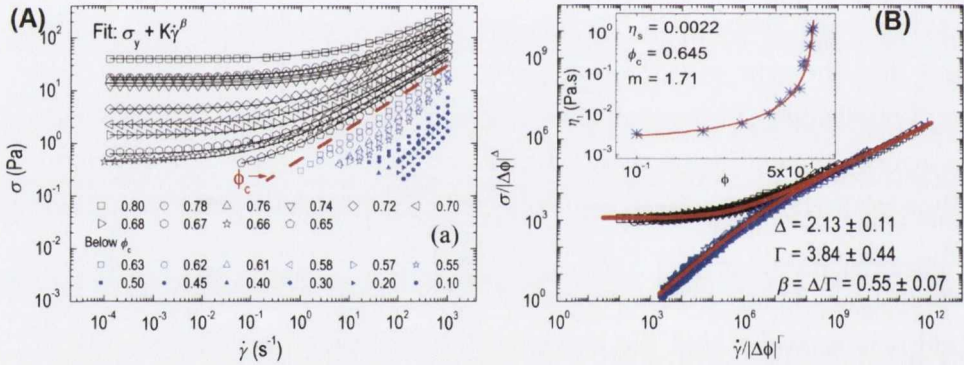


Figure 2.4: Figure taken from [86] (A) Flow curves obtained from a variety of packing fractions ranging from 0.1 to 0.8. (B) The two scaling regimes for flow curves measured above and below the jamming transition. The ratio red lines show a Herschel-Bulkley fit (with the HB exponent = β) and the Cross equation.

2.2 Exploring the Behaviour on the Bubble Scale

In order to understand how Herschel-Bulkley behaviour arises on the bubble scale, simulations had to be developed. In this vein the “Bubble Model” which was introduced by Durian in the mid-90’s and is still used widely today [92, 93, 94]. With

the Bubble Model Durian developed a method of simulating foams by treating the bubbles as overlapping discs confined in a given geometry, hence his model gained the name “The Soft Disc Model”. The overlapping discs are subject to two forces; a repulsive force that is a function of the overlap, and the dissipative force [92, 95]. Beginning with the simple approach Durian chose a harmonic repulsion related to the overlap of two discs and a mean field approximation for the viscous force. A constant strain-rate was imposed by a moving boundary and the dynamics, as well as the rheology, was measured. Durian found that the macroscopic rheology was described by the Bingham model, that is Herschel-Bulkley with exponent $n = 1$. The model was greatly improved by Langlois *et al.* [96, 97] when they, aside from increasing the system size by an order of magnitude, removed the mean field approximation. Now the viscous dissipation experienced by a bubble i in contact with a bubble j is directly proportional to the relative velocity between the two bubbles. This change provided a rheology that was much more representative of experimental data; a Herschel-Bulkley fit with exponent $n = 0.54 \pm 0.01$. The investigative power of Durian’s Bubble model was further highlighted in the work of Ono *et al.* [98, 62]. Before Langlois made the improvement herein mentioned, Ono and his team studied the velocity fluctuations of bubbles undergoing shear. They found that, transverse to the mean flow, the motion of individual bubbles was diffusive.

In an attempt to experimentally witness the bubble dynamics of a flowing foam Durian and Gopal performed diffusing wave spectroscopy (DWS) on a continuously sheared aqueous foam confined within a roughened, transparent Couette cell[99, 100, 101]. In DWS coherent light is transmitted through a foam and detected behind. Due to the refractive nature at the many interfaces composing a foam a speckled interference pattern will form on its obverse side. Intensity fluctuations of the pattern occur as scattering sites within the foam move, that is bubble rearrangements. Durian and Gopal were able to determine the characteristic relaxation time, t_r , of a foam by measuring the decay of the autocorrelation of the intensity fluctuations of the projected image. They found that the relaxation time as a function of strain corresponded to Equation 2.4, that is,

$$\frac{1}{t_r} = \frac{1}{t_{r0}} + \frac{\dot{\gamma}^\beta}{\gamma_{yield}^\beta}, \quad (2.6)$$

With $\beta = 1$. To highlight the agreement between the two approaches, SRFS and DWS, we have included a graph from Marze *et al* where they compare their work with Durian, Figure 2.5[80].

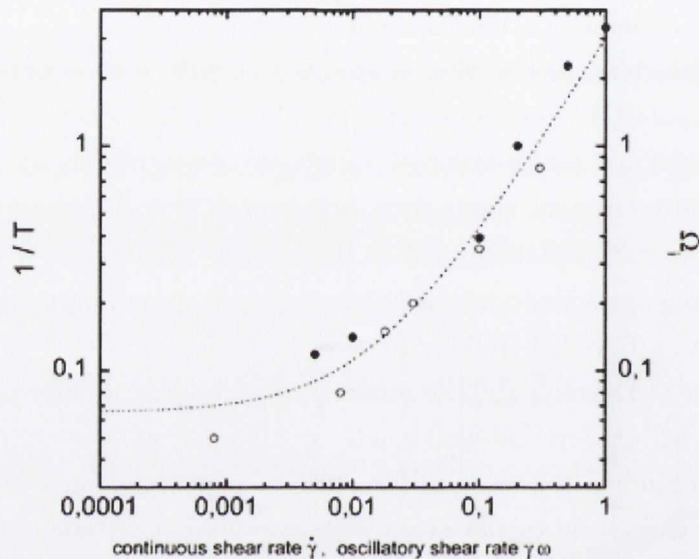


Figure 2.5: Figure taken from [80] comparing the inverse relaxation time obtained from Durian and Gopal diffusing wave spectroscopy measurements (open circles) and strain rate frequency superposition data (closed circles). As mentioned in the text both the data fit to the same functional form.

Continuing the investigation into behaviour at the bubble scale, Möbius *et al.* experimentally investigated the steady shear rheology of 2-dimensional foams in both linear and Couette geometries [59, 102, 103]. Taking advantage of the optical access of a 2D foam in a Couette geometry, they measured the viscous drag of bubbles sliding past each other as a function of relative velocity. In the linear shear cell they measured individual bubble displacements as a function of strain rate. The results from the Couette rheology showed that the dissipative force between two bubbles sliding past each other scale with their relative velocity to the power of 0.7. By measuring the bubble displacements in the linear cell, as shown in Figure

2.6, they were able to measure the change in mean square displacements, $\langle s^2 \rangle$ as a function of time, Δt via,

$$\Delta \mathbf{s}(\Delta t) = \mathbf{r}(t + \Delta t) - \mathbf{r}(t) - \langle \mathbf{V}(y) \rangle \Delta t \quad (2.7)$$

They also looked at the evolution of particle displacement distributions with the aim of identifying the onset of diffusive flow. The evolution of the displacements PDFs and the mean square displacements versus time are shown in Figure 2.7.

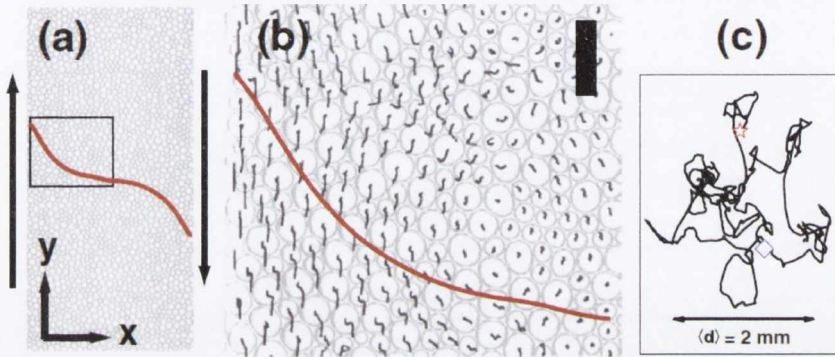


Figure 2.6: (a) Experimental image of a two dimensional flowing foam. (b) Magnified image from (a) with accompanying short time bubble trajectories. Red line indicates the velocity profile. (c) Long time bubble trajectory when mean flow has been subtracted i.e. random walk trajectory.

After sufficiently large Δt , the probability distribution became Gaussian indicating a diffusive regime. The diffusion constant was calculated from the mean square displacements. The characteristic relaxation time $t_r(\dot{\gamma})$ was defined to be the point at which the system changed from a super diffusive regime to a diffusive regime (Figure 2.7(B)), they found that the crossover between the two corresponds to the Lindemann criterion, a measure in thermodynamics that defines the onset of melting in a crystal. The results showed that it did not go as $\frac{1}{\dot{\gamma}}$ as had been assumed *a priori* and suggested by experiments conducted on three dimensional foams using diffusive wave spectroscopy[99, 100]. Instead it goes as $t_r \propto \dot{\gamma}^{-0.66}$. They showed that both the diffusion constant and the bulk viscosity scale with the relaxation time as $D \approx \frac{\langle d \rangle^2}{t_r}$ and $\eta \approx G t_r$.

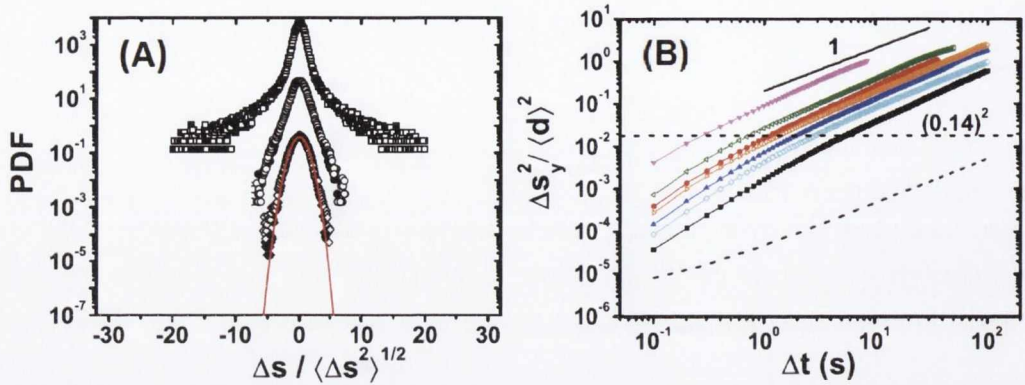


Figure 2.7: (A) PDFs of non-affine, normalised displacements with varying Δt from 2D experiments. Red line indicates Gaussian distribution. Δt decreases from top to bottom. Image taken from [59] (B) Mean square displacements as a function of Δt at different $\dot{\gamma}$. Dashed horizontal line indicates Lindemann criterion for melting in solids. This line is used to determine the relaxation time for a given $\dot{\gamma}$. Image taken from [59].

Taking the approach of Möbius *et al.* and using the improved Bubble Model, Sexton *et al.* performed simulations on 2D flowing foams. As well as confirming the experimental results of Möbius *et al.*, they investigated the microscopic behaviour at high strain rates, that is, at strain rates greater than the inverse relaxation time [60]. The analysis on the particle displacements followed the method of Möbius and the PDFs and mean square displacements are presented in Figure 2.8.

These simulations showed the applicability of the deformation-relaxation ansatz approach was verified up to a critical strain rate [104]. Beyond this critical strain the bubbles no longer undergo diffusive motion and are instead confined to lanes in the direction of flow (affine flow). This is because at these strain rates the bubbles do not have sufficient time to relax and thus diffusive rearrangements cannot occur, they termed this phenomenon "laneing". In this regime the flow is described by a local bubble-bubble drag law $\tau \propto \dot{\gamma}$. The simulations revealed an intermediate regime between these behaviours whereby the bubble dynamics change smoothly from non-affine, diffusive, flow to non-diffusive lane flow. This transition depicted in Figure 2.9 where the bubble trajectories at low and high strain rates are shown.

More recently, Knowlton *et al.* performed experiments on the droplet level of an emulsion. They investigated the onset of yielding using both rheology and optical

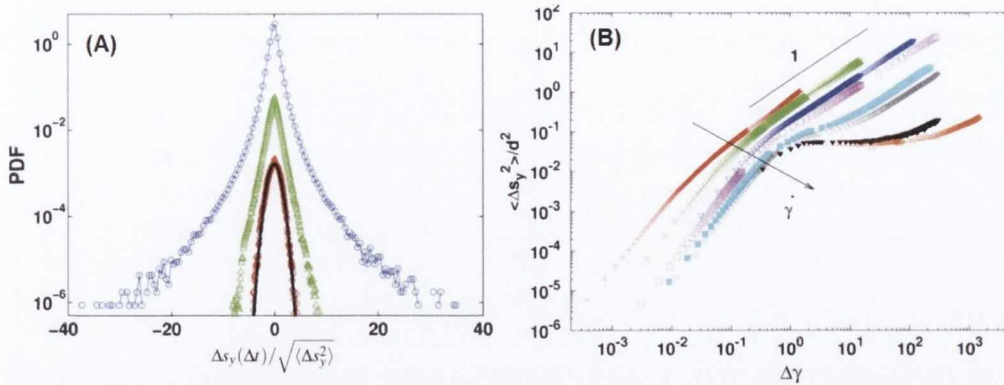


Figure 2.8: Simulations of steady sheared foam using the bubble model. (A) PDFs of non-affine, normalised displacements with varying Δt from 2D simulations. Black line indicates Gaussian distribution. Δt decreases from top to bottom. Image reproduced from [60] (B) Mean square displacements as a function of Δt at different $\dot{\gamma}$. Unlike as was seen in experiments the mean square displacements taper off at high strain rates which corresponds to laminar motion of bubbles which are confined to lanes at high strain rates. Images taken from [60].

microscopy [105]. By performing strain sweeps in a linear cell they determined the yield strain as a function of packing fraction of the emulsion. By also measuring the mean square displacement of droplets during oscillatory strain they determined the yield strain as the point at which the mean square displacement sharply increases. For clarity we have included a graph, Figure 2.10 of mean square displacement versus time to show this transition. What their results showed was that in the macroscopic rheology the transition is smooth whereas the increase in root mean square displacements on the microscopic level is sharp. The yield point was also consistently lower when determined microscopically. This suggests that particle rearrangements occur before the system has become fully fluidised. They also discovered the existence of both quiescent and ‘mobile’ and ‘supermobile’ particles in a fluidised emulsion.

Another attempt at accessing the local rheology of foams and emulsions is through the use of magnetic resonance imaging (MRI). Ovarlez *et al.* conducted such measurements on adhesive and nonadhesive emulsions in a wide-gap Couette geometry [106, 107]. Initially they looked at the velocity profiles for different strain rates. They were able to extract a constitutive law from the velocity profiles which related the

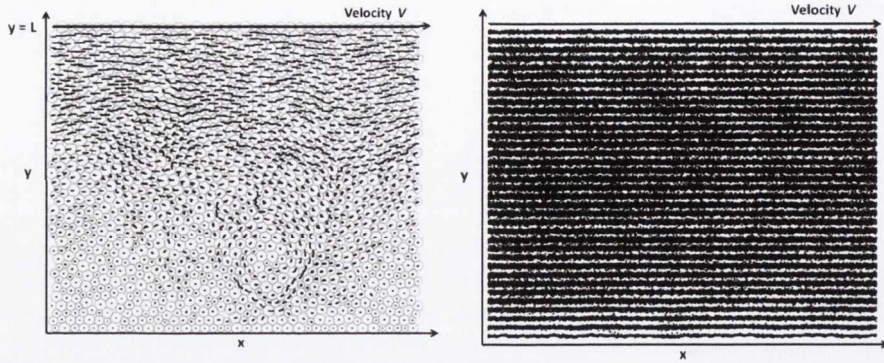


Figure 2.9: Image reproduced from [60]. Right: Bubble trajectories at a low/intermediate strain rate showing non-affine diffusive flow. Left: Trajectories at high strain rates showing how the bubble motion transitions to laminar flow.

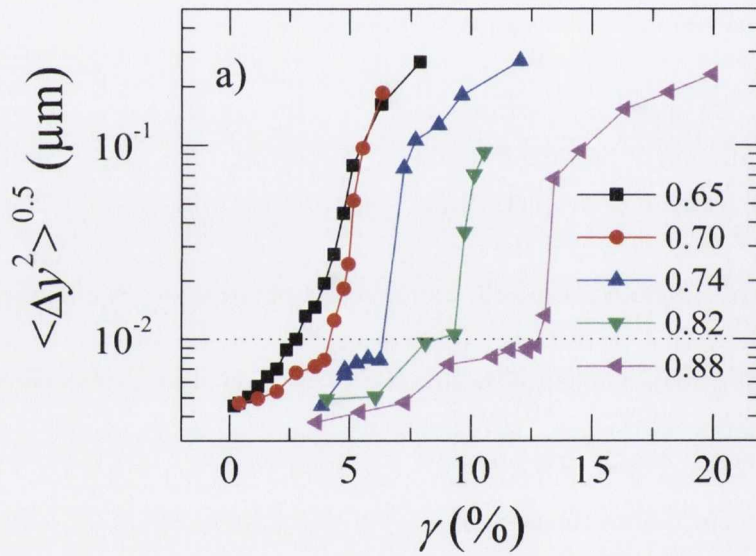


Figure 2.10: Figure taken from [105] showing the sharp increase in the root mean squared displacement, perpendicular to the shear direction, as a function of oscillatory strain amplitude for different packing fractions above jamming. The sharp increase corresponds to the yield strain of the emulsion

local stress to the local strain rate. They were able to uncover the Hershel-Bulkley relation from this law. They observed no major differences between adhesive and non-adhesive emulsions in this study.

2.3 Conclusions and Outlook

In this work we investigate the diffusive behaviour of droplets in a densely packed 3D emulsion. The 2D experiments and simulations, while providing a detailed description of the relaxation time and corresponding diffusive motion, are not optimal due to the boundary drag caused by confining the foam in two dimensions. It cannot be assumed that two dimensional behaviour can be simply extended to describe three dimensional systems. We also intend to examine the behaviour at high strain rates to see if affine motion occurs in real systems as observed in simulations by Sexton *et al.* [60]. Emulsions provide us with an excellent three dimensional experimental basis as by matching the refractive index of the continuous phase with the discrete phase we can obtain a transparent system. By suspending fluorescent tracer particles of similar size to the droplets we can measure non-affine displacements and hence diffusion. Here we place the index matched emulsion in a parallel plate geometry which is coupled to a rheometer. Rheometers have a precise control over the strain which is crucial for this investigation to be valid. We calculate the microscopic relaxation time by measuring particle trajectories at a given strain rate and the macroscopic relaxation time by conducting SRFS measurements.

Chapter 3

Materials and Methods

“To live only for some future goal is shallow. It’s the sides of the mountain that sustain life, not the top.”

-Robert Persig

In this chapter we will describe the method used to generate an index matched emulsion with a controlled packing fraction, ϕ . We will also describe the imaging techniques used to infer droplet dynamics, which when coupled to a rheometer are used to measure the diffusion constant, D , and the relaxation time, t_r , of a flowing emulsion. We describe how we complement this microscopic measurement of the relaxation time with strain rate frequency superposition measurements. Furthermore we will describe the rheological techniques used to measure the yield stress, σ_y , yield strain, γ_y , the shear modulus, G_0 , the relaxation time, t_r , and the Herschel-Bulkley parameters discussed in the preceding chapter. We will close with a list all of the experiments performed that comprise this research.

3.1 Emulsification

Emulsification is the process whereby the dispersed phase of the emulsion is introduced into the continuous phase with a desired droplet size distribution and packing fraction. To this end, membrane emulsification, followed by centrifuga-

tion is our chosen method. Membrane emulsification was chosen as it allows us to maintain a low polydispersity, which is the type of distribution we intend to study. A dispersion cell, shown in Figure 3.1, contains the sample during emulsification. Here 2ml of the continuous phase (Water/Glycerol/Tween20) is placed into the glass chamber. The stirrer is secured into position and set rotating at 1000 RPM. $\approx 40\text{mls}$ of silicone oil (dispersed phase) is then injected in through a hydrophilic membrane at $100\ \mu\text{l}$ per minute. The stirrer creates a flow field perpendicular to the passage of the oil through the micropores which are $10\ \mu\text{m}$ in diameter. This 'cross flow' separates the oil into droplets which are stabilised by inclusion of the non-ionic surfactant Tween20 in the continuous phase. After approximately 5 hours the two phases are combined into an emulsion which is removed and placed into a 50ml plastic tube for centrifugation.

3.1.1 Centrifugation

Centrifugation, followed by dilution, provides control over packing fraction of the emulsion. Once the emulsion is removed from the dispersion cell it is placed in a 50ml plastic tube and into a centrifuge for 90 minutes at 4000g. Post centrifugation the sample was placed in a vacuum oven at 70° and its mass measured every 30 minutes. Once the mass of the sample had ceased to change it was assumed that all the water had evaporated; as the silicone oil and glycerol both would require much higher temperatures for evaporation. Based on the mass difference we determined that after centrifugation the top 3cm of of the emulsion had a packing fraction of 0.99 In order to meet our desired packing fraction we diluted this with an appropriate volume of continuous phase (including tracer particles). At this point the sample was manually mixed with a spatula to ensure a homogeneous dispersion and centrifuged again at 250g for 15 minutes to remove any air bubbles trapped during stirring. The sample is slowly mixed again with the spatula to redistribute the continuous phase and placed into the rheometer. Once the diluted sample has been placed in the rheometer the batch sample is centrifuged and diluted again. This is done a total of three times for the 42ml emulsion generated in the dispersion chamber.

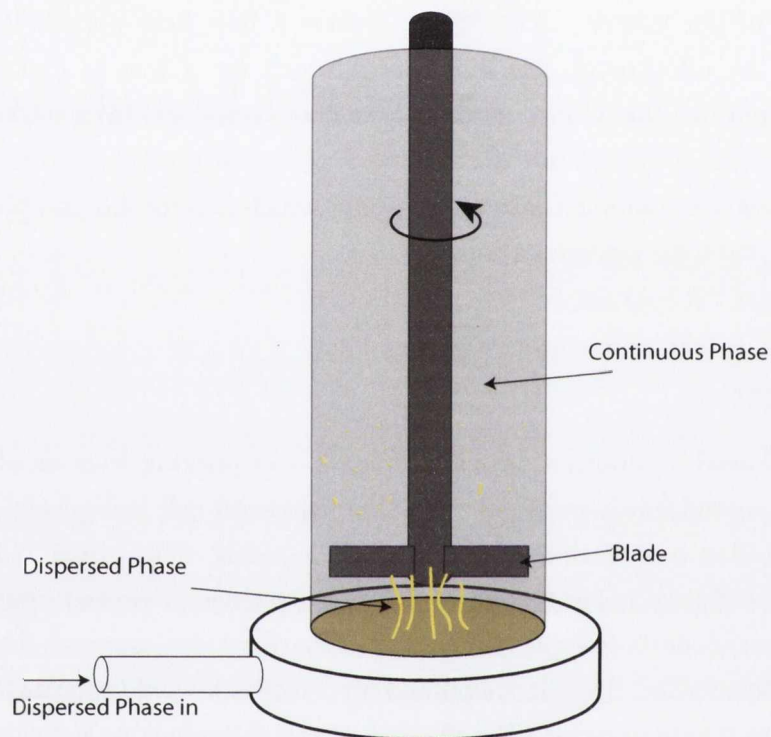


Figure 3.1: Graphic depiction of the emulsification process used throughout this research. Silicone oil is injected through the membrane at $100\text{ }\mu\text{l}$ per minute into the Glycerol/water continuous phase. The rotating blade creates a cross-flow which breaks the oil streams into droplets which pack into the continuous phase producing an index matched, oil in water emulsion.

3.1.2 Recipe

An appropriate recipe was chosen to achieve both refractive index matching and an emulsion stable against ripening and creaming within the time frame of the experiments, which are typically 3-24 hours. We use silicone oil as our dispersed phase which has an index of fraction $n = 1.4042$. In order to match this with a continuous immiscible phase we use a mixture of Glycerol ($n = 1.474$) and Millipore water ($n = 1.33$) and use the following equation to index match the two phases [108].

$$n_{mix} = \frac{\sum_i W_i \times n_i}{W_{Total}} \quad (3.1)$$

Where W is the weight of the fluid and subscript i refers to the substance used in the solution. This gives us a ratio of 52.6 : 47.4 Glycerol to water for the solution to have a refractive index of 1.4042 when the refractive index of tween 20(3.3% wt) is also taken into account. This surfactant concentration is approximately 300 times higher than the CMC value for Tween 20 making our emulsion an adhesive one due to the attractive depletion interaction. To calculate the magnitude of the depletion interaction we use the Vrij model [109],

$$\frac{U}{K_B T} = 4\pi a a_m^2 N_A (c - c^*) / v_m. \quad (3.2)$$

Where a is the average droplet radius, c is the surfactant concentration, c^* is the CMC, a_m is the micelle radius, v_m is the aggregation number, K_B is Boltzmann's constant, T is the temperature and N_A is Avogadro's number. Plugging the values for Tween20 we find that $U = 6.8 K_B T$.

3.2 Characterisation of the Emulsion

In order to extract, from the experimental results, the underlying physics, we need to ensure that the emulsion created from the process described above is well characterised and reproducible. In this section I will describe the methods employed to achieve this aim.

3.2.1 Size Distribution

The size distribution needed to be determined for the following reasons. Firstly to verify that the droplets are of a similar size to the tracer particles. Despite the fact that the tracer particles do not deform we make the assumption that they sufficiently represent droplet rearrangements in a flowing emulsion. We also need to be sure that the sample was sufficiently polydisperse so as not to form crystalline structures that would produce flow dynamics not in the scope of this research. As mentioned in the Introduction chapter the droplet size has an effect on the emulsion rheology and thus we also needed to confirm that the droplet radii were not changing significantly throughout the duration of the experiments (3-24 hours).

The distribution was obtained by first removing a sample of emulsion and diluting it with water. This changed the refractive index, giving optical access to the interface and allowing the droplets to become spherical. The diluted sample is then placed on a glass microscope slide and imaged under a microscope. The radius distribution is calculated using built in particle analysis algorithms in ImageJ. Figure 3.2 shows a typical image after processing with the circles found by ImageJ overlaid while Figure 3.3 shows the droplet radii distribution as well as a line indicated the radius of the monodisperse tracer particles. The mean droplet radius is $483\mu\text{m} \pm 1.87\mu\text{m}$ compared to $5.0\mu\text{m}$ for the tracers.

3.2.2 Surface Tension

In order to obtain a value for our surface tension we use the pendant drop method. Here we inject a drop of the continuous phase (water/glycerol/Tween20) through a capillary into a bath of oil. Using the open source software, OpenDrop, we calculate the surface tension using the Young-Laplace equation [110]. In Figure 3.4 we show the surface tension as a function of time obtained using this method. This data shows that after $\approx 10\text{s}$ the surface tension drops to 6.8 mNm^{-1} . This is the value of surface tension we use to calculate the Laplace pressure in our system. The time scale of 10 seconds is also worth noting as we will discuss it in section 5.1.1 when discussing surfactant kinematics. After approximately 3 hours the surface tension goes to 4.9 mNm^{-1} . As our emulsion takes over 5 hours to

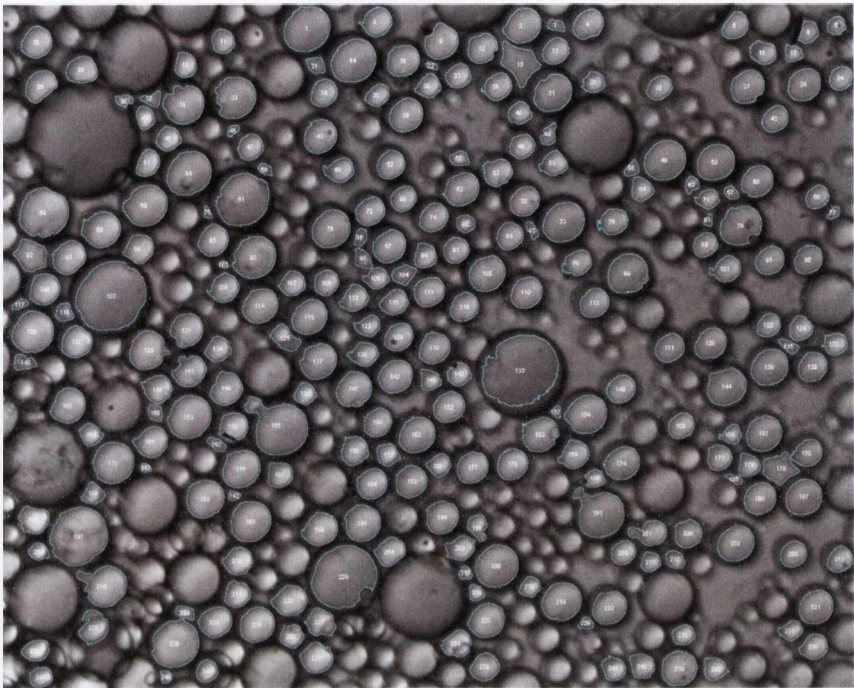


Figure 3.2: Processed image of emulsion sample with ImageJ particle analysis overlaid

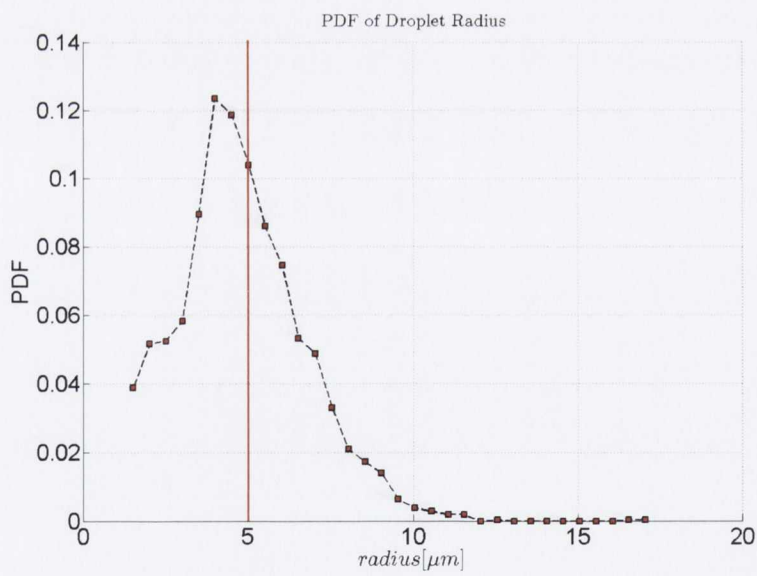


Figure 3.3: Plot of the droplet radius distribution. Red line indicates the radius of the monodisperse tracer particles. Mean droplet radius is $4.83\mu m \pm 1.87\mu m$

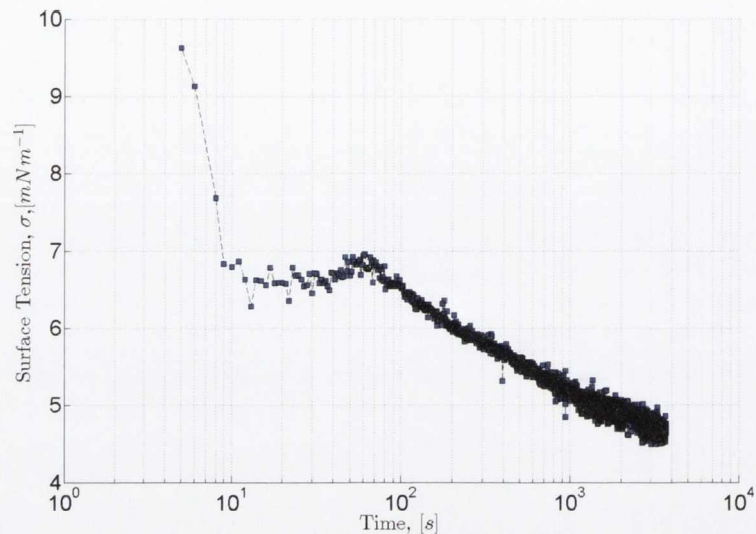


Figure 3.4: Surface tension of our emulsions as a function of time. We find that after ≈ 10 s the surface tension drops to 6.8 mNm^{-1} . Data courtesy of Steven Burke.

form in the membrane emulsifier this is the value we use when calculating the Laplace pressure.

3.2.3 Ripening

Ripening, the process whereby oil diffuses, from smaller droplets, across the water/Glycerol membrane, into larger droplets, alters the droplet size distribution over time. As mentioned above the droplet size distribution will impact the rheology and an investigation of ripening is needed to evaluate the accuracy of rheological data. The droplet size distribution method described above was implemented on our sample after emulsion generation, after centrifugation and after a 24 hour experiments (the longest experimental duration undertaken as part of this research) for each of the three samples generated from the original emulsion. The time between the first and final measurement is approximately four days. The distributions are plotted on top of each other and presented in Figure 3.5 and the mean radius for each sample is shown in Figure 3.6. From these plots we assume that there is no significant ripening in a our system and that the rheology wont be affected in this regard.

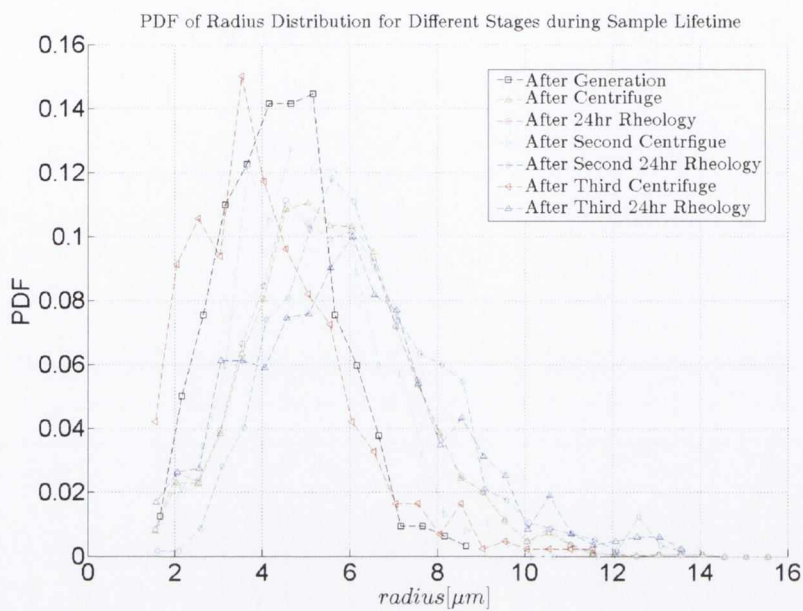


Figure 3.5: Plot of the radii distribution of the emulsion during different stages of the lifetime of the batch emulsion.

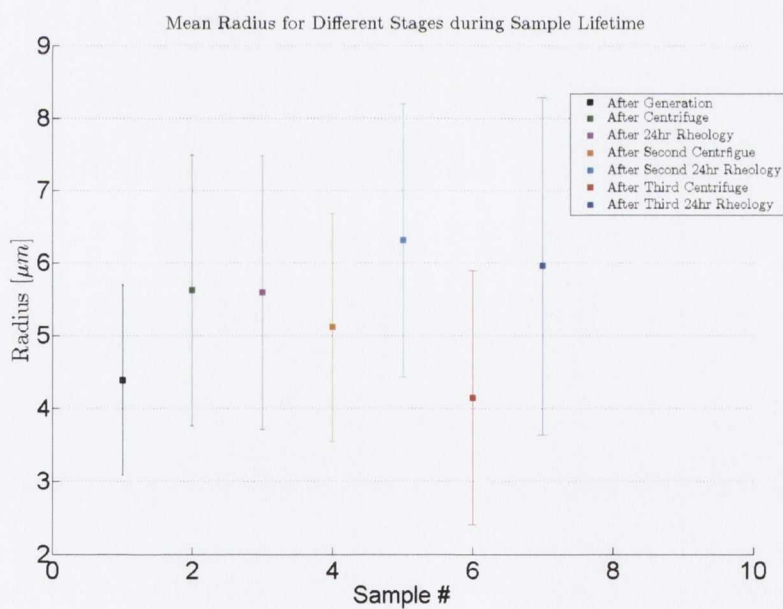


Figure 3.6: The mean and standard deviation of droplet radii for each sample taken through the lifetime of the batch emulsion.

3.2.4 Liquid Fraction Equilibrium

Drainage leads to a gradient in the packing fraction throughout the system. An inhomogeneous packing fraction alters the rheology of the sample and as part of this investigation consists in measuring rheological parameters as a function of varying liquid fraction, the drainage (or creaming) of the system must also be investigated¹. However, due to the transparent nature of the sample, and the low volume of the sample used in the rheometer, typical drainage experiments are not available to us. Instead we have opted to solve the drainage equation numerically to get a flavour of the drainage behaviour of our sample in the rheometer.

Before proceeding we must mention that in this section I have replaced the term packing fraction, ϕ , with liquid fraction, $\epsilon = 1 - \phi$, as within the context of these simulations it is a more appropriate term to use. The simulations are based on foam equilibration, that is, what does the final liquid fraction profile look like after the emulsion has equilibrated?

3.2.4.1 Osmotic Pressure Balancing

An emulsion comprised of droplets at a lower density than the continuous phase obtains equilibrium when the buoyancy force is balanced by the osmotic pressure. This is expressed in the equation:

$$d\Pi = (1 - \epsilon(z))\Delta\rho g dz \quad (3.3)$$

Where Π is the osmotic pressure, ϵ the liquid fraction, $\Delta\rho$ the density difference, g is acceleration due to gravity and z is the height into the gap beginning at the non-shearing wall.

For the purpose this approach we non-dimensionalise the variables. This is done by re-expressing the above quantities as follows:

¹Measures can be taken to reduce the rate of drainage by using liquids with a large viscosity, e.g. glycerol, in the continuous phase or shearing the emulsion at regular intervals during a long rheological experiment to homogenize the sample.

$$\tilde{z} = \frac{R}{l_c^2} z \quad (3.4)$$

$$\tilde{\Pi} = \frac{R}{\sigma} \Pi \quad (3.5)$$

Here R is the average droplet radius, σ , is the surface tension and l_c the capillary length, $l_c = \sqrt{\sigma/\Delta\rho g}$, i.e the ratio of surface forces to gravitational forces. Now we can express equation 3.3 in dimensionless form:

$$d\tilde{\Pi} = (1 - \epsilon) d\tilde{z} \quad (3.6)$$

which leads to:

$$d\tilde{z} = \frac{d\tilde{\Pi}}{(1 - \epsilon)} \quad (3.7)$$

Integrate to get $\tilde{z}(\epsilon)$

$$\tilde{z}(\epsilon) = \int_0^{\tilde{\Pi}(\epsilon)} \frac{1}{1 - \epsilon} d\tilde{\Pi} \quad (3.8)$$

To make this equation relevant to our investigation we express the osmotic pressure, Π , in terms of the liquid fraction, ϵ . This is achieved by the empirical equation [111]

$$\tilde{\Pi} = k \frac{(\epsilon_c - \epsilon)^2}{\sqrt{\epsilon}} \quad (3.9)$$

Where $k = 3.2$ and $\epsilon_c = 0.36$ have been empirically determined for disordered polydisperse foams. Differentiating with respect to ϵ gives:

$$\frac{d\tilde{\Pi}}{d\epsilon} = k \frac{(\epsilon - \epsilon_c)(\epsilon_c + 3\epsilon)}{2\epsilon^{\frac{3}{2}}} \quad (3.10)$$

Which we can now substitute into the above integral as follows:

$$\tilde{z}(\epsilon) = \int_0^{\tilde{\Pi}(\epsilon)} \frac{1}{1 - \epsilon} d\tilde{\Pi} = \int_0^{\tilde{\Pi}(\epsilon)} \frac{1}{1 - \epsilon} \frac{d\tilde{\Pi}}{d\epsilon} d\epsilon \quad (3.11)$$

Giving:

$$\tilde{z}(\epsilon) = k(\sqrt{\epsilon_c} - \sqrt{\epsilon})(3 + \sqrt{\frac{\epsilon_c^3}{\epsilon}}) + \frac{k}{2}(3 - 2\epsilon_c - \epsilon_c^2) \ln \left[\frac{(\sqrt{\epsilon} + 1)(\sqrt{\epsilon_c} - 1)}{(\sqrt{\epsilon} - 1)(\sqrt{\epsilon_c} + 1)} \right] \quad (3.12)$$

This equation produces the plot shown in Figure 3.7.

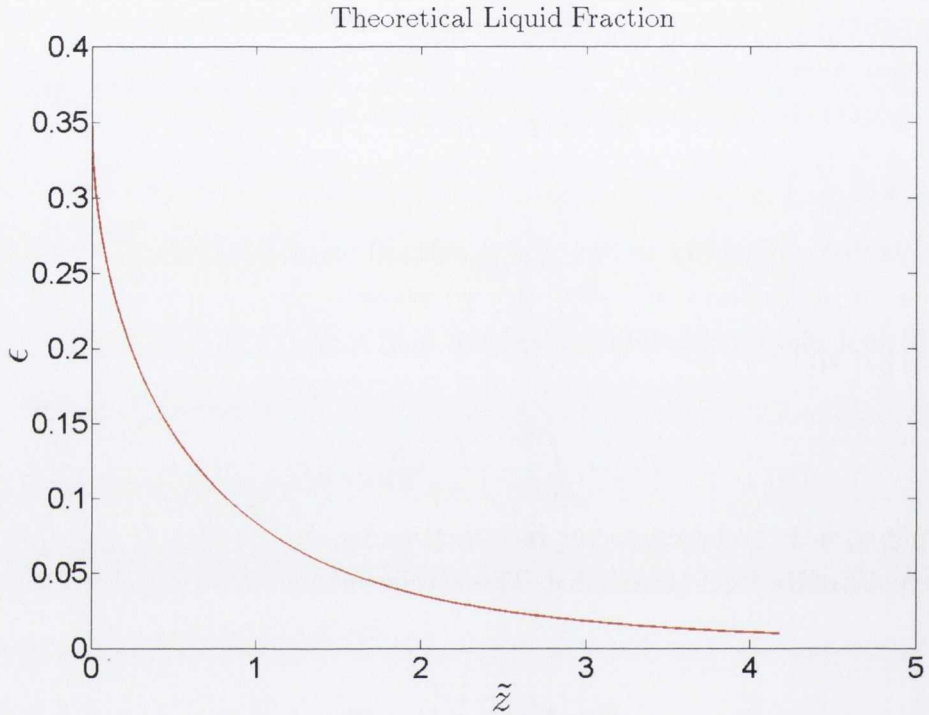


Figure 3.7: The non-dimensionalised liquid fraction as a function of non-dimensionalised height. Values obtained from equation 3.12

The limitations of expression 3.12 is that it is limited to a foam that is not constrained above and rests on a pool of surfactant solution below. Our system is compressed between two plates and an amendment must be made to obtain the equilibrium liquid fraction profile of our sample under experimental conditions.

To do this consider an emulsion contained within a cylinder of height l . The volume of liquid in the emulsion is expressed as:

$$V_{liquid} = A_{col} \int_0^l \epsilon dz \quad (3.13)$$

Here A_{col} is the cross sectional area of the confining cylinder. Given an initial liquid fraction, ϵ_0 , the volume of liquid in the sample can be simply expressed as:

$$V_{liquid} = \epsilon_0 V_{emulsion} = \epsilon_0 A_{col} l \quad (3.14)$$

which leads to:

$$\epsilon_0 = \frac{1}{l} \int_{\tilde{z}}^{\tilde{z}+\tilde{l}} \epsilon(\tilde{z}) d\tilde{z} \quad (3.15)$$

In order to solve this equation 3.12 must first be inverted. This is done numerically by invoking the Newton-Raphson method that is, obtaining $\epsilon(\tilde{z}_i)$ by finding the roots of the following equation:

$$\tilde{z}_i(\epsilon) - z_i = 0, \quad (3.16)$$

for each i . Once this is achieved we can find the relevant value of $\tilde{z}$ for equation 3.15 by again utilizing Newton-Raphson by finding the roots of:

$$\frac{1}{l} \int_{\tilde{z}}^{\tilde{z}+\tilde{l}} \epsilon(\tilde{z}) d\tilde{z} - \epsilon_0 = 0 \quad (3.17)$$

Once we know these values of $\tilde{z}$ we simply plot $\epsilon(\tilde{z})$ obtained by Newton-Raphson inversion for the range of $\tilde{z}$ extracted from equation 3.16. We do this for all packing fractions we investigate above ϕ_{RCP} as below this the emulsion has no osmotic pressure and the method does not hold. In Figure 3.8 we present the change in packing fraction through the gap as a function of initial packing fraction.

From the profile we see that for initial packing fractions $\phi \geq 0.70$ the packing fraction profile of the emulsion changes by no more than 0.1% when the emulsion has been equilibrated. We conclude from these results that the gradient in packing fraction is negligible and the sample can be considered homogeneous in our experiments.

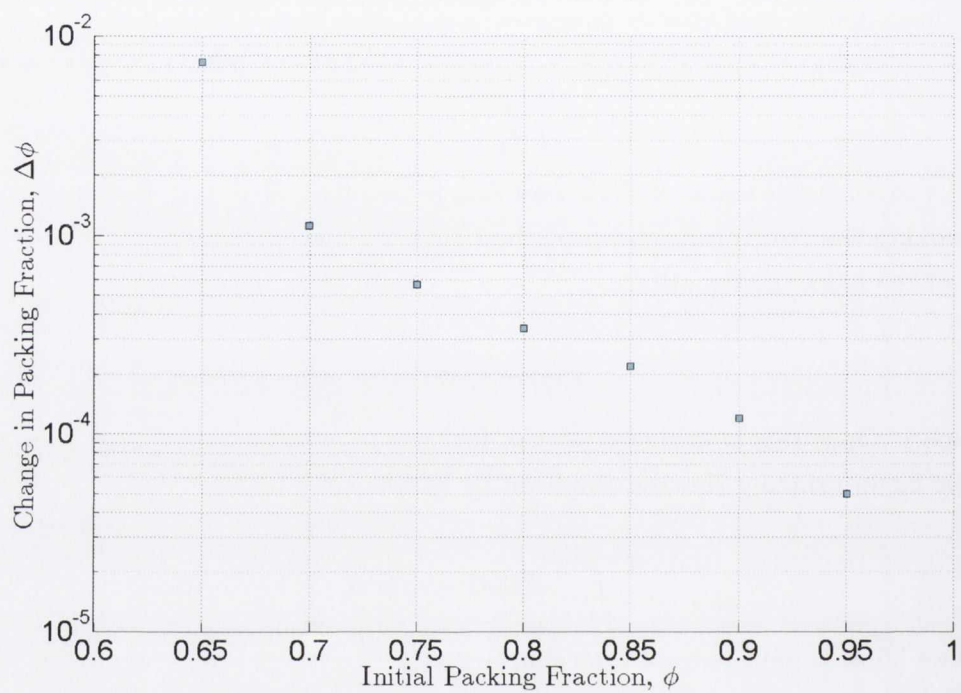


Figure 3.8: equilibrium packing fraction profile obtained by solving equation 3.15. This tells us that within the parameters of the experiment insignificant drainage occurs allowing us to rule out any rheological effects that might be caused by a severe packing fraction gradient throughout the sample.

3.2.5 Shear Test to Probe Stability

An indirect method for testing the stability of the system with regards to its influence on rheology is to put a fresh sample into the rheometer and pre-shear at $50s^{-1}$ to homogenise the sample. Immediately after the pre-shear an oscillatory test is performed whereby the strain amplitude is set such that the rheology will be in the linear regime. A graph of G' versus time will show the timescales during which the system response remains constant. The data from the shear test is presented in Figure 3.9 for illustration.

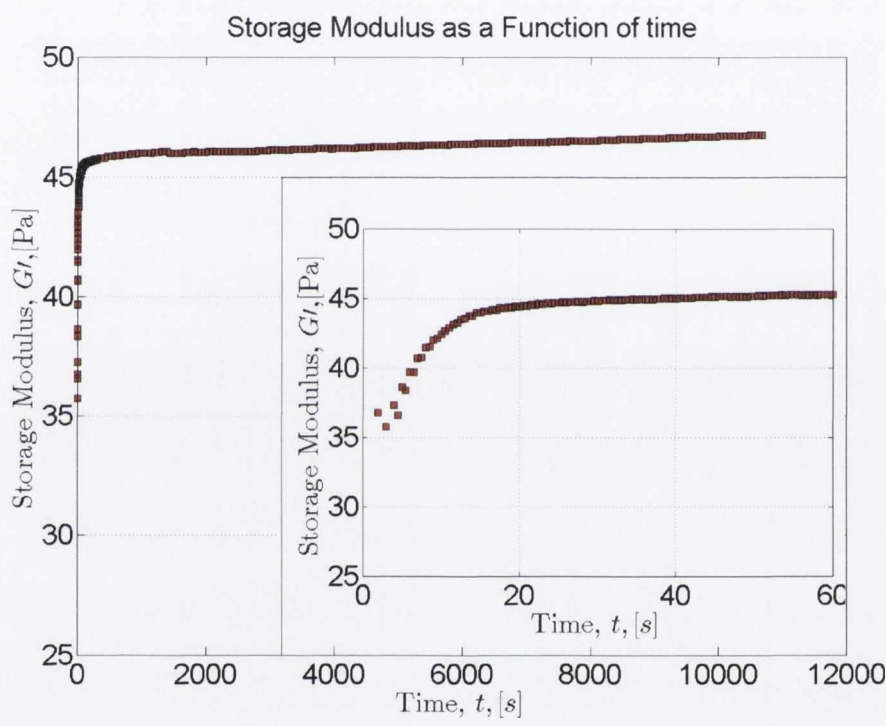


Figure 3.9: Shear test designed to provide a time for the experiment. Conducted on an emulsion at $\phi = 0.80$ with $\gamma = 0.01$ and $f = 1Hz$. Inset: Same plot cropped to first 60 seconds.

From this we conclude that within a 3 hour period the storage modulus only varies by 2% and thus we ensure that the emulsion is pre-sheared every 3 hours during long experiments. From the inset we see that after the pre-shear the emulsion takes approximately 25 seconds to recover. Therefore we wait 100 seconds after

pre-shear before beginning any measurement.

3.3 Imaging

As mentioned above the opaque nature of foam, arising from light scattering at the air-liquid interface, prohibits us from imaging foams within the bulk. An index matched emulsion seeded with fluorescent tracer particles allows us to infer droplets dynamics in the bulk of a flowing emulsion. In this section I will describe the custom built optical configuration which is attached to the rheometer and used to image the fluorescent beads in such an emulsion as well as the tracking techniques implemented on successive images.

Polystyrene fluorescent beads are deposited into the continuous phase of the emulsion during the emulsification process outlined in section 3.1. The radius of the beads is $5\mu m$ and the average droplet radius is $4.83\mu m \pm 1.87\mu m$ and as such, despite the hardness of the beads, we assume that they represent droplet dynamics. The beads emit fluorescent light with wavelength $\lambda_b = 605nm$ when light with $\lambda_i = 585nm$ is incident. Using the appropriate optical configuration we can obtain an image containing only the beads. Such a configuration is presented in Figure 3.10.

Here, the spectrum of the light source has a peak at $\lambda_s = 580nm$ which first passes through a collimator to intensify the beam. The intensified rays then pass through an excitation filter which allows only wavelengths, $\lambda = 570nm$, the excitation wavelength of the tracer particles, through². Once through the excitation filter the beam is reflected upwards into a $10\times$ objective via a dichroic mirror which reflects wavelengths $\lambda \leq 585nm$ and transmits $\lambda > 585nm$.

Once through the objective the beam passes through a viewing window, $area = 2mm^2$, and into the emulsion, which is contained in a parallel plate geometry. The fluorospheres react and emit light at $\lambda_e = 605nm$ which is collected by the

²This minimises any photo-bleaching of the beads that additional, unnecessary wavelength can induce

objective and passed through the dichroic mirror and emission filter, which only allows light with $\lambda > 590nm$, minimizing the background light.

After the final filter the light is refocused by a lens ($f = 20cm$) and directed towards a CCD sensor via a prism and captured. The field of view allowed by the system is $0.35mm^2$. The camera, Baser ACa2000-340kc, has a resolution of 2046 pixels $\times$ 1086 pixels which means that the imaged beads have a diameter of 14 pixels. A typical image is shown in Figure 3.11. The CCD camera is attached to the rheometer allowing signals to be sent to capture images.

3.3.1 Tracking

Before the captured images can be analysed they must first be processed. This is done by implementing a bandpass filter on each frame. Bandpass filtering works by suppressing pixel noise on short and long-wavelength image variations while retaining information of a characteristic size (bead diameter). This results in the image shown in Figure 3.12.

Next all the local maxima are found by examining the pixel intensity of all pixels within the neighbourhood of any pixel above a prescribed threshold. The radius of this neighbourhood is slightly larger than the radius of the bead. The pixel with the maximum intensity in the neighbourhood is taken to be centre of the bead. The centres are further refined to sub pixel accuracy by fitting a Gaussian to the intensity distribution and taking the peak as the centre.

Once all the centres are determined for each frame particle tracking is implemented. The tracking works by determining the particle within a prescribed neighbourhood which is most likely to correspond to the same particle in the previous image. The radius of the neighbourhood is decided by looking at two consecutive images and measuring maximum particle displacements manually. An example of tracked particles is presented in Figure 3.12. This code is a modification of the IDL particle tracking program written by John C. Crocker and Eric R. Weeks that has been

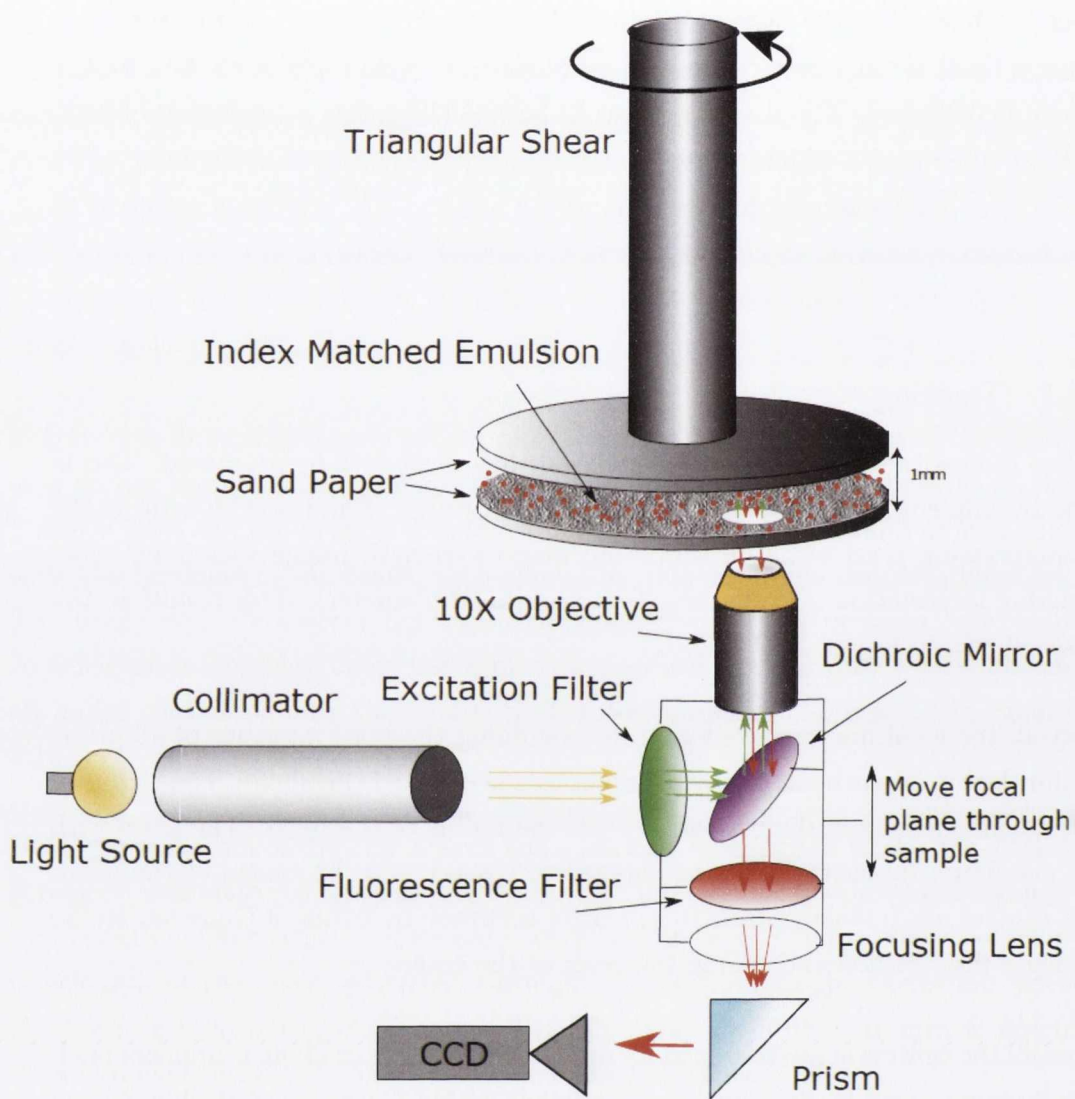


Figure 3.10: Fluorescence imaging configuration.

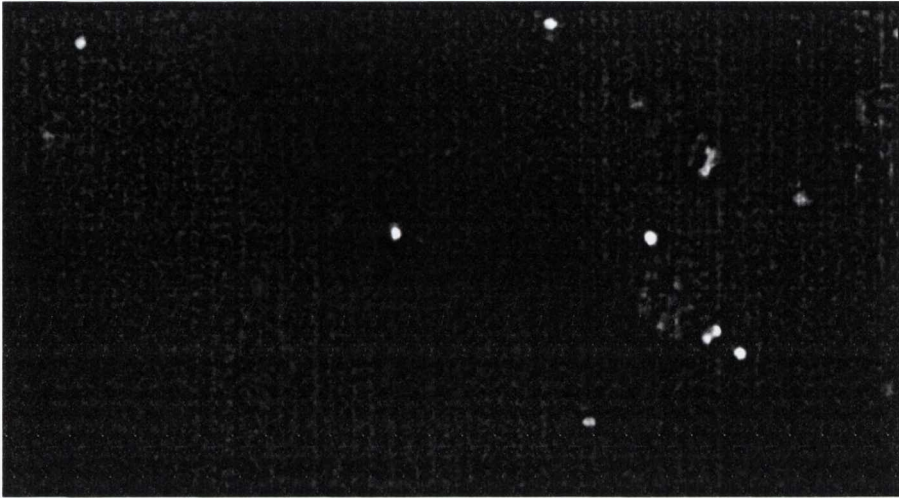


Figure 3.11: Processed image of the $10\mu\text{m}$ beads in the index matched emulsion.

widely used to track colloidal particles [112].

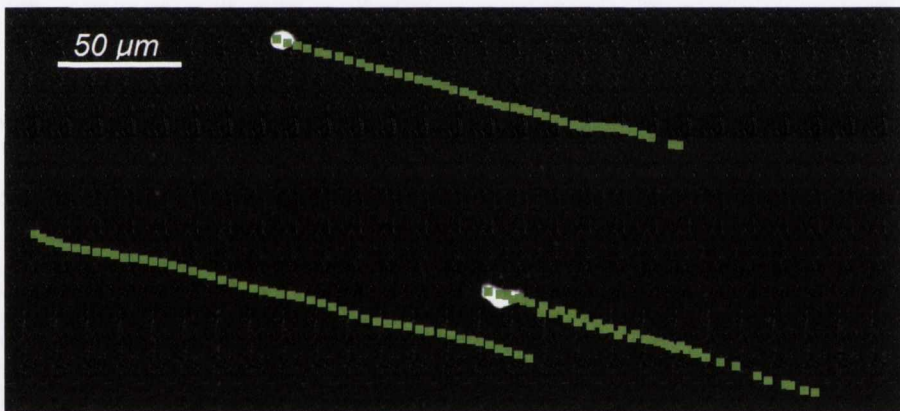


Figure 3.12: Processed image of the $10\mu\text{m}$ beads in the index matched emulsion with corresponding particle tracks (green).

3.3.1.1 Tracking Accuracy

In order to determine the lower bound of our measured particle displacement we needed to test the accuracy of the particle finding algorithm. This was conducted by placing the seeded emulsion in the rheometer and focusing the objective half-

way ($250\ \mu\text{m}$) into the sample. The rheometer holds the emulsion in place so that no shear is imposed on the sample. The centre positions were recorded for 60 seconds and the standard deviation of particle centres is taken to be the limiting tracking accuracy. A plot of particle centres for all frames measured is displayed in Figure 3.13 for clarity. From this measurement we conclude that the uncertainty in our coordinates is $6.4 \times 10^{-2}\ \mu\text{m} = 6 \times 10^{-3} d_{\text{tracer}}$. This sets the noise floor of the mean square displacements.

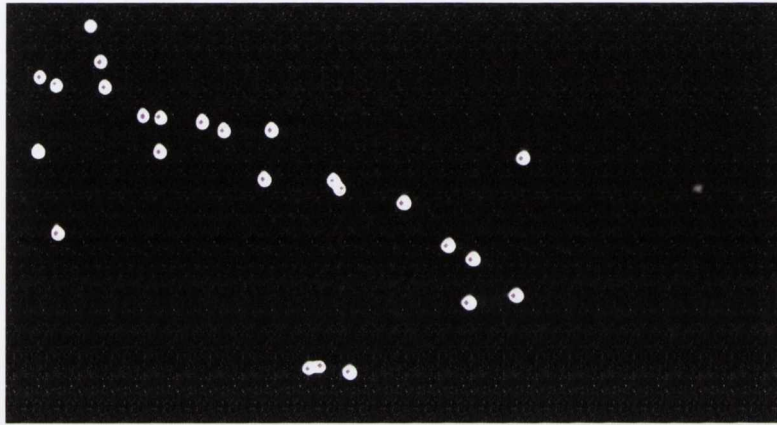


Figure 3.13: Processed image of the $10\ \mu\text{m}$ beads with their measured centres for 120 frames.

3.3.2 Coordinate System

Due to the cylindrical geometry we use polar coordinates in our analysis. Cartesian coordinates are transformed to polar coordinates via the following equations:

$$r = \sqrt{(x - x_c)^2 + (y - y_c)^2} \quad (3.18)$$

$$\theta = \tan^{-1}\left(\frac{x - x_c}{y - y_c}\right) \quad (3.19)$$

the centre position (x_c, y_c) must be measured. This is done by adhering beads with sellotape to the rotating plate, recording their trajectories and fitting a circle to

the arc they create. Using this centre and the Equations 3.18 and 3.19 the particle trajectories are transformed into tangential and azimuthal displacements.

3.3.2.1 Validating the Tracking Algorithm

In order to ensure that the modified tracking code developed would provide accurate measurements of the experimental images we generated diffusing particles using the programming language Processing and ran the tracking code on the images generated. The simulation begins with white discs with 25 pixel radius (the same radius as the experimental tracer particles in pixels) assigned random positions on a grid. The particle density is 0.0017. The grid rotates around its central axis, imposing a flow, and after each time step the particles are displaced in x and y with a value taken from a uniform distribution of $[-15 \text{ pixels}, 15 \text{ pixels}]$. A window is created at a position equivalent to the imaging window in the experimental system and images are recorded for 1000 frames. The modified tracking code is run on these images and the particle positions recorded and analysed for each image. In order to validate the accuracy of the particle tracking code we analytically derive the diffusion constant and compare with the results. For comparison with experimental images shown above we plotted an image of the simulated diffusing particles along with their tracks and particle identification labels in Figure 3.14

Given that the particles are displaced by a value randomly taken from a uniform distribution in the interval of $[-15 : 15]$ we can calculate the mean square displacement as the variance, σ^2 , by:

$$\sigma^2 = \int_{-15}^{15} \frac{x^2}{30} dx. \quad (3.20)$$

This gives us a value of 75 *pixels*. Taking the particle diameter, 25 *pixels*, gives us a variance of $0.12d^2$. The diffusion constant is given by:

$$\frac{\langle s^2 \rangle}{d^2} = 2Dt \quad (3.21)$$

$$\Rightarrow D = \frac{\langle s^2 \rangle}{2\Delta t} \quad (3.22)$$

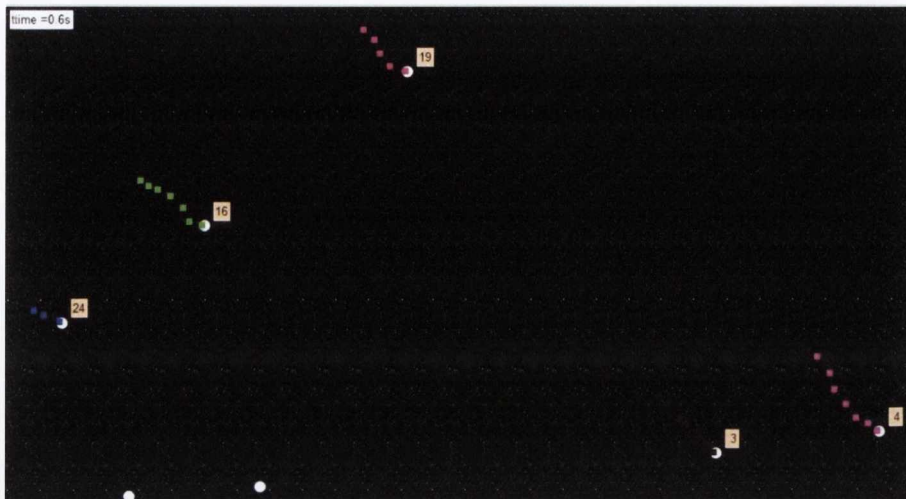


Figure 3.14: Snapshot of simulated diffusing particles along with their tracks and particle identification labels for comparison with experimental images shown above.

Where $\Delta t = 0.1s$. Plugging everything in we get a diffusion constant $D = 0.6d^2s^{-1}$. When we run the tracking code on our simulated diffusion and fit the mean square displacements to the frame rate we get a value of $D = (0.54 \pm 0.08)d^2s^{-1}$. We conclude that the modified tracking algorithm used in this research is capable of measuring the diffusion constant of a sequence of binarized experimental images. A plot of the mean square displacement versus time with the fit used is presented in Figure 3.15.

After centre finding, we decided to test the sensitivity to the centre finding algorithm we used, that is, how would much would an incorrect centre coordinate affect the mean square displacements measured by our tracking algorithm? From the same data set used in the previous argument we ran the tracking code using a range of centre co-ordinates for Cartesian to polar conversion. We chose a range of possible centres to be within a grid corresponding to $6mm \times 6mm$ which is approximately ten times the size of the error in our center finding algorithm (erring on the side of caution we initially chose an extreme range). We calculated the diffusion constant using each of the centre coordinates on the grid. All of the mean square displacement versus time plots are presented in Figure 3.16. We found that the diffusion constant varied by a maximum of 0.3% within the chosen range showing

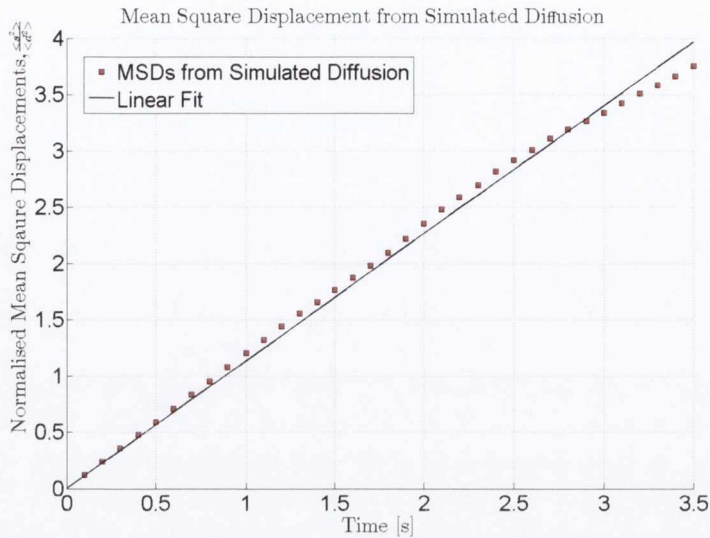


Figure 3.15: Mean square displacements versus time for simulated diffusive particles. A linear fit to this data provides a diffusion constant, $D = (0.54d^2 \pm 0.08)d^2s^{-1}$, which, within error, compares to the analytically derived diffusion constant, $D = 0.3d^2s^{-1}$.

us that we can accept the results of our centre finding algorithm without concern.

3.4 Rheological Experiments

So far we have described the sample preparation and how the internal particle dynamics are measured. In this section I will describe the rheological experiments performed on the emulsion created by the procedure described above. We often use the term bulk rheology to remind the reader that the rheological experiments, which give a measure of the global mechanical response of the system, are an investigation conducted in parallel, or complementary, to the microscopic measurements described above with the aim of correlating the droplet dynamics to the bulk flow behaviour.

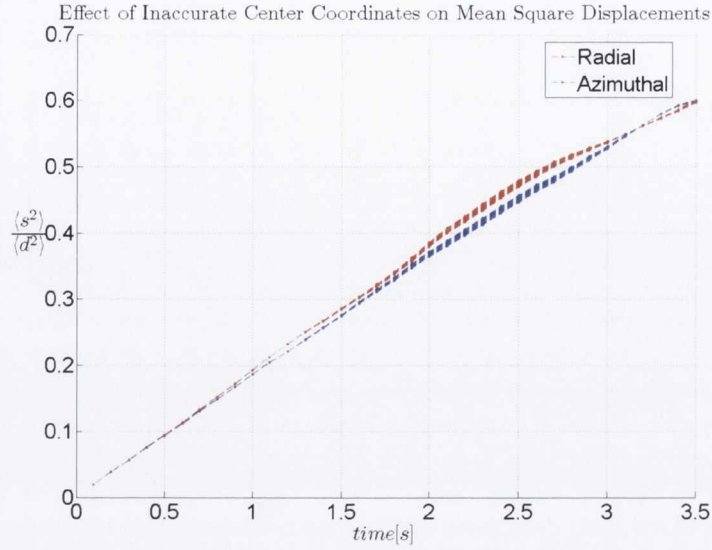


Figure 3.16: Mean square displacements versus time for simulated diffusive particles for a range of centre positions differing from the correct one. Linearly fitting each of the data sets shows us that the diffusion constant does not vary by any more than 0.3%

3.4.1 Bulk Rheology

3.4.1.1 Strain Sweep

Strain, or amplitude, sweeps are a common rheological test of a systems response to varying deformation. In this technique the shear stress, τ , which is proportional to torque, is measured as a function of a stepwise increasing strain amplitude, γ . In this measurement the angular frequency is kept constant. Using the relationship expressed in equations 1.11 and 1.12 the storage modulus, G' , and the loss modulus G'' are obtained as a function of strain amplitude. The typical behaviour of $G'(\gamma), G''(\gamma)$ for a jammed ($\phi \geq 0.64$) emulsion is presented in Figure 3.17. When the storage modulus exceeds the loss modulus, $G' \gg G''$ we say that the the system is behaving elastically, or solid-like. This is known as the linear regime as the shear stress is linearly proportional to the strain. In the solid-like regime the storage modulus corresponds to the shear modulus, G_0 in elastic materials. Conversely, when $G'' > G'$ the system is in the viscous regime, or liquid-like and undergoing plastic flow (irreversible, dissipative rearrangements). There are sev-

eral definitions used to define the yield point of the material. One is point at which $G' = G''$. Another is the intersection of the two regimes from a stress versus strain plot obtained from amplitude sweeps (see Figure 3.18 for clarity). This yield point corresponds to the end of the plateau in Figure 3.17. When $G' = G''$ we argue that the system is fully fluidised is not an appropriate point to define yielding. Instead we maintain that taking the crossover in the stress versus strain data describes the onset of dissipative rearrangements which is a convenient definition of the yield point for this study.

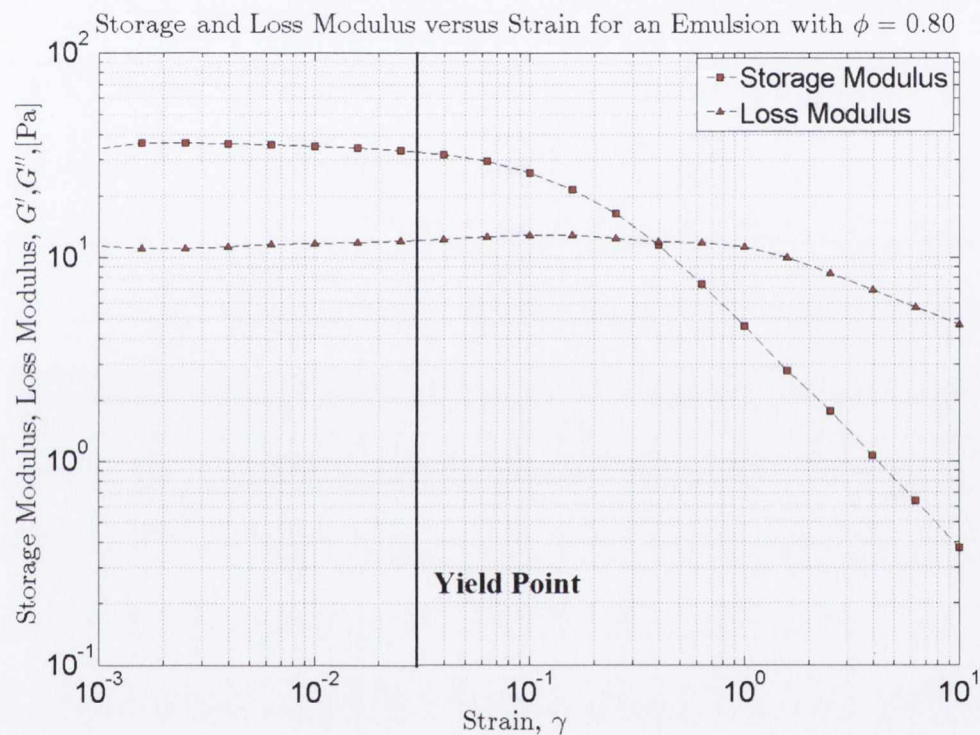


Figure 3.17: Storage modulus (squares) and loss modulus (triangles) obtained from a strain sweep performed on an emulsion with $\phi = 0.8$ conducted at a constant frequency of 1 Hz.

3.4.1.2 Strain-Rate Frequency Superposition

While strain sweeps determine the yield point of a system as a function of strain, they do not keep the strain rate constant. As the droplet rearrangement rate

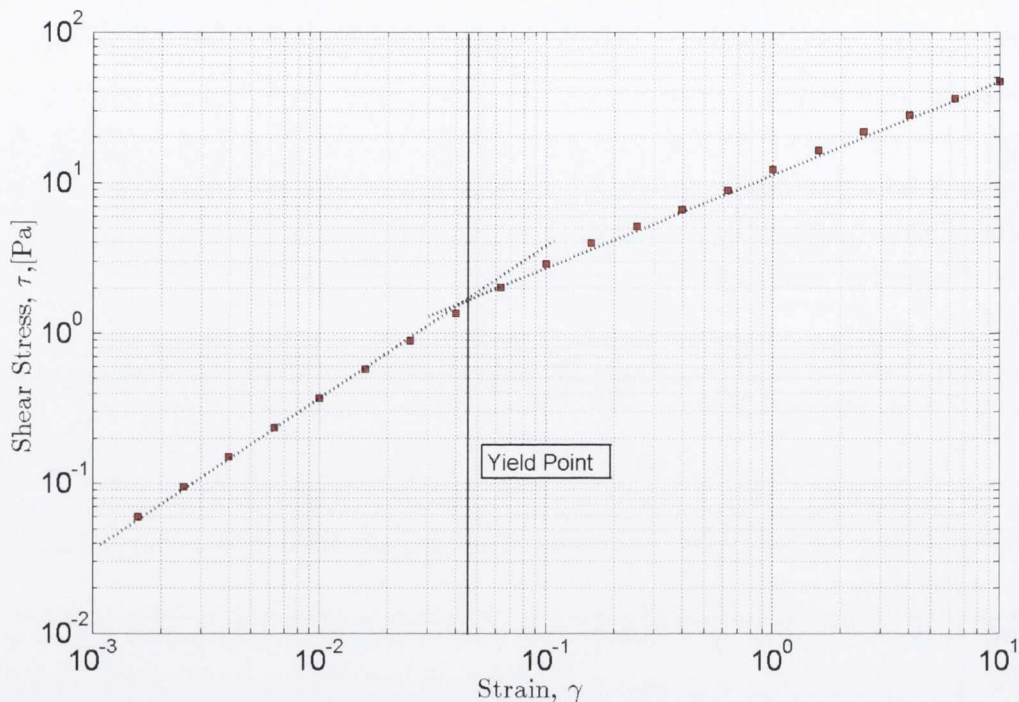


Figure 3.18: Stress versus strain data obtain from the strain sweep for an emulsion with $\phi = 0.8$ conducted at a constant frequency of 1 Hz.

is set by the strain rate [60, 59, 100] a new measurement, strain rate frequency superposition (SRFS) was introduced to the field to probe the system response as a function of strain rate [79]. For this study it gives us a complementary method of measuring the relaxation time as a function of strain rate. In SRFS we keep the strain rate constant by varying both the strain amplitude and the frequency. By doing multiple SRFS for different strain rates we can measure the relaxation time as a function of strain rate which is a very useful measurement to have in the context of this research. The relaxation time obtained from this kind of measurement we call t_r^{SRFS} . A sample SRFS graph is plotted in Figure 3.19

3.4.1.3 Flow Curve

It is also of interest to the rheologist to know how the system behaves under continuous shearing conditions. In such a protocol we measure the shear stress as

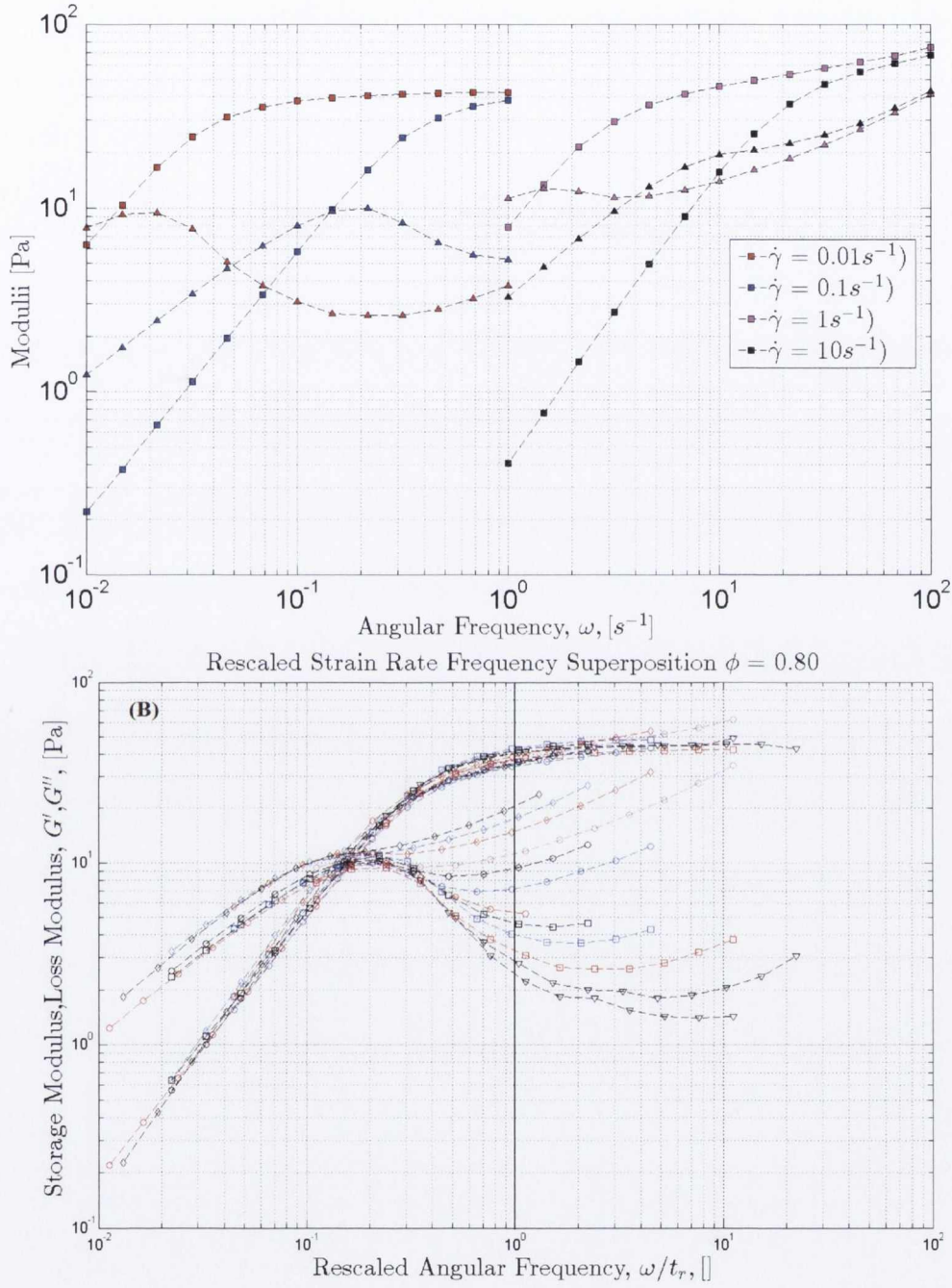


Figure 3.19: (A) Storage modulus (squares) and loss modulus (traingles) obtained from sdnstant strain rate frequency sweep from a sample of strain rates (as indicated in the legend) measured on an emulsion with $\phi = 0.80$. (B) Strain rate frequency superposition for all strain rates measured on an emulsion with $\phi = 0.80$. All the data has been rescaled such that $G', G'' \rightarrow \frac{G_0}{a}$ where G_0 is the shear modulus at the lowest strain rate measured and $\frac{\omega_c(\dot{\gamma})}{t_r(\dot{\gamma})} = 1$.

a function of increasing strain rate $\dot{\gamma}$. This is used to measure the constitutive relationship between stress and strain rate, otherwise known as a flow curve. For emulsions this relationship is well described by the empirical Herschel-Bulkley expression (Equation 1.16). A typical flow curve is shown in Figure 3.20

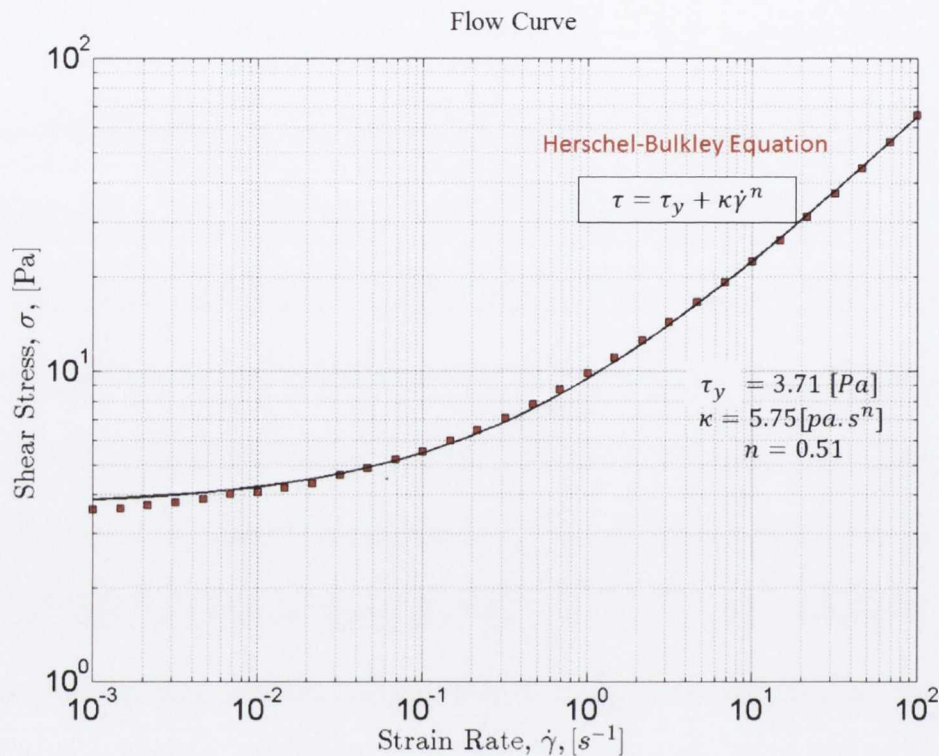


Figure 3.20: Flow Curve of an emulsion with $\phi = 0.80$.

3.4.1.4 Summary of Bulk Rheological Experiments

Before moving on to discuss the microscopic measurements of flowing emulsions conducted as part of the is work we will describe the exact rheological experiments performed on the emulsion created using the emulsification process described above.

We performed strain rate frequency superposition measurements, amplitude sweeps and flow curves for $0.65 < \phi < 0.95$ with a strain rate range of $0.001s^{-1} \geq \dot{\gamma} \geq 100s^{-1}$ with three points per decade. This allowed us to calculate the relaxation time, t_r^{SRFS} , for each strain rate which was compared with the relaxation time obtained from microscopic measurements described in the next section. Amplitude sweeps were conducted for $0.50 < \phi < 0.95$ to probe the presence of elasticity below ϕ_{RCP} and to obtain the shear modulus, yield stress and yield strain as a function of packing fraction. Flow curves were also performed as part of the investigation for $0.50 < \phi < 0.95$ with a strain rate range of $0.001s^{-1} \geq \dot{\gamma} \geq 100s^{-1}$ to determine the Herschel-Bulkley parameters as a function of strain rate.

3.4.2 Diffusion Measurements

The imaging of droplet dynamics has been described in the previous section. Here I will mention how the shear is imposed on the emulsion as it is imaged. To get a clear image of the tracer particles we are restricted to a frame rate of 10 per second. This limits the maximum strain rate we can impose on the system before the circular beads appear as streaks. To overcome this limitation we use two different protocols for measuring the mean square displacements. For low/intermediate strain rates, $\dot{\gamma} \leq 0.5s^{-1}$, we use steady shear whereby we impose the desired strain rate and begin recording the tracer trajectories as soon as the system has surpassed the yield strain, as determined from amplitude sweep data. Two examples of particle trajectories during steady shear are presented in Figure 3.21. For high strain rates, $\dot{\gamma} \geq 0.5s^{-1}$ we utilize triangular strain. Here we strain at a constant strain rate for a period of time chosen such that the total strain is much greater than the yield strain, i.e. $\dot{\gamma}t \gg \gamma_{yield}$. Once this strain has been reached the rheometer holds the system in place for 1 second. The strain rate is then reversed bringing the plate back to its original starting position and holds for 1 second. Each time the rheometer returns to this starting position and the one second interval has elapsed, a voltage sent from the rheometer to the camera triggers an image to be taken. This way we measured the trajectories of the particles after they have undergone a strain of $\Delta\gamma = 2\dot{\gamma}t$. This is an analogue

of kinematic reversibility seen in Stokes flow. An example of particle trajectories measured in this regime, as well as the strain as a function of time, is presented in Figure 3.22. Combining these two methods we explore a strain rate range from $0.01s^{-1} \geq \dot{\gamma} \geq 100s^{-1}$.

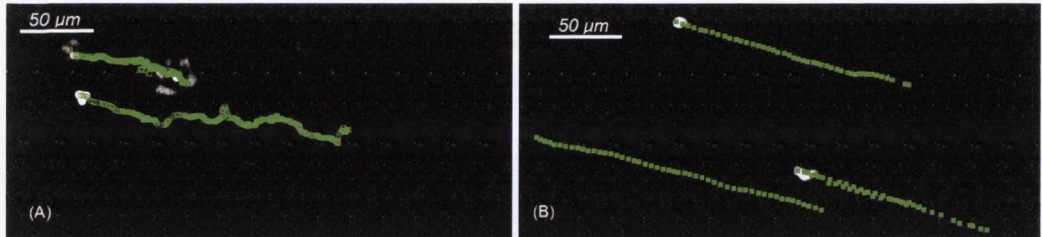


Figure 3.21: (A) Plots of particle positions during steady state flow at a shear rate, $\dot{\gamma} = 0.01s^{-1}$, overlaid on the image taken at t_0 . The total strain in this trajectory is $\gamma = 1$. (B) Plots of particle positions during steady state flow at a shear rate, $\dot{\gamma} = 0.5s^{-1}$, overlaid on the image at t_0 . The total strain in this image is $\gamma = 15$.

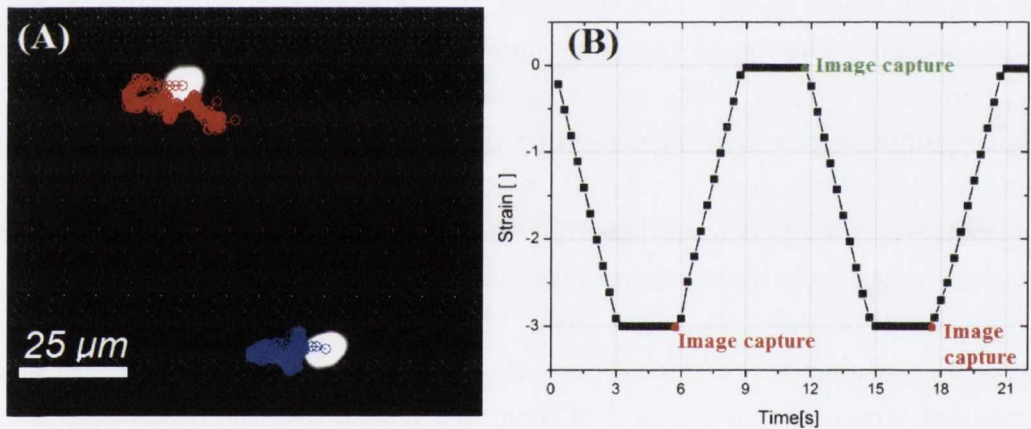


Figure 3.22: (A) Plots of particle positions obtained over an hour of triangular strain intervals overlaid onto an image of the original positions of the beads. (B) The strain as a function of time using the triangular protocol. Image capture occurs at the end of the rest interval.

3.4.3 Measuring Local Strain Rate

While a strain rate is imposed by the rheometer, it is pertinent to investigate whether this is the actual strain rate experienced by the emulsion during shear. It is also important to measure the local strain rate as it can indicate whether slip is present in the measuring geometry. While sandpaper was used to prevent slip it cannot be assumed that slip is entirely absent. In order to measure this local strain rate throughout the gap the azimuthal velocity of the beads in each plane was measured as a function of height i.e. $v_a(z)$. This was done for various imposed strain rates so as to compare the imposed with the local strain rate. For this measurement the rheometer was set to shear at a given strain rate, $\dot{\gamma}$, corresponding to the values used for a given diffusion or SRFS measurement. Enough time was allowed to pass so that the emulsion was in steady state flow, that is $\dot{\gamma}t \gg \gamma_{yield}$, as determined by strain sweep data. The focal plane was moved through the gap in $50\mu m$ intervals and images were captured for approximately one minute³. The local strain rate is calculated via,

$$\dot{\gamma}_l = \frac{\delta v_a(z)}{\delta z} \quad (3.23)$$

We also measured the local strain rate in oscillatory rheology to test if slip was dependant on the type of measurement imposed.

3.4.3.1 Velocity Profiles and Local Strain Rate Measurements

As the results from this measurement impact the treatment of our data in the proceeding chapter we have included the results as part of the Materials and Methods chapter. By measuring the tracer particle velocity at different heights in the sample we have calculated the local strain rate and determined that there is slip in our system. The velocity profiles were measured in the steady shear and oscillatory regimes. We imposed strain rates of 0.01, 0.05, 0.1 and 0.5 s^{-1} and measured the velocity as a function of height into the sample, $v(z)$. The velocity for a given position was taken as the averaged velocity of all tracked particles that entered the field of view throughout the duration of experiment. These velocity profiles, from

³This time decreased for higher strain rates due to limitations in the computer's RAM

the steady shear measurements, for each imposed strain rate, $\dot{\gamma}_G$, are presented in Figure 3.23.

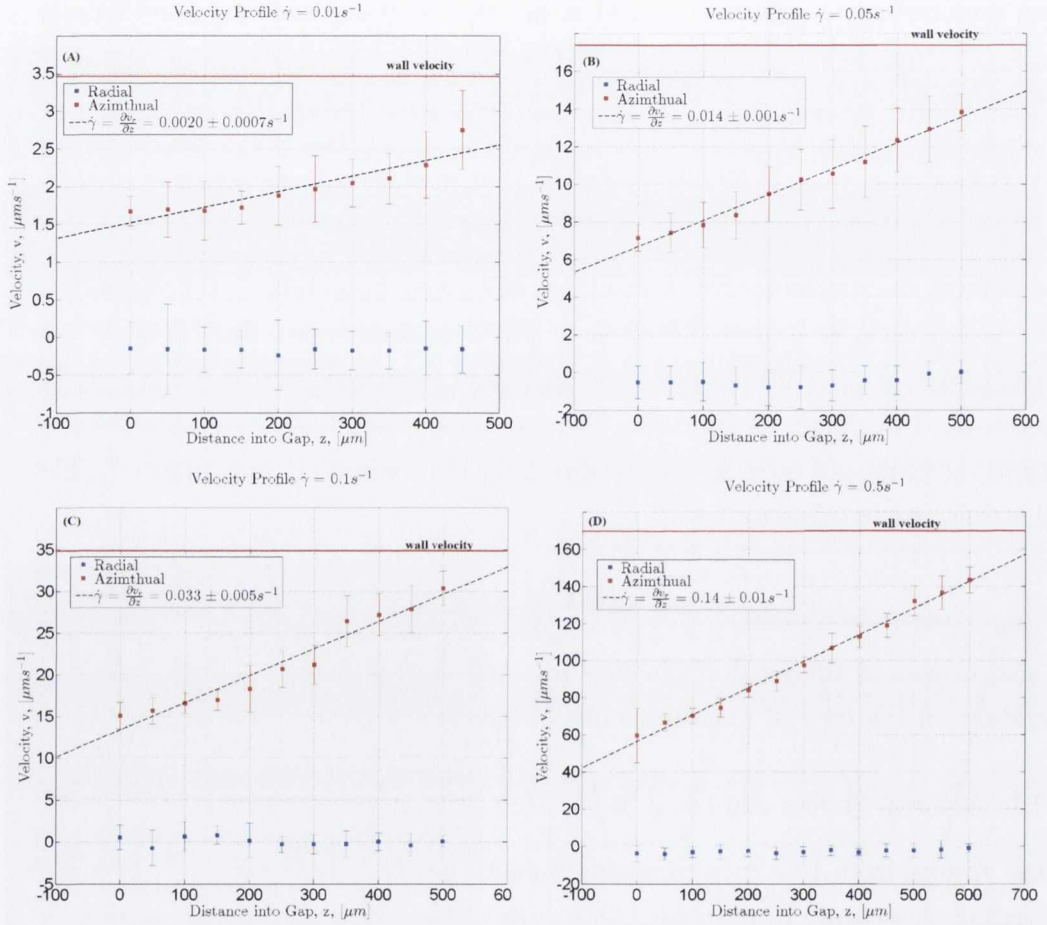


Figure 3.23: Average tracer particle velocity as a function of distance into the sample in the radial direction (blue) and the azimuthal direction (red) for a imposed strain rate. (A) $\dot{\gamma} = 0.01 \text{ s}^{-1}$, a linear fit to the azimuthal velocity (dashed line) gives the local strain rate, $\dot{\gamma}_l = 0.0020 \pm 0.0007 \text{ s}^{-1}$. (B) $\dot{\gamma} = 0.05 \text{ s}^{-1}$, a linear fit to the azimuthal velocity (dashed line) gives the local strain rate, $\dot{\gamma}_l = 0.014 \pm 0.001 \text{ s}^{-1}$. (C) $\dot{\gamma} = 0.1 \text{ s}^{-1}$, a linear fit to the azimuthal velocity (dashed line) gives the local strain rate, $\dot{\gamma}_l = 0.033 \pm 0.005 \text{ s}^{-1}$. (D) $\dot{\gamma} = 0.5 \text{ s}^{-1}$, a linear fit to the azimuthal velocity (dashed line) gives the local strain rate, $\dot{\gamma}_l = 0.14 \pm 0.01 \text{ s}^{-1}$.

As apparent from the figures the profiles behave linearly as one would expect in this geometry. However there is also an element of slip present as the velocity does

not go to zero at the base plate or as high as the wall velocity at the top of the sample. From these profiles we calculate the local strain rate via,

$$\dot{\gamma}_l = \frac{dv(z)}{dz} \tag{3.24}$$

Due to the limiting frame rate of our optical configuration (10FPS) we can only measure the velocity at low strain rates, $\dot{\gamma}_G \leq 0.5s^{-1}$. However we plot the local strain rate as a function of the imposed strain rate, to find a general relationship between the two. This data is presented in Figure 3.24. A linear fit between the imposed strain rate and the measured, local strain rate, gives the following relationship,

$$\dot{\gamma}_l = (0.29 \pm 0.03)\dot{\gamma}_G \tag{3.25}$$

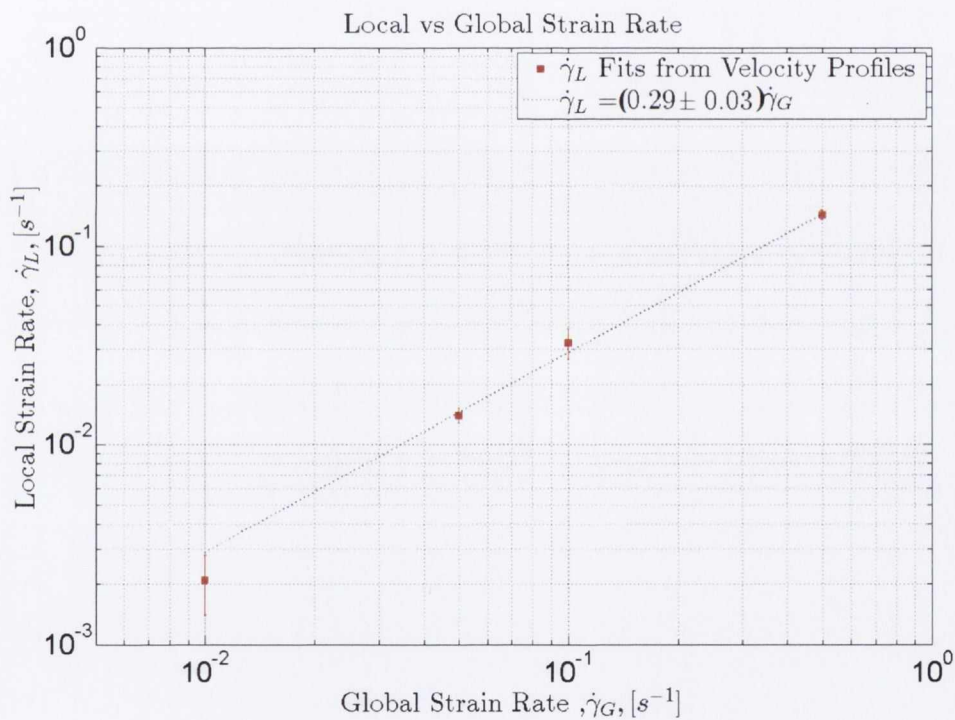


Figure 3.24: Local strain rate, as determined by the linear fits to the velocity profiles, as a function of global (imposed) strain rate, $\dot{\gamma}_G$. A linear fit (dashed line) indicated that the local strain rate is given by $\dot{\gamma}_l = (0.29 \pm 0.03)\dot{\gamma}_G$

We also measured the velocity profile in oscillatory flow and found that in this regime the slip has a smaller impact on the local strain rate. We found that in the case of oscillatory motion,

$$\dot{\gamma}_l = (0.45 \pm 0.05)\dot{\gamma}_G \quad (3.26)$$

From this we conclude that when the emulsion is being continuously sheared that the actual strain rate is 0.29 times the imposed strain rate and 0.45 times the local strain rate for oscillatory shear. This is an important finding as despite the presence of sandpaper the actual strain rate experienced by the emulsion is not the same as what is imposed by the rheometer. We however find that this is not the case. In the proceeding analysis we have corrected the strain rate based on these findings.

3.5 Conclusion and Outlook

Now that we have described all the methods employed in generating the emulsion and measuring its rheology and droplet dynamics we will conclude this chapter with a table of the exact experimental protocol used as well as the outcome or information obtained from each step.

3.5.1 Role of Packing Fraction

The table below contains the protocol used on a given sample to obtain the relaxation time and diffusion constant as a function of packing fraction, ϕ .

3.5.2 Role of Strain Rate

Below we provide the protocol used to obtain the diffusion constant and microscopic relaxation time as a function of strain rate $\dot{\gamma}$.

#	Measuremnt	Outcome
1	$\dot{\gamma} = 50s^{-1}$ for 60s	Homogenise the sample after loading.
2	$\dot{\gamma} = 0s^{-1}$ for 100s	Rest period to allow recovery after shear.
3	Amplitude Sweep	Shear Modulus, Yield Strain.
4	Steady Shear Diffusion $\dot{\gamma} = 0.1s^{-1}$	Microscopically measured relaxation time, $t_r(\dot{\gamma} = 0.1s^{-1})$ and diffusion constant, $D(\dot{\gamma} = 0.1s^{-1})$
5	Flow Curve $\dot{\gamma} = 0.001...100s^{-1}$	Functional form of stress - strain rate relationship.
6	Strain Rate Frequency Superposition (SRFS) $\dot{\gamma} = 100s^{-1}, 50s^{-1}, 25s^{-1}$	Relaxation time $t_r(\dot{\gamma} = 100s^{-1}, \dot{\gamma} = 50s^{-1}, \dot{\gamma} = 25s^{-1})$
7	$\dot{\gamma} = 50s^{-1}$ for 60s	Homogenise the sample to compensate for any ageing effects.
8	$\dot{\gamma} = 0s^{-1}$ for 100s	Rest period to allow recovery after shear.
9	SRFS $\dot{\gamma} = 10s^{-1}, 5s^{-1}, 2.5s^{-1}$	Relaxation time $t_r(\dot{\gamma} = 10s^{-1}, \dot{\gamma} = 5s^{-1}, \dot{\gamma} = 2.5s^{-1})$
10	$\dot{\gamma} = 50s^{-1}$ for 60s	Homogenise the sample to compensate for any ageing effects.
11	$\dot{\gamma} = 0s^{-1}$ for 100s	Rest period to allow recovery after shear.
12	SRFS $\dot{\gamma} = 1s^{-1}, 0.5s^{-1}, 0.25s^{-1}$	Relaxation time $t_r(\dot{\gamma} = 1s^{-1}, \dot{\gamma} = 0.5s^{-1}, \dot{\gamma} = 0.25s^{-1})$
13	$\dot{\gamma} = 50s^{-1}$ for 60s	Homogenise the sample to compensate for any ageing effects.
14	$\dot{\gamma} = 0s^{-1}$ for 100s	Rest period to allow recovery after shear.
15	SRFS $\dot{\gamma} = 0.1s^{-1}, 0.05s^{-1}, 0.025s^{-1}$	Relaxation time $t_r(\dot{\gamma} = 0.1s^{-1}, \dot{\gamma} = 0.05s^{-1}, \dot{\gamma} = 0.025s^{-1})$
16	$\dot{\gamma} = 50s^{-1}$ for 60s	Homogenise the sample to compensate for any ageing effects.
17	$\dot{\gamma} = 0s^{-1}$ for 100s	Rest period to allow recovery after shear.
18	SRFS $\dot{\gamma} = 0.01s^{-1}, 0.005s^{-1}, 0.0025s^{-1}$	Relaxation time $t_r(\dot{\gamma} = 0.01s^{-1}, \dot{\gamma} = 0.005s^{-1}, \dot{\gamma} = 0.0025s^{-1})$
19	Amplitude Sweep	Can indicate if the emulsion has aged since beginning of experiment.

#	Measurement	Outcome
1	$\dot{\gamma} = 50s^{-1}$ for 60s	Homogenise the sample after loading.
2	$\dot{\gamma} = 0s^{-1}$ for 100s	Rest period to allow recovery after shear.
3	Amplitude Sweep	Shear Modulus, Yield Strain.
5	Steady Shear for a chosen strain rate measured throughout the gap, $z = 0...500\mu m$	Velocity profile $\rightarrow$ Local strain rate, $\dot{\gamma}_l$
6	Steady Shear/triangular diffusion for one decade of strain rate $\dot{\gamma} = 0.01..100s^{-1}$	Diffusion constant and relaxation time for those Strain rates
7	Amplitude Sweep	Can indicate if the emulsion has aged since beginning of experiment.

Chapter 4

Macroscopic Characterisation of the Yielding and Flow Behaviour of Adhesive Emulsions

*“No man ever steps in the same
river twice, for it is not the same
river and he is not the same
man.”*

-Heraclitus

We begin our discussion by focusing first on the macroscopic rheology of adhesive emulsions. First we look at the strain sweep measurements from which we infer the shear modulus, yield stress and yield strain. We then proceed to discuss the behaviour of our emulsion when it is undergoing steady shear flow. Before introducing the data obtained from the flow curves we present the measurements of the local strain rate as this information is important when analysing the behaviour of our system in the steady shear regime. From there we explore how the Herschel-Bulkley fitting parameters vary with packing fraction, ϕ . We will conclude this chapter with an overview of the macroscopic response of an adhesive emulsion.

4.1 Solid-Like Response

4.1.1 The elastic Shear Modulus

Strain sweeps allow us to probe the elastic response of the system, and the transition to the non-linear response regime where the emulsion starts to yield, as a function of stepwise increasing strain. In Figure 4.1 we present the storage and loss moduli as functions of strain for a selection of packing fractions measured.

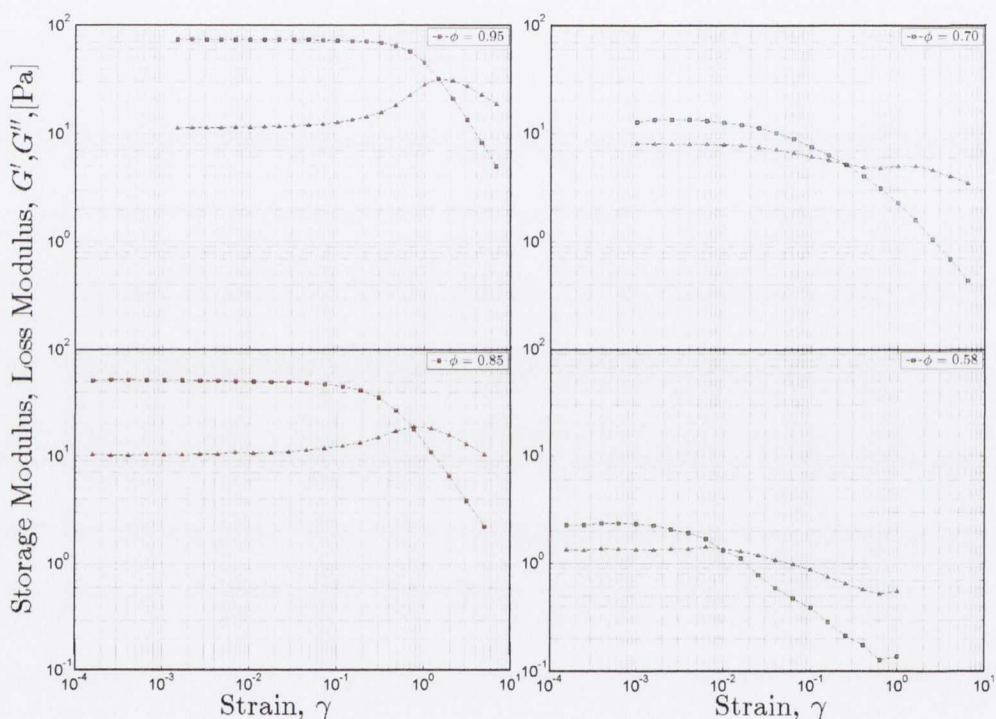


Figure 4.1: Storage modulus (squares) and loss modulus (triangles) obtained from strain sweeps conducted at a frequency of 1 Hz for different packing fractions as indicated in legend. This data can be rescaled by the shear modulus and the yield strain.

A few things are apparent from this data. First the value of the storage modulus plateau increases with packing fraction, as does the yield point (and the crossover point, that is where $G' = G''$). The storage modulus can be explained by considering what happens to the droplets as you strain the system. The droplets

deform, that is they increase their surface area. Due to surface tension they wish to return the minimal surface. It is from this that foam and emulsion elasticity arises. The increase in the shear modulus can be partly explained by the increase in the number of droplets per unit volume. However in our packing fraction range the number of bubbles per unit area increases by at most a factor of two, while the shear modulus increases by an order of magnitude. This change may better be explained if we think not only of the increase in droplet density but also of the increase in number of contacts per droplet as you increase the packing fraction thereby adding additional constraints on the system. The increase in the yield strain can be explained by reduction in free space as you increase packing fraction. The system yields when droplets begin undergoing dissipative rearrangements. As you increase the packing fraction the amount of available space in which rearranges can occur decreases. More strain is needed to induce yielding in this densely packing state.

The values of the shear modulus and the yield strain can be obtained from the storage modulus data. The shear modulus can be calculated from the average value of G' in the plateau. We obtain the yield strain by rescaling the strain axis such that the departure of the storage modulus plateau begins at 1. In other words we rescale the strain axis such that the shoulder of G' lands on 1. We also rescale the storage modulus with the shear modulus, such that, $\frac{G'}{G_0} = 1$. The rescaled data for all packing fractions investigated is presented in Figure 4.2.

Evident from the rescaling is that all packing fractions possess a linear response regime, that is they all respond elastically up to a certain yield strain. Also apparent from the rescaling is the decay of the storage modulus beyond the yield strain. At low packing fractions the storage modulus decays with a log slope -1 and the decay decreases at higher packing fractions to a log slope -3. Viscoelasticplastic models give the slope as -2/3 [113]. However this has not been extensively studied as a function of packing fraction nor with the presence of depletion interaction[13] and we suggest that this be considered in the evaluation of any models attempting to describe the non-linear response of an emulsion to oscillatory strain.

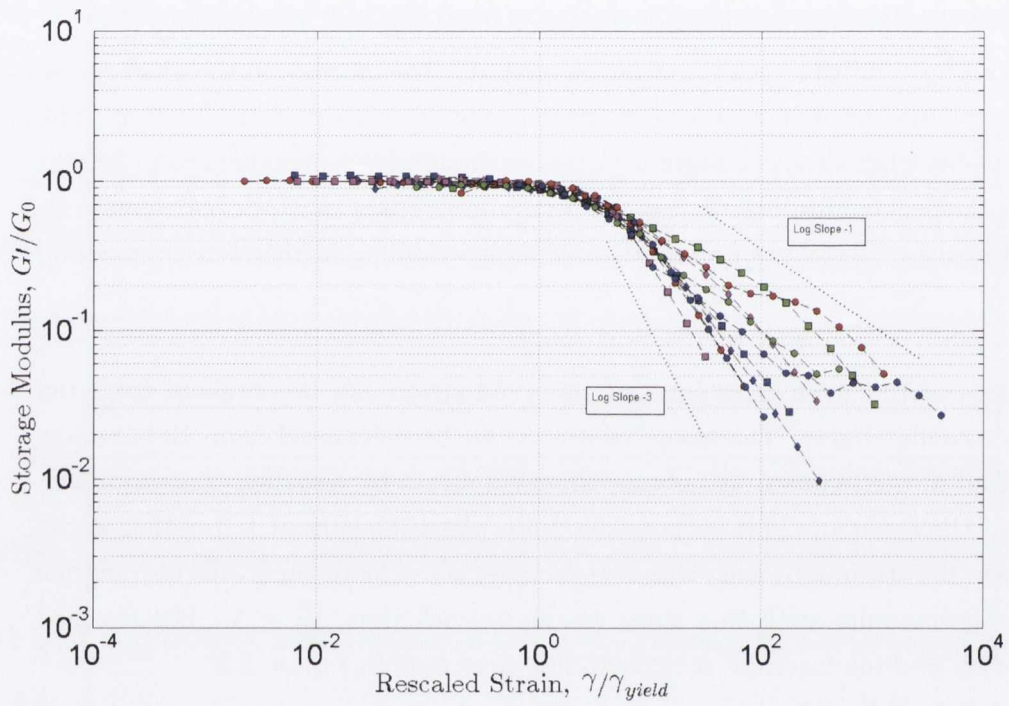


Figure 4.2: Rescaled storage modulus all packing fractions measured. The storage modulus scaling factor is the shear modulus and the strain scaling factor is the yield strain. Also apparent from this rescaling is the decay of the storage modulus beyond the yield strain. At lower packing fraction the shear modulus decays with a log slope -1 and decreases to -3 at the highest packing fraction.

Now we return to the linear, elastic regime and look at the shear modulus, normalised by the Laplace pressure, as a function of packing fraction and compare our data with what has been found in the literature. The shear modulus as a function of packing fraction is presented in Figure 4.3

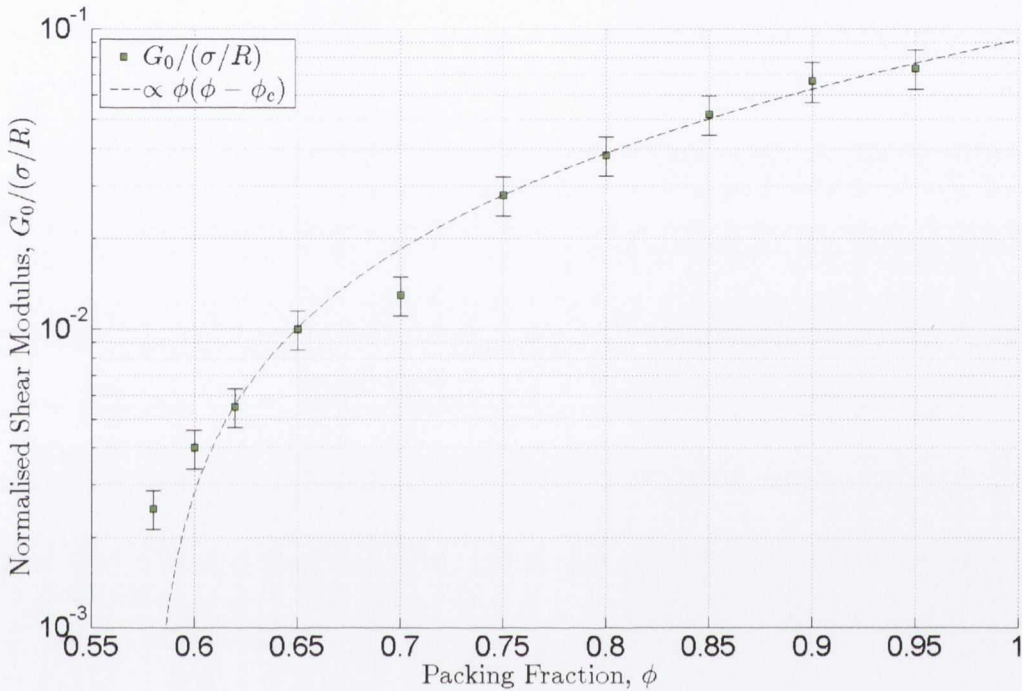


Figure 4.3: The shear modulus, normalised by the Laplace pressure, as a function of packing fraction. The dashed line is a fit to Mason's equation, $\phi(\phi - \phi_c)$ [78], with ϕ_c given as an open fitting parameter. This fit gives a critical packing fraction $\phi_c = 0.57 \pm 0.025$.

What is clear from this data is the existence of a well defined shear modulus below random close packing, $\phi_{rcp} = 0.64$. This is not surprising in the case of attractive emulsions as reported in the literature whereby entropic effects caused by the presence of micelles creates an attractive force between neighbouring droplets which continues to exist below ϕ_{RCP} [36]. By fitting the shear modulus to Mason's equation, $\frac{G_0}{\sigma/R} \propto \phi(\phi - \phi_c)$ [78], and leaving ϕ_c as an open parameter, we find that our data adheres to this relationship and gives a critical packing fraction, $\phi_c = 0.57 \pm 0.025$, which is lower than the critical packing fraction found for purely repulsive foams and emulsions, that is $\phi = 0.64$ [13, 70]. From here on,

unless otherwise stated we use $\phi = 0.57$ as our critical packing fraction. In Figure 4.4 we compare our values of the storage modulus with literature values measured using both attractive and repulsive emulsions.

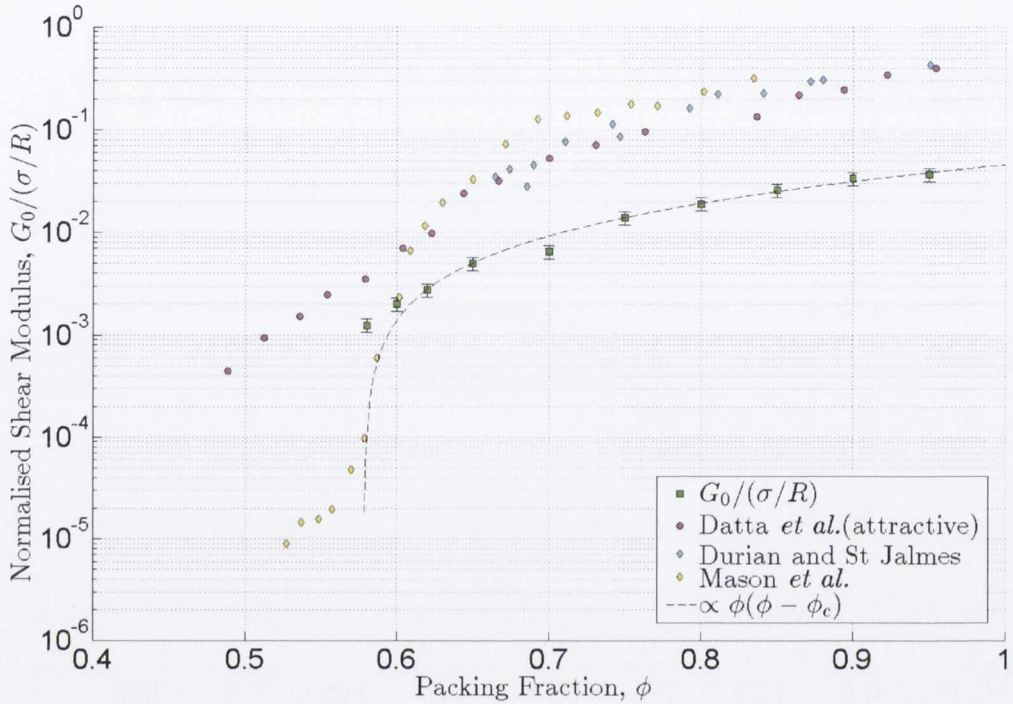


Figure 4.4: The shear modulus, normalised by the Laplace pressure, as a function of packing fraction. The dashed line is a fit of our data to Mason's equation, $\phi(\phi - \phi_c)$, with ϕ_c left as an open fitting parameter. Here we compare our values with those found in the literature: Datta *et al.* (pink) (attractive) [36], Durian and Saint-Jalmes (repulsive) (blue), Mason *et al.* (weakly attractive) (yellow) [78].

From this plot there appears to be a discrepancy between our data and what has been found in the literature. This is not alarming as it has been discussed previously by Rouyer *et al.* [72]. They found that when comparing results presented in the literature not all the shear modulus data falls onto the same curve when normalised by the Laplace pressure. In that review paper they argue that the discrepancies are likely due to inconsistencies in the experimental method across the literature. In our case it is likely due to slip at the plates. They found that the data falls onto a master curve when normalised by the yield stress instead of

the Laplace pressure. We discuss this further towards the end of Section 4.2.1. Another observation from this data is that Mason *et al* find a similar trend to ours. Upon reviewing their work one can find that their surfactant concentration is $\approx 1.5\times$ the CMC which may make their emulsion weakly attractive and allow for elasticity below ϕ_{RCP} . When we compare our data with that of Datta *et al.* we see that their emulsion allows for elasticity much lower than ours (in our measurements $\phi = 0.55$ was completely fluid like) which is surprising as our interaction potential was similar to theirs (see Section 3.1.2)[36]. We do not attempt to explain this discrepancy and proceed with the knowledge that our system is an adhesive emulsion that allows for rigidity at $\phi \geq 0.57$.

4.1.2 The Yield Stress

As described in detail in Section 1.5 G' and G'' are calculated from the stress measured when imposing an oscillatory strain. However other system parameters can be obtained by looking at the stress strain curves directly. In Figure 4.5 we present stress versus strain data taken for two packing fractions. Note that these two graphs have corresponding G', G'' plots in Figure 4.3.

As evident in this figure two lines can be fitted to the data. One that is linear, which represents the elastic response of the system, that is, $\tau = G_0\gamma$ and one that is non-linear. We use the crossover of these two lines to provide a definition of the yield stress and an additional definition of the yield strain. Presented in Figure 4.6 is the yield stress as a function of packing fraction obtained from the intersection of two fitted lines are shown in Figure 4.5.

We will return to this data in Section 4.2.1. However for now we see from the line of log slope 2 that the quadratic relationship in $(\phi - \phi_c)$ reported in the literature is consistent with our data. It does however appear to rise more sharply as $\phi \rightarrow 1$. This has been reported from previous experiments and was attributed to fracturing, as opposed to yielding, that occurs as the emulsion becomes more densely packed [73]. At low packing fractions, the yield stress has a shallow slope. It appears that when $\phi < \phi_{RCP}$ different yielding mechanisms are in place. Instead of overcoming geometric constraints, as happens in yielding when $\phi > \phi_{RCP}$ the imposed strain instead breaks bonds created by the depletion interaction.

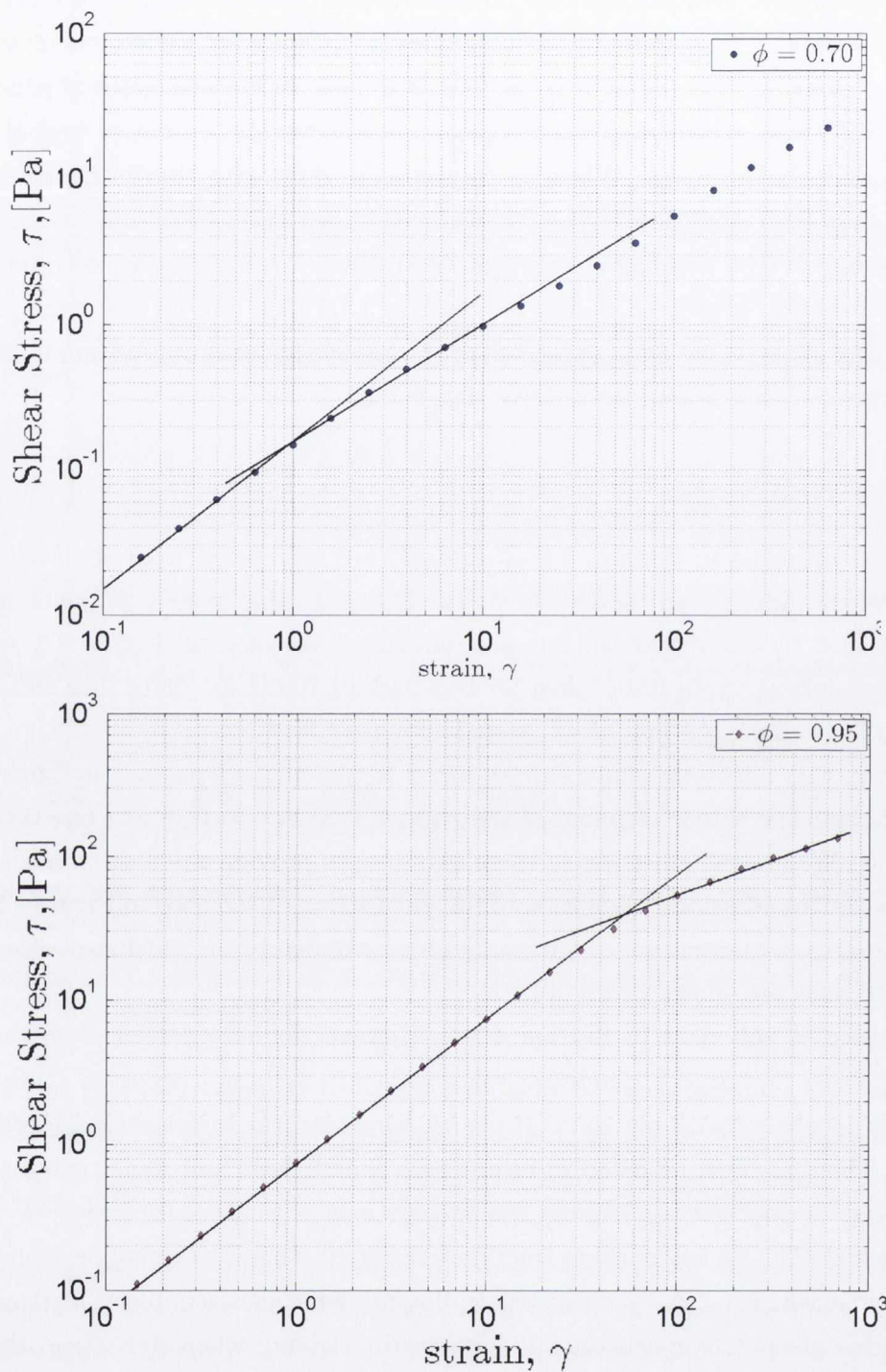


Figure 4.5: Stress versus strain data from oscillatory amplitude sweeps for packing fractions $\phi = 0.70$ and $\phi = 0.95$. The intersection of the two lines gives the yield stress and the yield strain.

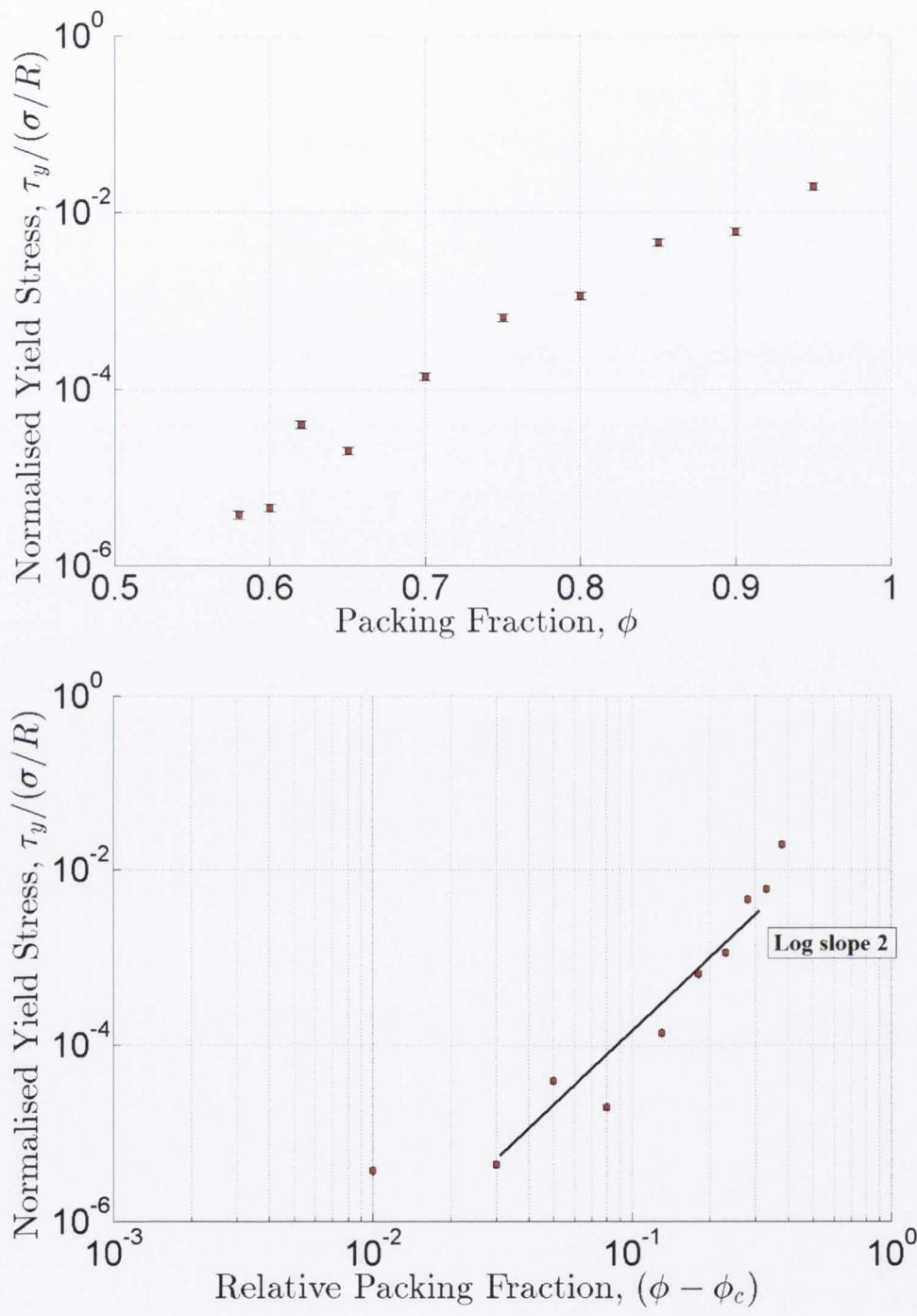


Figure 4.6: The yield stress, normalised by the Laplace pressure, as a function of packing fraction. The solid line is a log slope 2 and inserted as a guide to the eye as this is the established trend.

4.2 Steady Shear Rheology

In this section we discuss the results obtained from measurements conducted by applying a continuous strain rate to the emulsion, that is, the flow curves.

4.2.1 Flow Curves and the Herschel-Bulkley Equation

With the corrected strain rate we can now move on to the flow curves, which expresses the stress measured on an emulsion as a function of strain rate, that is, the system is always in a steady shear regime. We present the raw data for all packing fractions in Figure 4.7. Not that all in all the plots presented in this section the strain rate was corrected using Equation 3.25

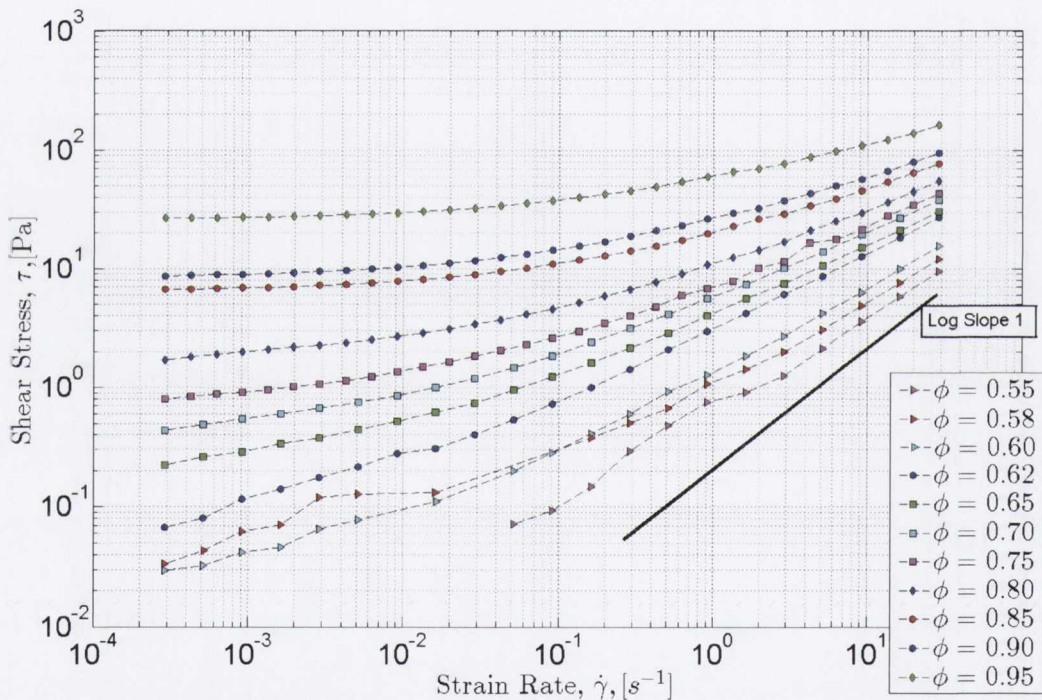


Figure 4.7: Stress versus strain rate data from continuously increasing strain rate for different packing fractions, indicated in the legend. Evident from this data is the stress measured on a flowing emulsion increases with packing fraction.

Before we proceed to fit this data to the empirical Herschel-Bulkley equation,

$\tau = \tau_y + \kappa \dot{\gamma}^n$, we can immediately make a few observations from this plot. First it is clear that the yield stress increases with packing fraction. Again we argue that this is likely due to the increase in droplets per volume and number of contacts as you increase the packing fraction. Also noticeable from this plot is that, as the yield stress decreases, the flow curve approaches that of a Newtonian liquid. Note that at the lowest packing fraction we approach the stress resolution of the rheometer and have less data. To further elucidate the stress response to strain rate of a flowing emulsion we fit the data to the empirical Herschel-Bulkley equation. In Figure 4.8 we show the raw data along with fits to the Herschel-Bulkley Equation.

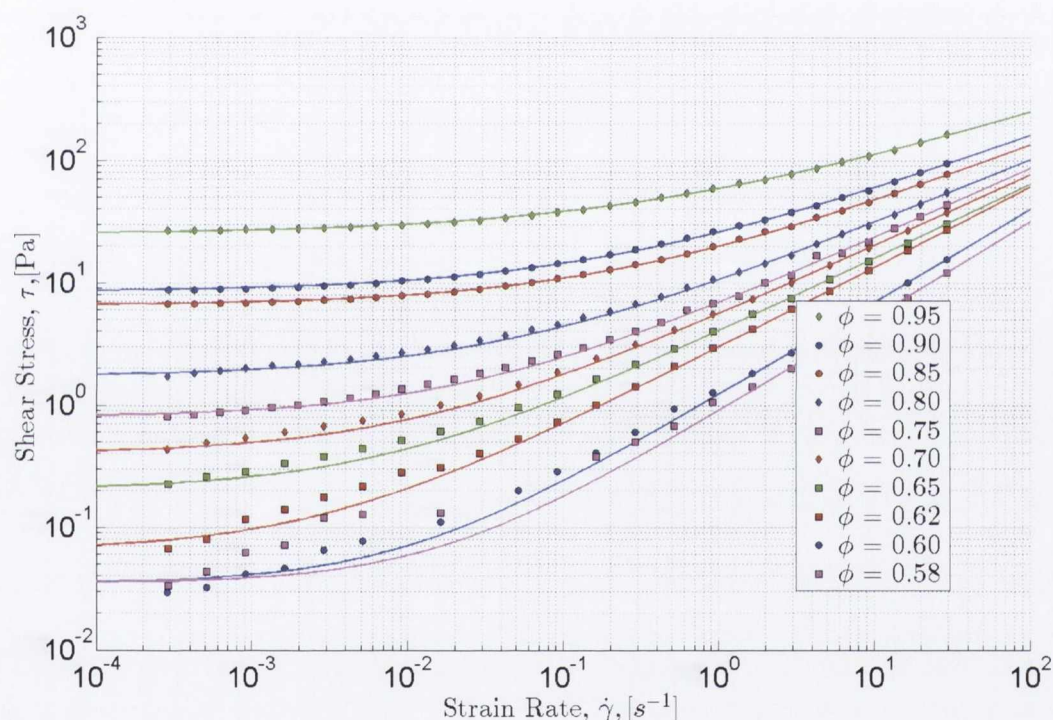


Figure 4.8: Stress versus strain rate data with corresponding Herschel-Bulkley fits (solid lines). By fitting to the Herschel-Bulkley equation we can find the yield stress, consistency, and power-law exponent as a function of packing fraction.

We can see that the empirical Herschel-Bulkley relationship best describes the data above ϕ_{RCP} but still produces adequate fits below. Again, we hypothesize that despite still being a yield stress fluid the mechanisms that govern the flow below ϕ_{RCP} are slightly different than above. However to a first approximation we still

take the Herschel-Bulkley description as adequate for all our data. By fitting to this equation we obtain, the yield stress, τ_y , the consistency, κ , sometimes referred to as the Herschel-Bulkley viscosity, and the power-law exponent, n , as a function of packing fraction. We present the relationship between these parameters and the packing fraction in Figures 4.9, 4.10 and 4.11 respectively. The yield stress is presented both as a function of packing fraction and the relative packing fraction, that is, this distance from the critical packing fraction, $\phi_c = 0.57$.

In Figure 4.9 we point to the log slope 2, which is placed as a guide to the eye and suggests that the yield stress follows the same trend that has been reported in the literature for repulsive foams, that is $\phi_c = 0.64$ [72]. Again, we highlight that the yield stress does not adhere to this relationship beyond $\phi = 0.90$ which we have discussed in Section 4.1.2. We will now proceed with the consistency, that is the Herschel-Bulkley viscosity. In Figure 4.10 we present the data as a function of ϕ and $(\phi - \phi_c)$.

Both of these plots show a smooth increase in the Herschel-Bulkley consistency. If we look at the $(\phi - \phi_c)$ data we can see that the consistency goes as $(\phi - \phi_c)^2$, similar to the yield stress. Next we discuss the power law exponent, n . In Figure 4.11 we present the power law exponent as a function of packing fraction, ϕ .

Figure 4.11 shows that the Herschel-Bulkley power-law exponent decreases linearly with packing fraction. What this says is that the shear stress increases more rapidly with imposed strain rate as you get closer to the critical packing fraction as is evident in Figure 4.8. A similar relationship has been reported in simulations using the bubble model[114], however to our knowledge this is the first time it has been explicitly shown from experimental data.

As mentioned in Section 2.1.2 rescaling the stress and the strain axis onto a master curve has been used to study flow curves conducted at various packing fractions [86, 90]. This approach arose from theoretical models suggesting that jamming is analogous to second order phase transitions in thermal systems¹. Motivated by such an analogue power law behaviour of rheological variables with regard to some control parameter, in this case the critical packing fraction, ϕ_c , that is, they take the form $(\phi - \phi_c)^x$ is proposed.

¹An example of such behaviour is found in magnetisation when $M \propto (T - T_C)^x$

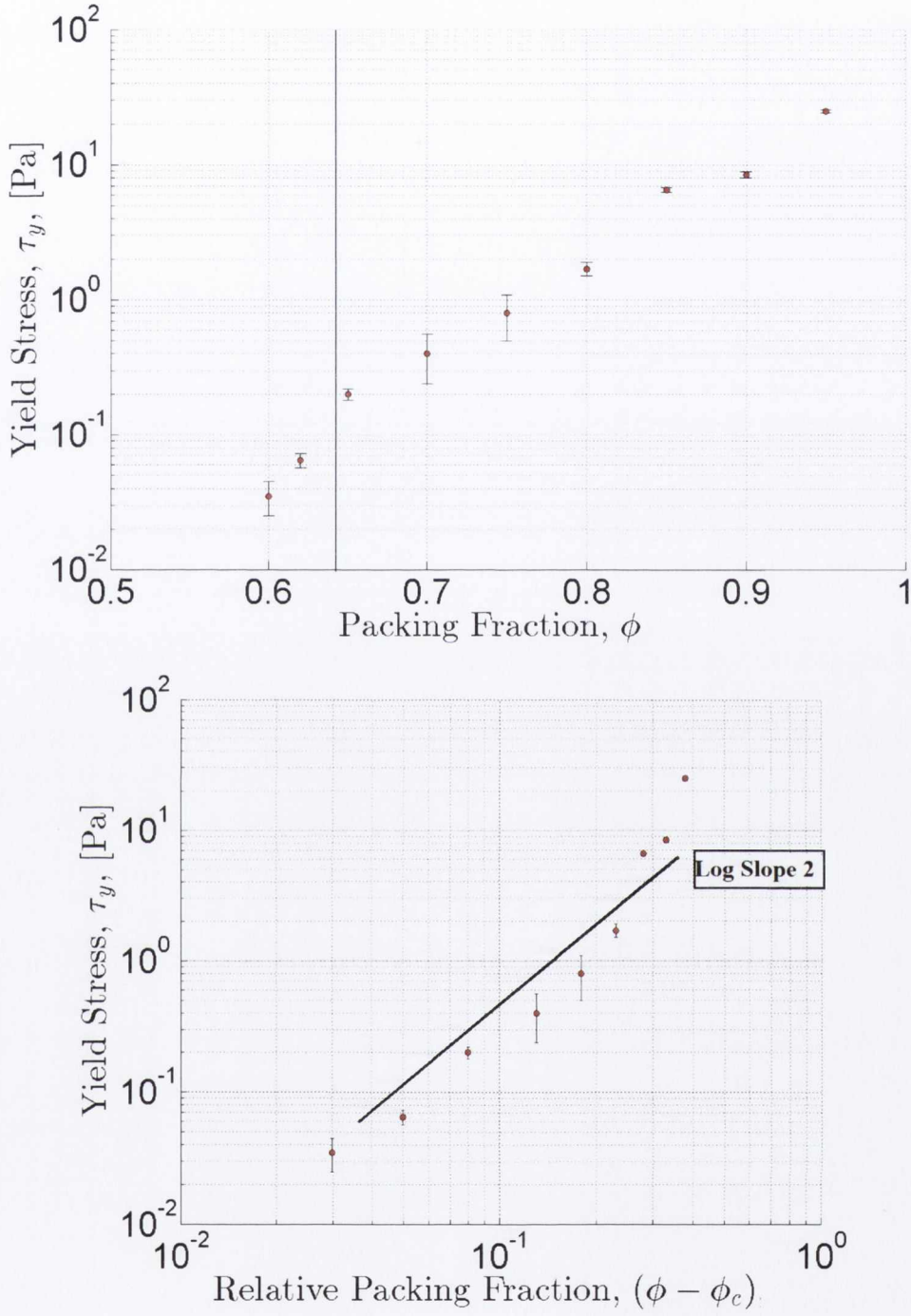


Figure 4.9: The yield stress as a function of packing fraction obtained by fitting to Herschel-Bulkley. A log slope 2 is included in the loglog plot as this is the trend that has been reported in the literature.

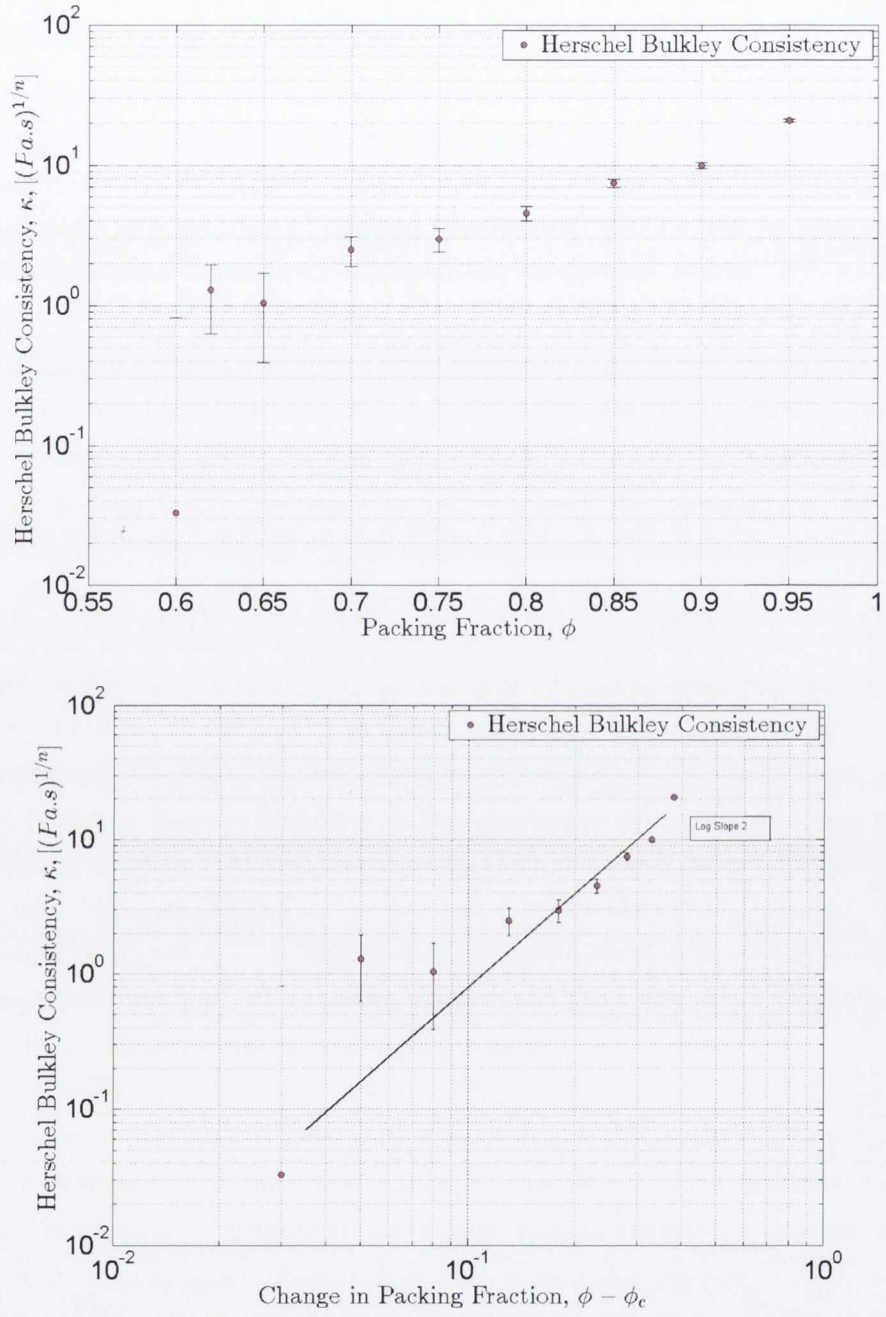


Figure 4.10: Consistency, sometimes known as effective viscosity, obtained from fits to the Herschel-Bulkley equation as a function of packing fraction in both a log-lin and log-log ($\phi_c = 0.57$) scaling. From the loglog graph it seems the Herschel-Bulkley consistency increases with a log slope 2 as a function of distance from the critical packing fraction

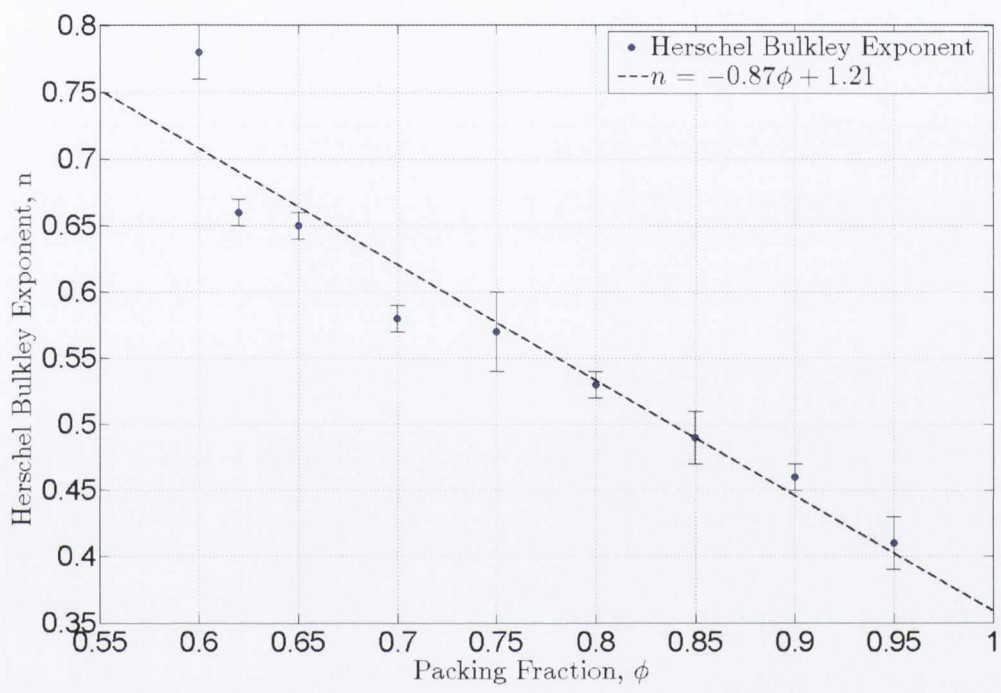


Figure 4.11: Herschel-Bulkley exponent as a function of packing fraction. Dashed line is a linear fit to the data, showing that the exponent decreases linearly with packing fraction is increased meaning the stress experienced by a flowing foam increases with strain rate more dramatically as you decrease the packing fraction.

Figure 4.12 shows the collapse of the flow curves using the flowing scale parameters:

$$\tau(\dot{\gamma}) \rightarrow \frac{\tau(\dot{\gamma})}{\tau_y} \quad (4.1)$$

$$\dot{\gamma} \rightarrow \frac{\dot{\gamma}}{\dot{\gamma}_c} \quad (4.2)$$

Where $\dot{\gamma}_c$ is chosen such that all the data falls onto a master curve after the stress has been normalised by τ_y . Figures 4.13 and 4.14 show these scaling factors, τ_y and $\dot{\gamma}_c$, as a function of both ϕ and $(\phi - \phi_c)$.

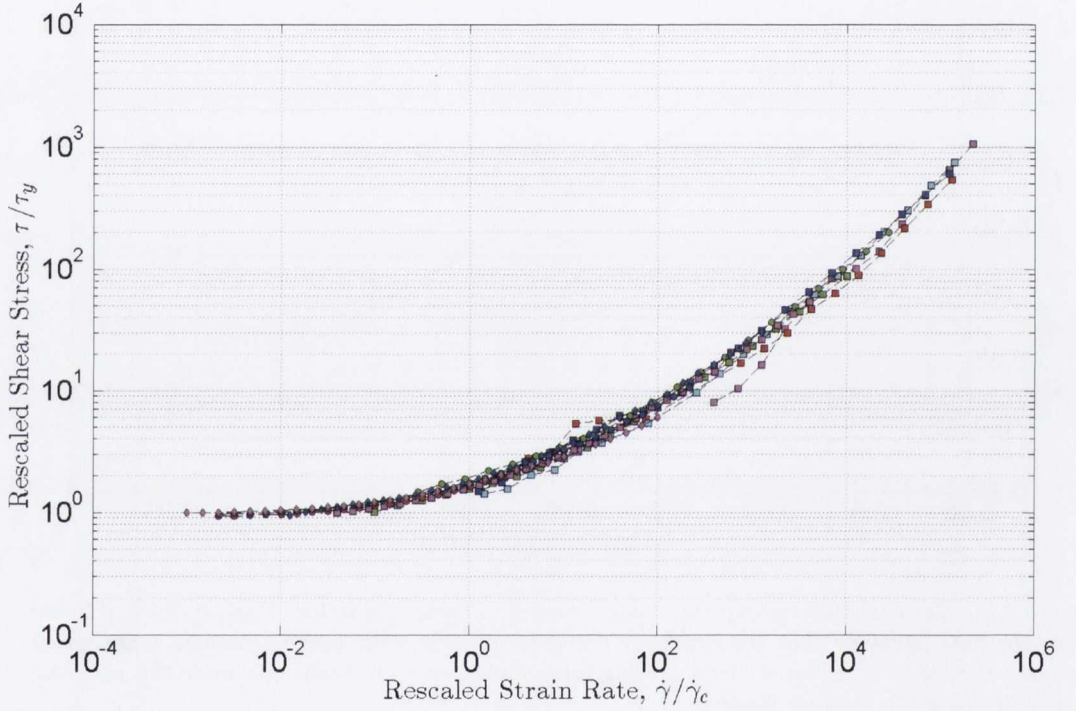


Figure 4.12: Stress versus strain rate data rescaled onto one master curve by the yield stress and critical strain rate.

This plot shows that one master curve can be produced from all packing fractions investigated. In the experimental work of Parades *et al.* this is not the case. Below ϕ_{RCP} the data scales onto a second curve (See Figure 2.4). However it is not surprising that ours is different as in their case they use a repulsive emulsion

which does not exhibit a yield stress flow below ϕ_{RCP} . Now we look at the rescaling factors, which for the stress axis is the yield stress τ_y and for the strain rate axis we call it $\dot{\gamma}_c$, a characteristic strain rate which identifies the point at which the flow curve begins to depart from the plateau. We can identify two different regimes in both cases as indicated by a vertical straight line through the data. Below ϕ_{RCP} , τ_y and $\dot{\gamma}_c$ seem to plateau. This corroborates the arguments we have already made regarding the possible existence of different mechanics below ϕ_{RCP} . However, τ_y and $\dot{\gamma}_c$ above ϕ_{RCP} have exponents, which we call α and β which are consistent with those found by Paredes *et al.*[86] and which we have indicated on the plots. As mentioned this rescaling approach has been used as two independent models both suggested that the ratio of α and β correspond to the Herschel-Bulkley exponent. [86, 90]. α and β from these two research groups did not agree, which is no surprise as Paredes *et al.* conducted experiments on emulsions while Teitel *et al.*[90] used the Bubble Model, but the ratio of the two in both cases were found to be ≈ 0.5 , which our data is also consistent with above ϕ_{RCP} .

Before we proceed we can now collect all our measurements of the yield stress. We have, the intersection of the two regimes in stress versus strain from oscillatory strain sweeps, Figure 4.5, the yield stress as obtained by fitting stress versus strain rate data to the empirical Herschel-Bulkley equation, Figure 4.13, and we have, β , the stress rescale values from Figure 4.12, and the yield stress as determined from fitting to the Herschel-Bulkley Equation, Figure 4.9. We present the comparison of these values as well as some from the literature, all of which have been normalised by the Laplace pressure, in Figure 4.15.

By placing a Log slope 2 as a guide to the eye it would seem that the quadratic relationship holds for our system also. As in the shear modulus data our results fall below the literature values. We can resolve this by returning to Rouyer *et al* and their attempt to normalise the yield stress by the shear modulus as in this case the Laplace pressure cancels out. Presented in Figure 4.16 are our values of shear modulus normalised by the yield stress and compare with what values we could obtain from the literature and attempt to fit to $\frac{\tau_y}{G_0} = \frac{(\phi - \phi_c)^2}{\phi(\phi - \phi_c)} = \frac{\phi - \phi_c}{\phi}$, using both $\phi_c = 0.57$ and $\phi_c = 0.64$.

By normalising in this fashion we find that the data scales onto one curve as shown by Rouyer *et al.* However, the fit, $\frac{\phi - \phi_c}{\phi}$, does not seem to capture our data very

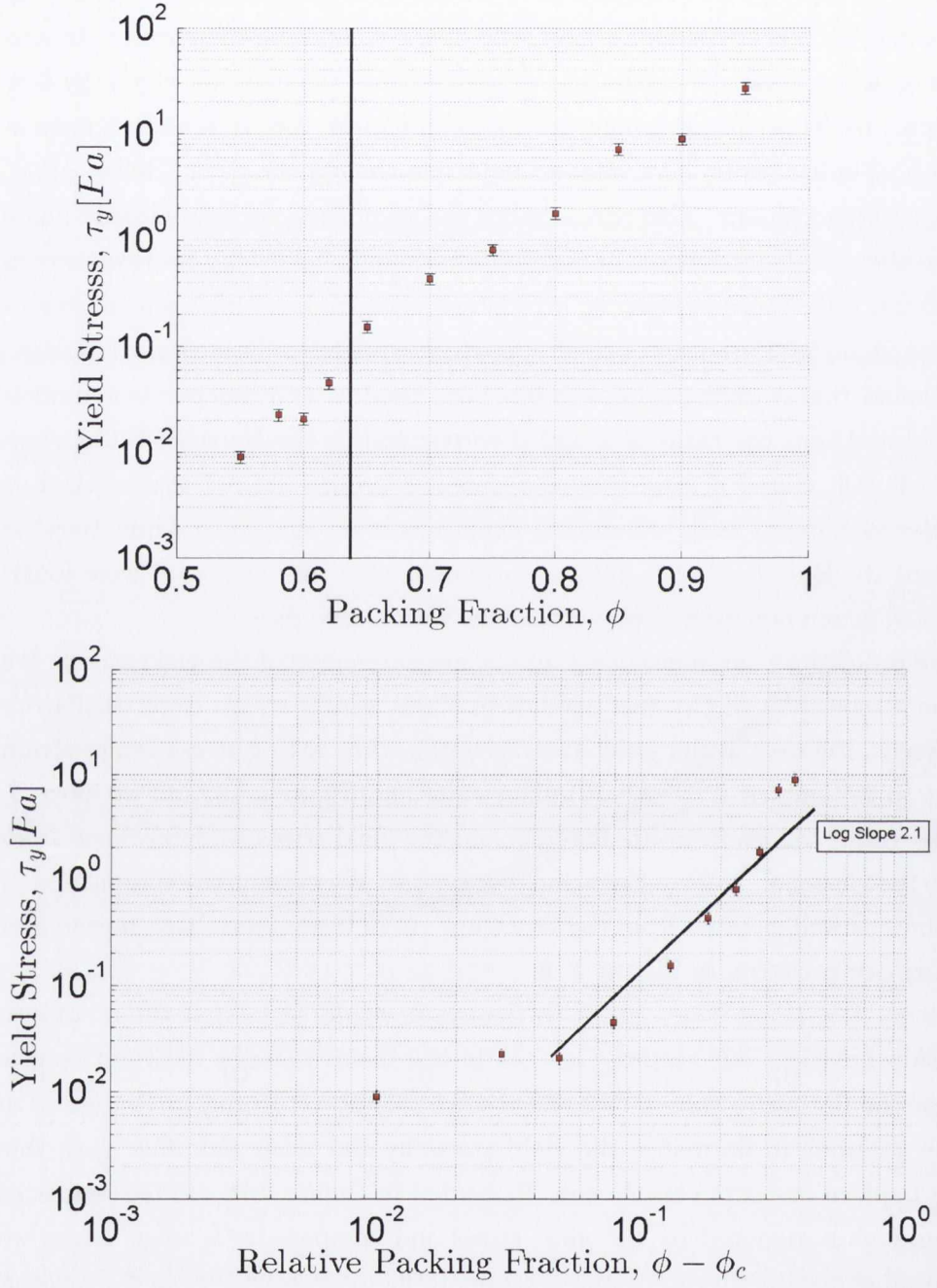


Figure 4.13: Yield Stress, τ_y from rescaling stress versus strain rate data, for both packing factors and as a function of $\phi - \phi_c$. Solid line in the loglog graph is log slope of 2.1 as measured by Paredes *et al.* [86] and consistent with the $\tau_y(\phi)$ relationship found using oscillatory rheology (See Figure 4.6).

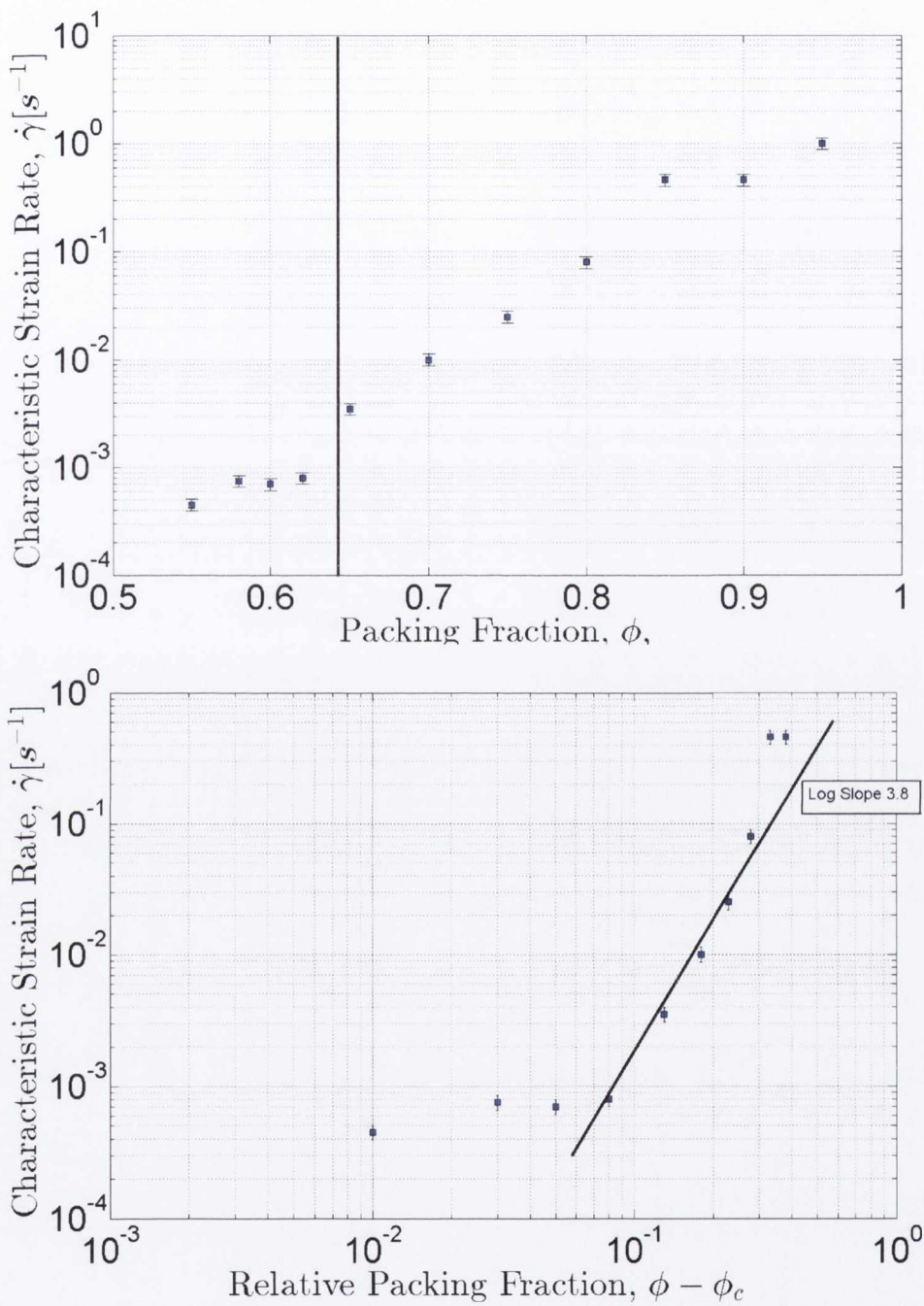


Figure 4.14: Strain rate rescale values, $\dot{\gamma}_c$, from stress versus strain rate data as both a function of ϕ and $(\phi - \phi_c)$. Solid line in the loglog graph is log slope of 3.8 as measured by Paredes *et al.* [86].

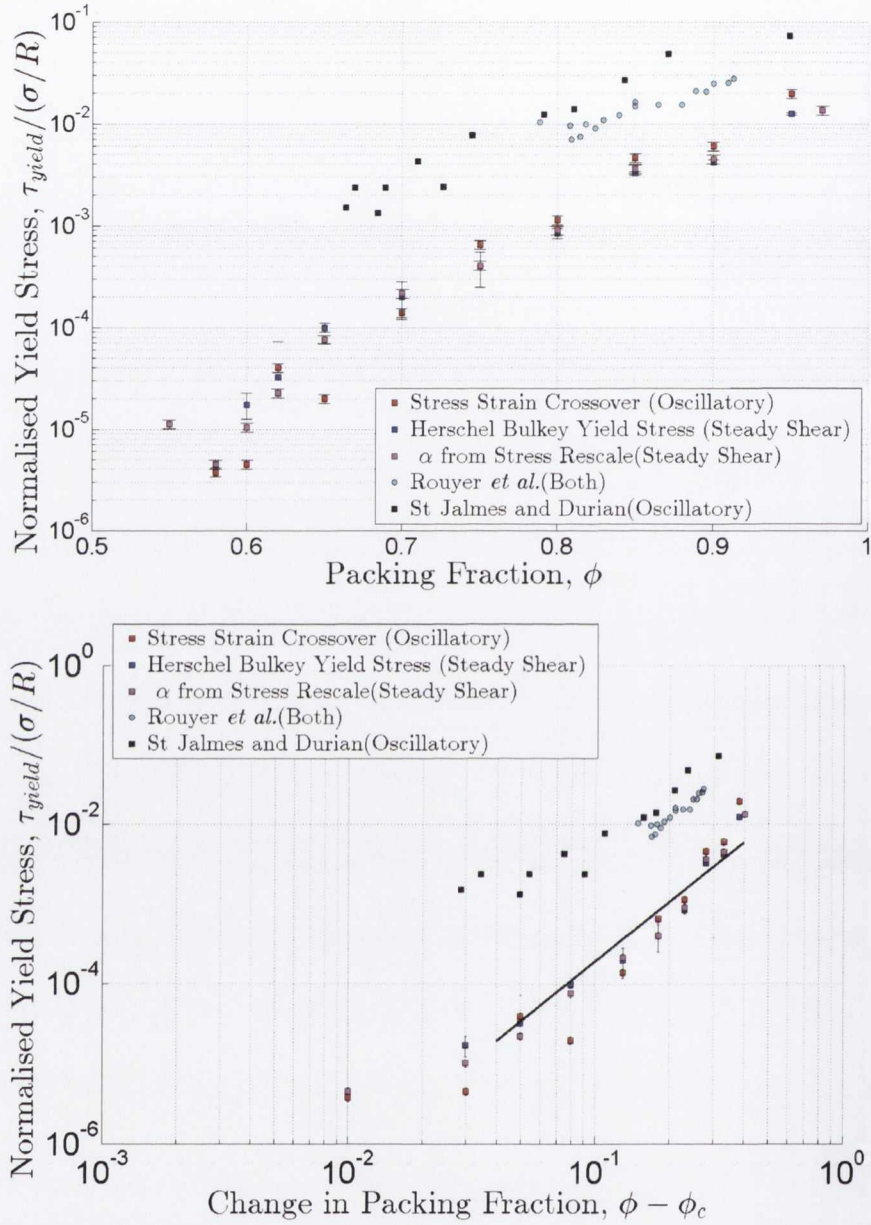


Figure 4.15: The yield stress as obtained from crossover in stress versus strain oscillatory measurements (red) as shown in Figure 4.6, by fitting to Herschel-Bulkley (blue), as shown in Figure 4.9, by rescaling the stress from the flow curve (pink), as shown in Figure 4.13, compared to the values obtained by Rouyer using both steady shear and oscillatory measurements [72] and St Jalmes using oscillatory measurements [70]. The yield stress has been plotted as both a function of packing fraction and distance from ϕ_c . A log slope 2 shows that our data adheres to the well established quadratic trend.

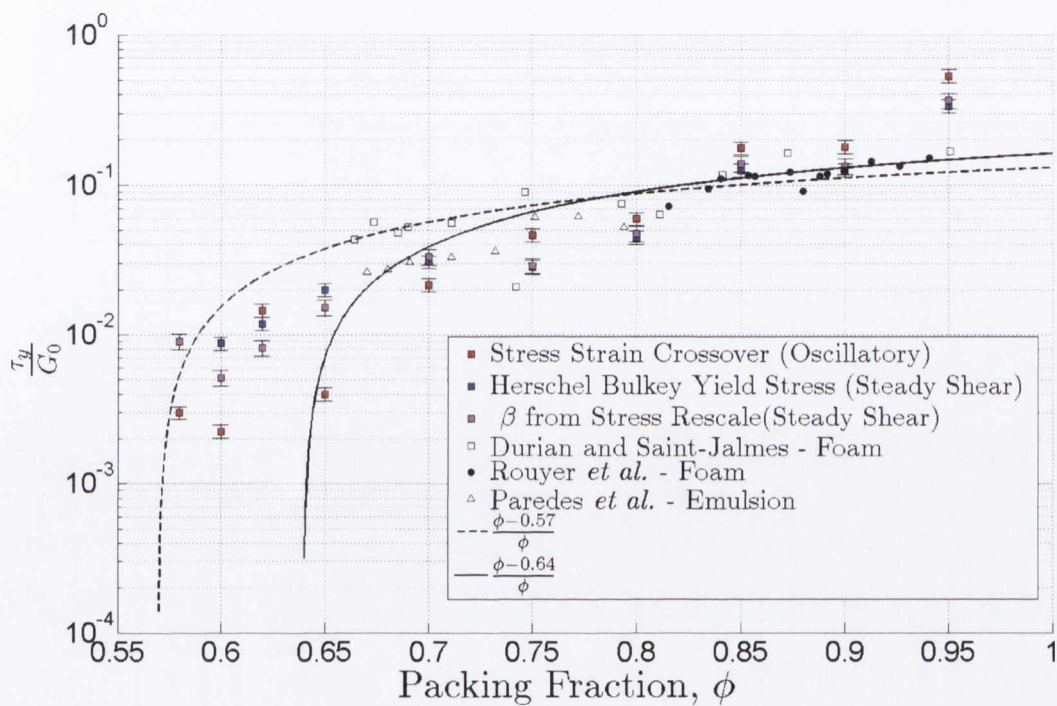


Figure 4.16: The shear modulus normalised by the yield stress and compared with values measured by Saint-Jalmes (squares) Rouyer (circle) and Bonn (triangles). We fit the the function used by Rouyer, $\frac{\tau_y}{G_0} \propto \frac{(\phi - \phi_c)}{\phi}$, using $\phi_c = 0.57$ and $\phi_c = 0.64$.

well when we use $\phi_c = 0.57$. This is not surprising as we have shown several times that the behaviour below ϕ_{RCP} is different than above. We leave this fit in to show the reader that when using attractive emulsions, behaviour above ϕ_{RCP} is consistent with what has been found for purely repulsive emulsions but new models need to be suggested to describe elastic behaviour below ϕ_{RCP} . Note that we had to remove the final data point from this fit. We justify this by acknowledging the findings of Gardiner whose experiments suggest that at packing fractions close to unity the measured stress increases rapidly due to fracturing [73]. We conclude this section by once again reiterating that above ϕ_{RCP} the behaviour of an attractive emulsions mirrors that of a repulsive emulsion. However despite the existence of elasticity this behaviours does not simply continue below ϕ_{RCP} .

4.3 Conclusions and Outlook

So far we have characterised the macroscopic rheology as a function of packing fraction of an attractive emulsion using conventional techniques, that is amplitude sweeps and flow curves. Our first finding was that elasticity exists below ϕ_{RCP} and the shear modulus follows Mason's trend, $G_0 \propto \phi(\phi - \phi_c)$ where we found $\phi_c = 0.57 \pm 0.015$. However when we attempted to fit our yield stress data to the accepted trends, that is $\tau_y \propto (\phi - \phi_c)^2$ or $\frac{\tau_y}{G_0} \propto (\phi - \phi_c)/\phi$ we found that they fit best when we take $\phi_c = \phi_{RCP}$, suggesting the existence of different yielding mechanisms below ϕ_{RCP} for attractive emulsions. The most important finding presented in this chapter however was the slip measured in our system despite the use of sandpaper. We found that the actual strain rate experienced by the emulsion is 0.29 times the strain rate imposed by the rheometer. This is highly significant as it is the custom in the field of foam and emulsion rheology to assume that the use of sandpaper or roughened surfaces completely removes this slip. This clearly is not the case and strain rates reported in the literature may not correspond to the real ones. Now that we have characterised our emulsion and identified the critical packing fractions as well as two different yielding mechanisms we are in a position to discuss the relaxation time of an adhesive emulsion.

Chapter 5

The Relaxation Time of an Adhesive Emulsion

*“The only way to make sense out
of change is to plunge into it,
move with it, and join the dance.”*

-Alan Watts

Now that we have characterised the macroscopic properties of our emulsion we can take a look at the internal time scale that govern these responses, namely the relaxation time. How is the relaxation time affected by packing fraction? Can the relaxation time be used in conjunction with the deformation-relaxation ansatz to describe the Herschel-Bulkley type stress versus strain-rate relation? What does the non-equilibrium Stokes-Einstein relation tell us about the elastic fluctuations in a flowing emulsion? We begin this chapter with a discussion of the relaxation time as measured by strain rate frequency superposition. We will then discuss the results obtained by measuring the mean square displacements of the tracer particles at a given strain rate. We will conclude by comparing the results of the two measurements and exploring their implication in the deformation-relaxation ansatz and the non-equilibrium Stokes-Einstein relation.

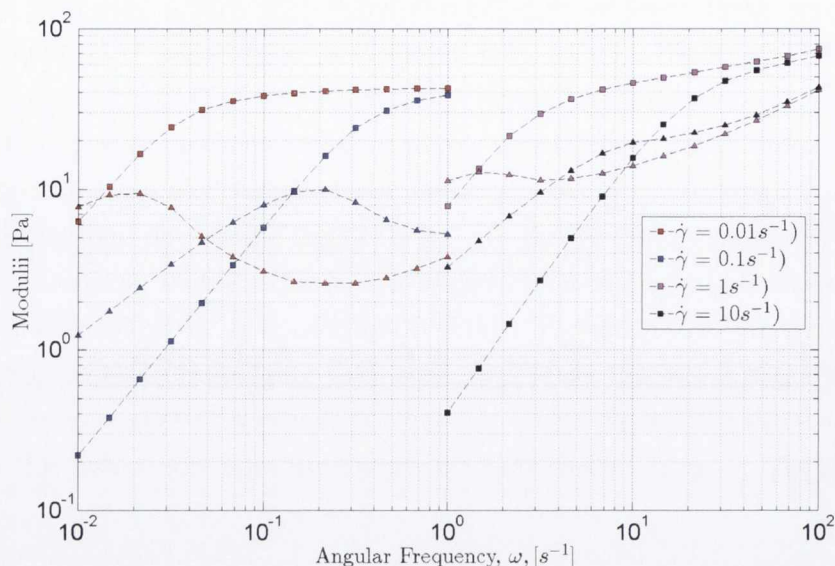


Figure 5.1: Storage modulus (squares) and loss modulus (triangles) from constant strain rate frequency sweeps (SRFS) as a function of angular frequency for four different imposed strain rates as indicated in legend

5.1 Strain Rate Frequency Superposition

Strain rate frequency superposition measurements allow us to directly measure the relaxation time as both a function of packing fraction and strain rate. By varying both the strain amplitude and frequency we can perform constant strain rate oscillatory measurements. Presented in Figure 5.1 is the raw data for a sample of strain rates investigated for $\phi = 0.95$.

To make sense of this plot we remind the reader of strain sweeps (Figure 3.17 in Section 4.1.1). In SRFS the strain rate is the product of the strain amplitude and the frequency, $\dot{\gamma} = \gamma\omega$, so if we divide the frequency by the strain rate we have a constant strain rate strain sweep. G', G'' versus strain from the data shown in Figure 5.1 is presented in Figure 5.2.

In the same way we defined the yield strain in the amplitude sweeps we define the relaxation time as the inverse frequency at which the departure from the G' plateau occurs. In Figure 5.3 we show rescaled strain rate frequency superposition

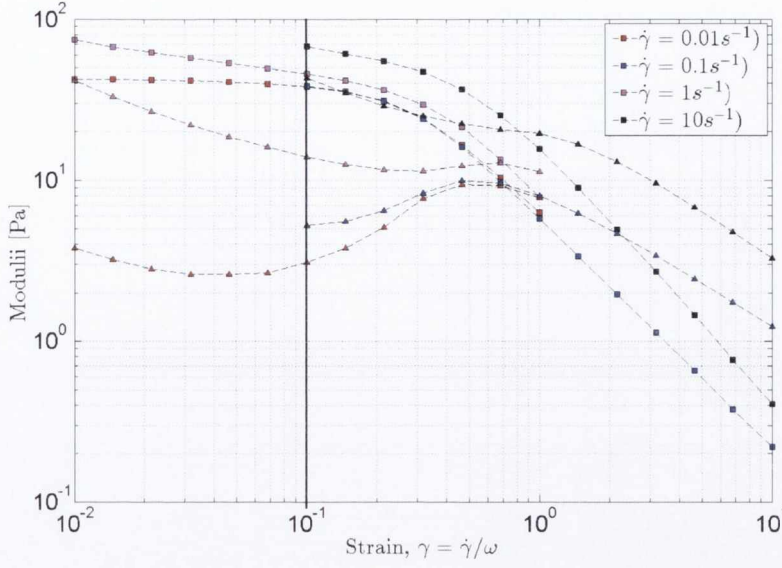


Figure 5.2: Storage modulus (squares) and loss modulus (triangles) from versus strain from constant frequency sweeps (SRFS) for four different imposed strain rates as indicated in legend. The solid line signifies the departure from the linear response regime which we have used to define the onset of yielding (See Section 4.1.1).

graphs for $\phi = 0.95$ and $\phi = 0.75$. The rescaling was done in the following way,

$$G', G'' \rightarrow \frac{G_0}{a}, \quad (5.1)$$

where G_0 is the shear modulus at the lowest strain rate measured and

$$\frac{\omega_c(\dot{\gamma})}{t_r^{SRFS}(\dot{\gamma})} = 1. \quad (5.2)$$

In Figure 5.4 we plot the relaxation time obtained from equation 5.2 as a function of strain rate for all packing fractions investigated. Note that the strain rate has been corrected using Equation 3.26.

Before proceeding we will briefly discuss why the number of data points per curve decreases as the packing fraction decreases. This is due to the relationship between the yield strain and the packing fraction. There is a frequency limit of 100 Hz on the rheometer. Recall that the strain rate is set by $\dot{\gamma} = \gamma_0 \omega$. We show in Figure 5.23 that as the packing fraction decreases the yield strain decreases. In SRFS

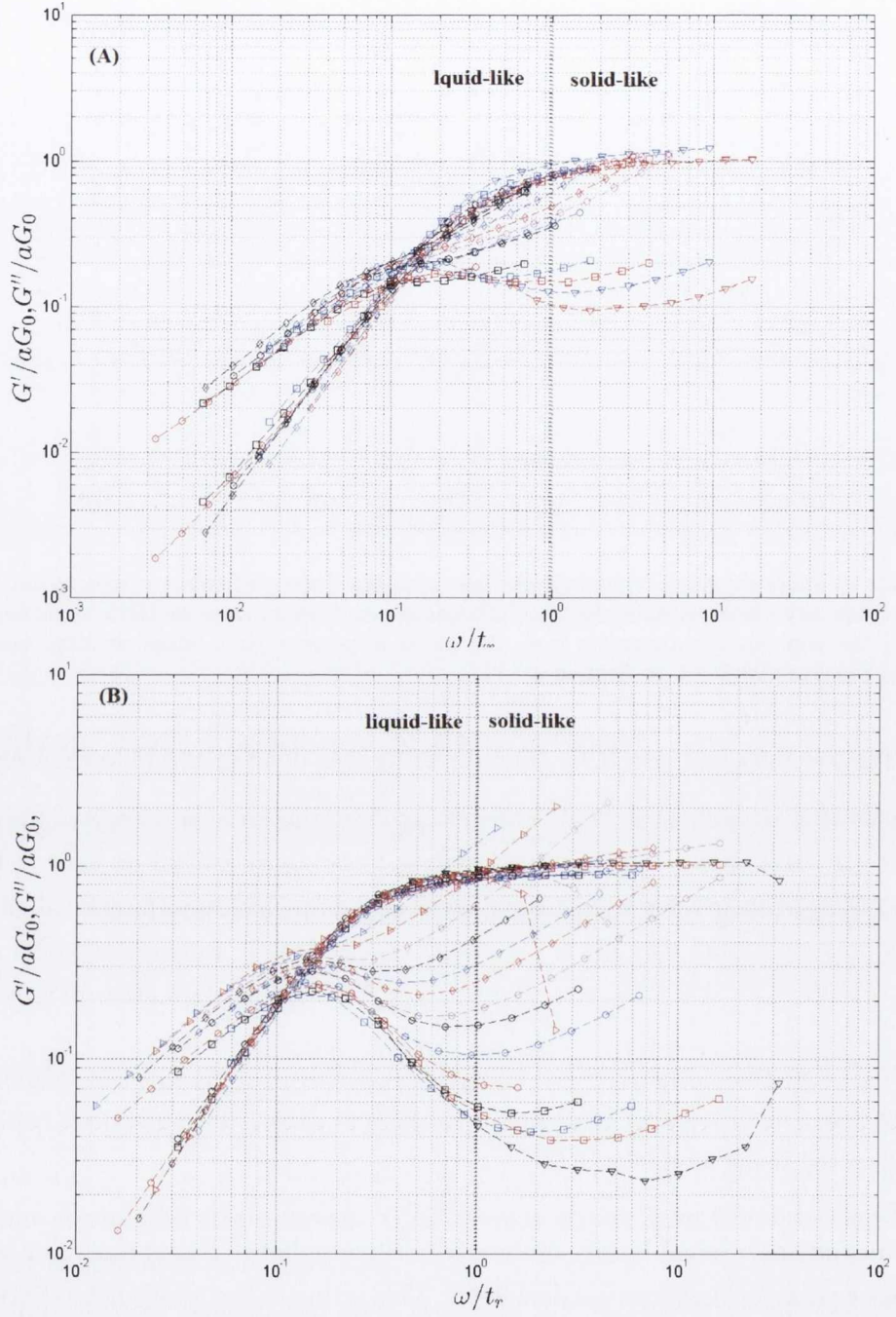


Figure 5.3: Rescaled strain rate frequency superposition graphs for $\phi = 0.75$ (A) and $\phi = 0.95$ (B). Here the Loss and Storage modulus have been rescaled by aG_0 where a is a prefactor that varies with strain rate and the frequency has been rescaled by the relaxation time t_r .

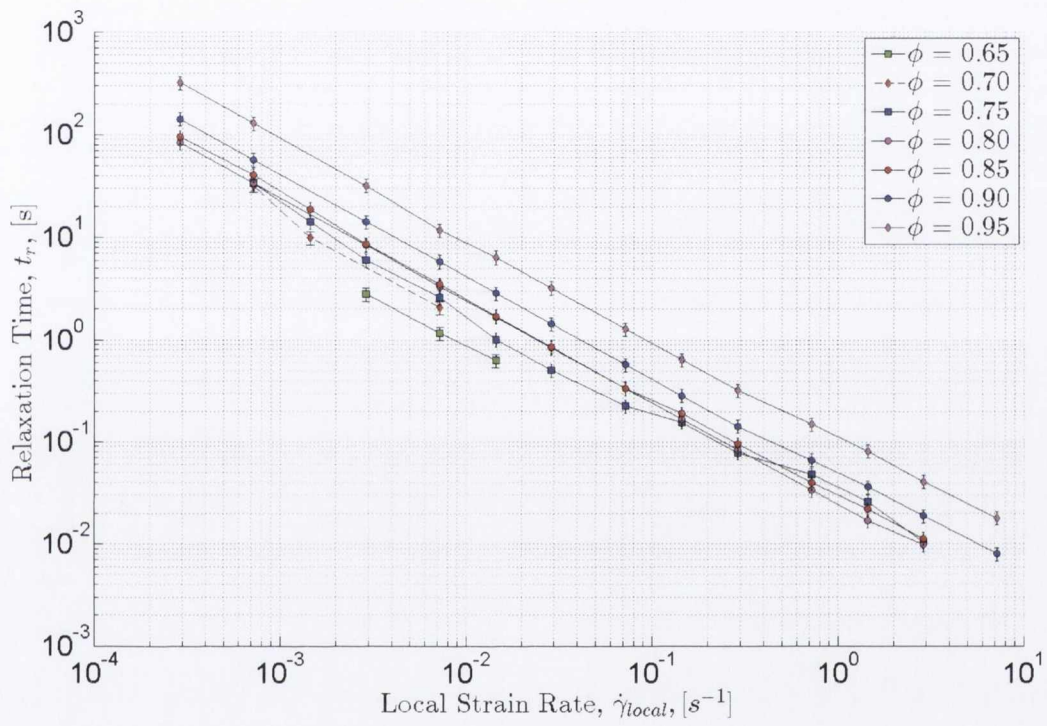


Figure 5.4: Relaxation time versus strain rate for different packing fractions as indicated in the legend. The relaxation time is taken as the inverse characteristic frequency in strain rate controlled frequency sweeps (SRFS).

measurements the range of the strain amplitude has to be both above and below the yield strain so that the liquid-like to solid-like transition can occur. If the strain amplitude is always above the yield strain the system will exhibit a liquid like response throughout the entire frequency range. As we reduce the packing fraction we reach the frequency limit and the system only exhibits a solid-like to liquid-like transition at lower strain rates where γ_0 can be below the yield strain. Returning to Figure 5.4 we observe that all the packing fractions appear to exhibit a similar trend. As such, we rescale the data onto a master curve and plot the scaling factors as a function of packing fraction. We call the non-dimensional scale factor ζ and is defined by,

$$\zeta(\dot{\gamma}) = \frac{t_r^{SRFS}(\dot{\gamma}, \phi)}{t_r^{SRFS}(\dot{\gamma}, \phi = 0.65)}. \quad (5.3)$$

We plot the rescaled relaxation time, ζt_r^{SRFS} , as a function of strain rate in Figure 5.5 where the strain rate has been corrected using Equation 3.26.

By fitting this rescaled data to a power law we find that $t_r^{SRFS} \propto \dot{\gamma}^{-0.97 \pm 0.015}$. This is in agreement with what Marze *et al.* found for repulsive emulsions [80]. Datta *et al.* also found a similar relationship for attractive emulsions, $t_r \propto \dot{\gamma}^{-0.95}$, when $\phi > \phi_{RCP}$ [36]. Before moving on we plot the rescaled values as a function of ϕ to examine how the relaxation time varies with packing fraction. In Figure 5.6 we plot the relaxation time as a function of ϕ and $(\phi - \phi_c)$.

We observe that no clear power law exists but for $\phi < 0.95$, ζ , appears to go as,

$$\zeta \propto (\phi - \phi_c) \quad (5.4)$$

Based on this we can now sum up the relaxation time dependence on strain rate and packing fraction as measured by strain rate frequency superposition via,

$$t_r^{SRFS}(\dot{\gamma}, \phi) \propto \zeta \dot{\gamma}^{-0.97 \pm 0.015} = \frac{(\phi - \phi_c)}{\dot{\gamma}^{0.97 \pm 0.015}} \quad (5.5)$$

We will examine this further in Section 5.2.2 when we discuss the relaxation time as measured microscopically. Before we move onto the microscope dynamics we

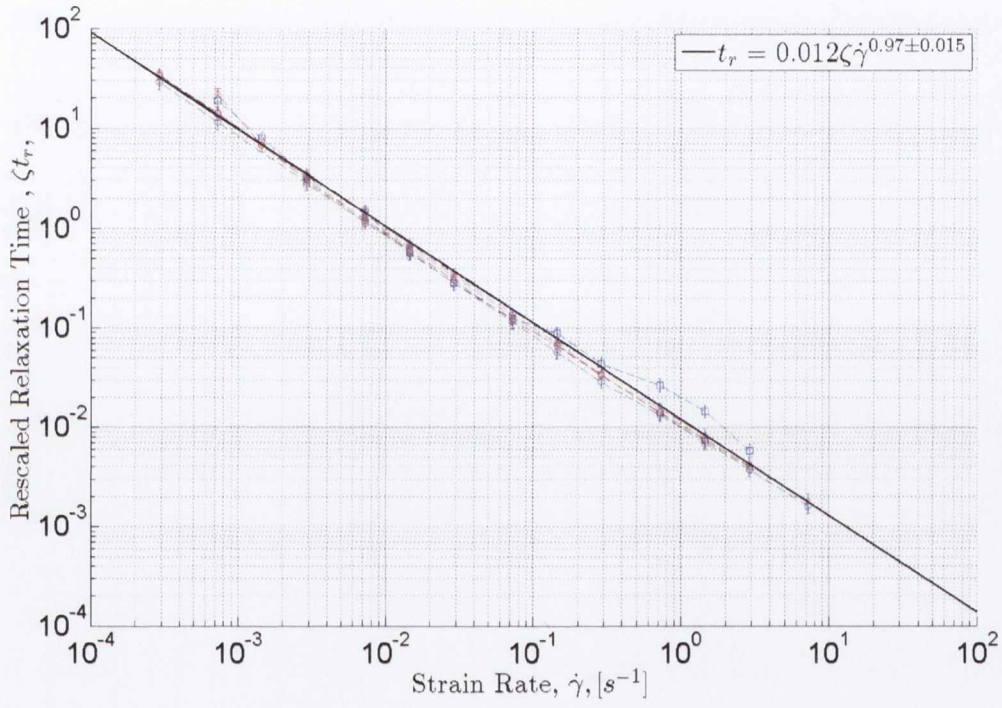


Figure 5.5: Rescaled relaxation time, ζt_r^{SRFS} , as a function of strain rate for different packing fractions with a fit to $\dot{\gamma}^{0.97 \pm 0.015}$ (dashed line).

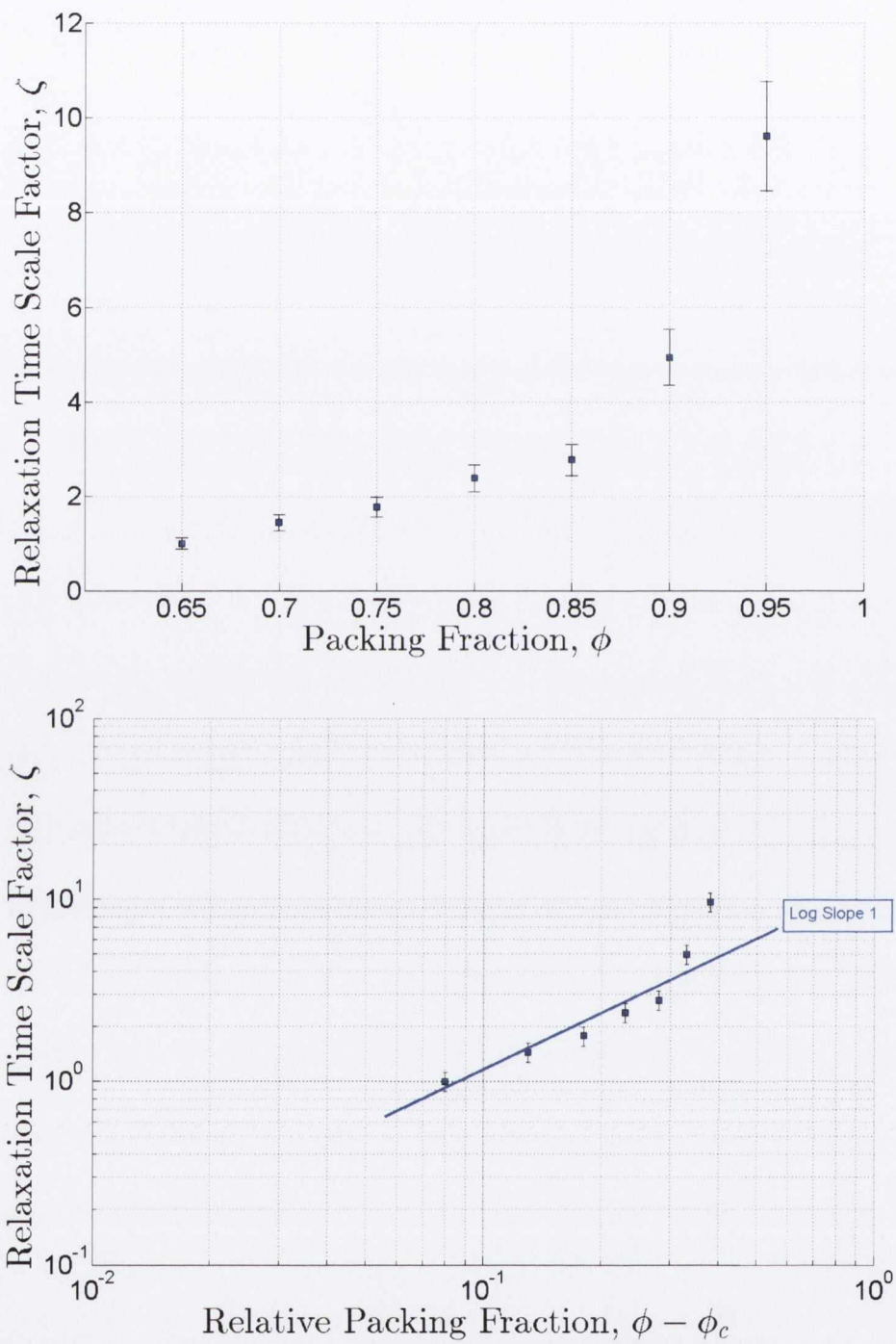


Figure 5.6: Rescaling factors for the relaxation time for different packing fractions. Blue line is a log slope 1 as a guide to the eye

will discuss how the G' axis also scales with strain rate.

5.1.1 How the Storage Modulus Changes with Strain Rate

As mentioned the storage modulus in SRFS measurements was also rescaled such that the plateau falls onto a single curve (See Figures 3.19 and 5.3). To explore how the shear modulus changes with strain rate in SRFS measurements we plot aG_0 as a function of strain rate for all packing fractions in Figure 5.7.

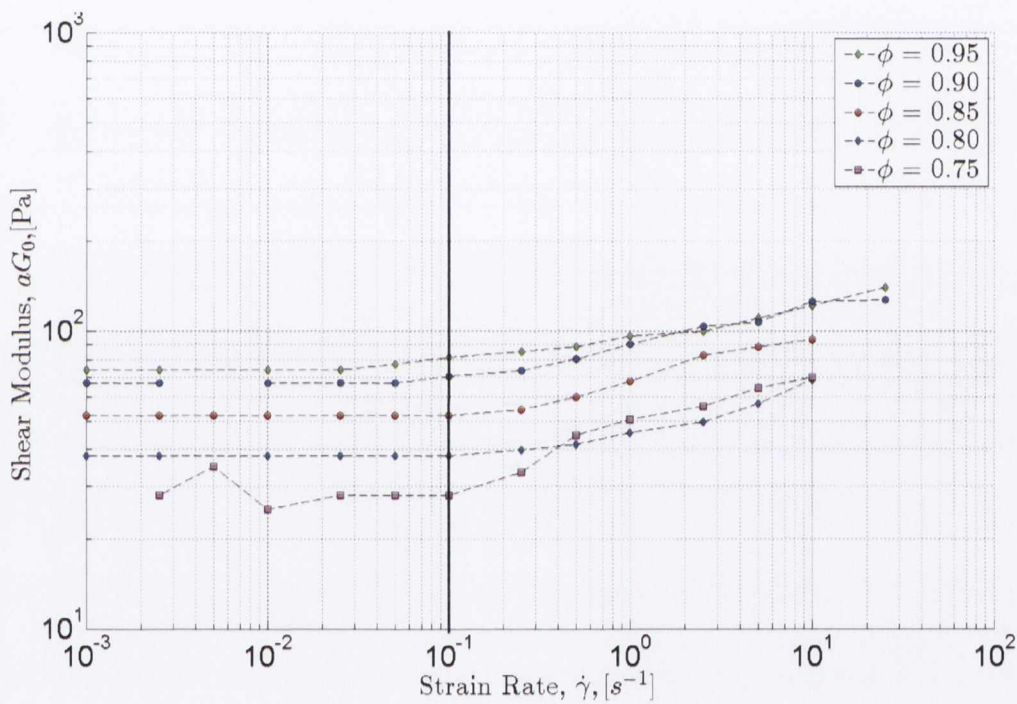


Figure 5.7: Rescaling factors for the storage modulus for different packing fractions, as indicated in legend. The line is placed to highlight the range in which no change is observed in the shear modulus beyond which it appears to increase with strain rate.

The first thing to note is that we have excluded data for $\phi \leq 0.70$ as there are few values and they are non-monotonic. As we have ruled out the effects of coarsening or drainage we find this puzzling. However as we are limited in the volume of data we can acquire at lower packing fractions, as we explained above, we are not in

a position to discuss the possibility of a trend at these packing fractions. What is worth discussing however is, for $\phi > 0.70$, at low strain rates, $\dot{\gamma} \leq 0.1s^{-1}$ the shear modulus is strain rate independent. At what seems to be a packing fraction independent strain rate, $\dot{\gamma} \approx 0.1$, (as indicated by a vertical straight line through the data) it begins to increase. We hypothesize that this arises from surfactant adsorption kinetics at the interfaces during shear. As the system is strained the films expand. This reduces the number of surfactant molecules on the interface per unit area, which would have an effect on the interfacial tension. At low strain rates the molecules in the bulk have time to adsorb on the surface while the system is perturbed, that is the adsorption time $\ll \frac{1}{\dot{\gamma}}$. This means that the surface tension remains unchanged, which as explained in Section 2.1.1 would result in a constant shear modulus. However, we argue, when the adsorption time $\gg \frac{1}{\dot{\gamma}}$ the surfactant molecules do not adsorb to the interface while the film is perturbed. This will increase the surface tension, which in turn increases the shear modulus of the system.

Patist *et al.* have studied surfactant kinetics of Tween20 saturated solutions (i.e. well above CMC) [115]. They studied the slow micellar time constant, which they call τ_2 and is associated with the lifetime of a micelle. For Tween20 they found $\tau_2 = 6s$. Micelles are not static systems and continuously break up and reform at a timescale that is independent of shear, that is, τ_2 . Below this time the surfactant molecules will remain part of a micelle and not be free to adsorb to an interface. At times $\frac{1}{\dot{\gamma}} > \tau_2$ the micelles will break apart and before they reform there will be free molecules in the solution ready to adsorb to the interface. We argue that it is this time scale that sets the increase in shear modulus in SRFS measurements. When the film is stretched at frequencies higher than this slow micellar time constant, $\frac{1}{\dot{\gamma}} < \tau_2$, there will be no free molecules to adsorb and thus the surface tension of the film increases. This in turn causes the shear modulus to increase because $G_0 \propto \frac{\sigma}{R}$. Systematic measurements, with different surfactants with different τ_2 values, would be required to validate this hypothesis. For now we proceed to describe the functional form of this data.

We remind the reader of the deformation-relaxation ansatz (Equation 1.24) which relates the viscosity and the relaxation time via the shear modulus. In previous

studies the shear modulus in this expression was considered to be constant [60, 59]. However in light of these new findings we can no longer say this is so. We use an empirical fit for $G_0(\dot{\gamma})$ that we will use in Section 5.3 when discussing the deformation relaxation ansatz. We fit G_0 to,

$$G_0(\dot{\gamma}) = a + b(\dot{\gamma})^c. \quad (5.6)$$

In Figure 5.8, we present the same data from Figure 5.7 with fits to Equation 5.6.

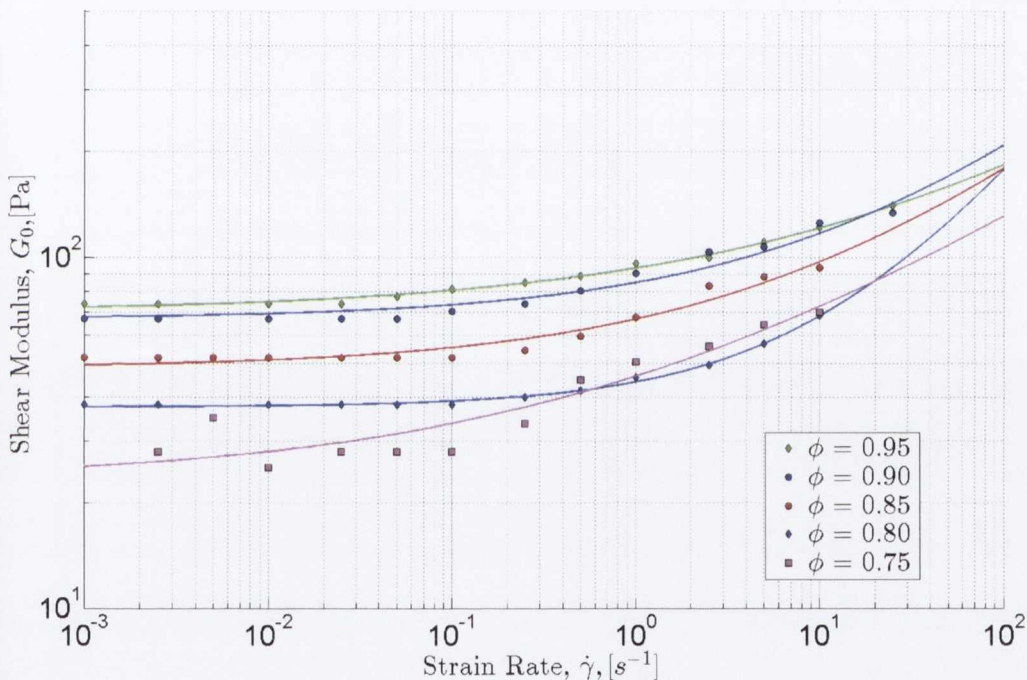


Figure 5.8: Rescaling factors for the storage modulus for different packing fractions, as indicated in legend, along with fits to the functional form of the Herschel-Bulkley relaxation, that is, $G_0(\dot{\gamma}) = G_0(a + b\dot{\gamma}^c)$.

We find that this fits the data well for all packing fractions and can now use this relationship when we discuss the deformation-relaxation ansatz. We also highlight that to the best of our knowledge this phenomenon has not been discussed in the literature.

5.2 Microscopic Droplet Dynamics

In this section we discuss the relaxation time as measured by microscopic tracer particle dynamics which we henceforth call t_r^{micro} . We begin with the relaxation time as a function of strain rate, measured at a constant packing fraction, $\phi = 0.80$, and compare our findings with t_r^{SRFS} . We then discuss the relaxation time as a function of packing fraction, measured at a constant strain rate, $\dot{\gamma} = 0.1s^{-1}$, and compare with t_r^{SRFS} .

5.2.1 Measuring the Diffusion Constant as a Function of Strain Rate

We conducted experiments that allow us to examine the influence of strain rate on the droplet dynamics. Before we can uncover these dynamics we must first look at how the particle dynamics evolve through time at a given strain rate, or equivalently, as a function of strain. The first thing we can do to get an idea of the internal dynamics of this system undergoing increasing strain is to look at the evolution of particle displacement distributions. Figure 5.9 shows the distribution of particle displacements, normalised by the width, at four different times (strains) under steady shear conditions for an imposed strain rate of $\dot{\gamma} = 0.1s^{-1}$.

As evident in this plot at short times the distribution has fat tails, this is suggestive of the presence of only a small number of local rearrangements that give rise to the large displacements found in the tails. This distribution eventually evolves into a Gaussian which reflects many rearrangements giving rise to random walk dynamics, that is, the emulsion is undergoing plastic flow. The insets show the corresponding Kurtosis (right) and mean square displacements (left) both which are defined below in Equations 5.11 and 5.7.

We want to investigate the change in the mean square displacement as a function of time, or strain, from which the relaxation time and the diffusion constant can be inferred. We calculate the radial mean square displacements, $\langle \Delta s_r^2 \rangle$, and azimuthal radial mean square displacements, $\langle \Delta s_a^2 \rangle$, from the moments of the displacement distributions via,

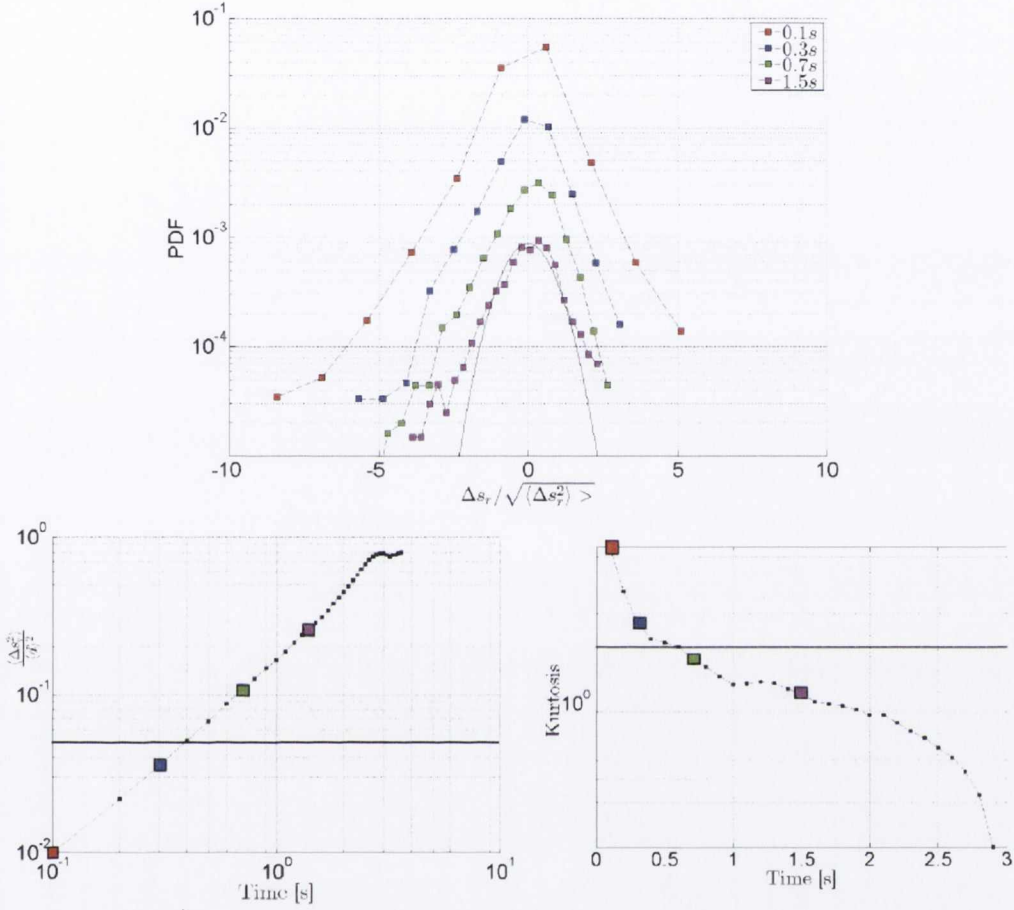


Figure 5.9: Evolution of tracer particle displacement distributions, normalised by the width and shifted for clarity, for difference times (strain) for an imposed strain rate, $\dot{\gamma} = 0.1s^{-1}$ with corresponding mean square displacements (left inset) and excess Kurtosis(right inset). At $t = 0.1s$ (red) the distribution exhibits fat tails indicating the presence of only a few droplet rearrangements. At larger times, $t = 1.5s$ the distribution has become fully Gaussian indicative of diffusive dynamics (plastic flow). The MSD and Kurtosis for the PDFs are indicated by corresponding colours in the inset. Note: Horizontal line in the Kurtosis inset it at 3, the point at which we define the onset of flow and the horizontal line in the mean square displacements is the Lindemann criterion for our system, the threshold beyond which the system is undergoing dissipative rearrangements.

$$\langle \Delta s_r(\delta t)^2 \rangle = \langle s_r(\delta t)^2 \rangle - \langle s_r(\delta t) \rangle^2, \quad (5.7)$$

$$\langle \Delta s_a(\delta t)^2 \rangle = \langle s_a(\delta t)^2 \rangle - \langle s_a(\delta t) \rangle^2 \quad (5.8)$$

were s_r is the in the radial displacement and s_a the azimuthal displacement defined by

$$s_r(\delta t) = r(t + \delta t) - r(t), \quad (5.9)$$

$$s_a(\delta t) = (R + \frac{s_r(\delta t)}{2})(\theta(t + \delta t) - \theta(t)) - \langle s_a(\delta t) \rangle \quad (5.10)$$

were R is the distance to the centre of the rotating plate geometry and $\langle s_a(\delta t) \rangle$ is the mean displacement in the shear direction. As there is no mean flow in the radial direction, $\langle s_r(\delta t) \rangle = 0$ (see Figure 3.23). Presented in Figure 5.10 are the mean square displacements versus time in the radial direction for a selection of strain rates. A log slope 1 has been placed on this plot as a guide to the eye as this relationship is expected for diffusive dynamics.

Next we present the mean square displacements measured in the azimuthal direction, that is, in the direction of shear. Figure 5.11 shows a selection of azimuthal mean square displacements as a function of time. The dashed line shows that $\langle \Delta s_a^2 \rangle \propto t^{1.5}$ indicating that there are additional mechanisms at play that contribute to droplet dynamics such as Taylor dispersion which leads to super-diffusive behaviour due to the shear flow [116]. In Taylor dispersion the shear flow effectively smears out the concentration distribution in the direction of flow which would lead to the observed super-diffusivity. To simplify our analysis we focus only on diffusion in the radial direction, that is diffusion perpendicular to the shear flow, where the mean flow is zero.

Before we can proceed we need to define the onset of diffusive motion. One way is to look at the Kurtosis to determine the shape of the displacement distribution. The radial excess Kurtosis, K_r , is defined as,

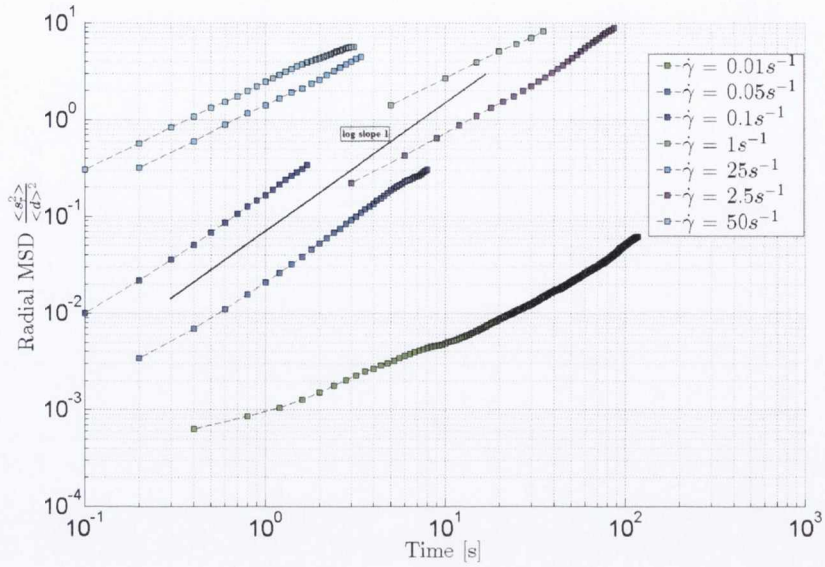


Figure 5.10: The radial mean square displacements, normalised by the average droplet diameter, as a function of time (equivalent to strain) for some strain rates investigated as indicated in legend. Black dashed line is a guide for the eye with a log slope 1 indicating that the behaviour is diffusive.

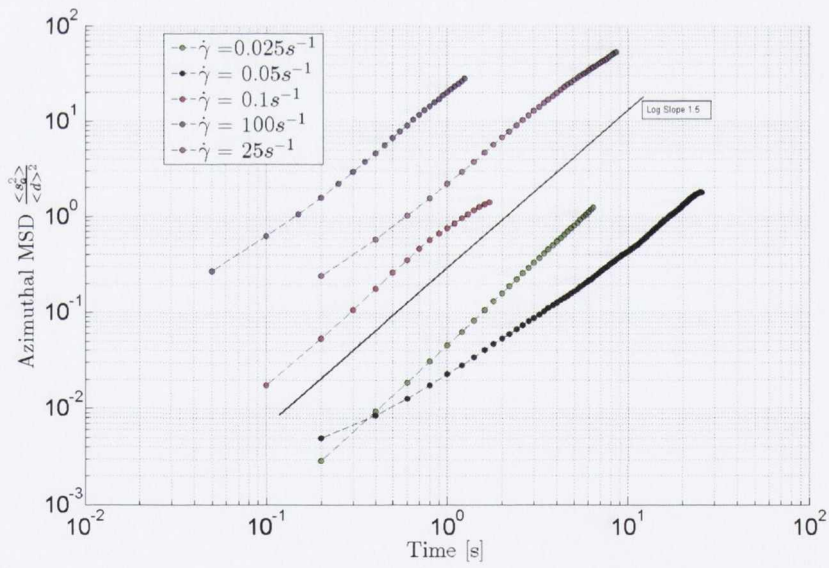


Figure 5.11: The azimuthal mean square displacements, normalised by the average droplet diameter, as a function of time (equivalent to strain) for some strain rates investigated as indicated in legend. Black dashed line is a guide for the eye with a log slope 1.5.

$$K_r = \frac{\langle \Delta r^4 \rangle}{\langle \Delta r^2 \rangle^2} - 3. \quad (5.11)$$

The kurtosis measures the “tailedness” of a distribution and has well defined values for various distributions. A Gaussian distribution has an excess Kurtosis of 0. In our case the kurtosis decreases monotonically. We use the exponential distribution to define the onset of flow which has an excess kurtosis = 3. Presented in Figure 5.12 is the excess kurtosis as a function of root mean squared displacement for a selection of strain rates investigated.

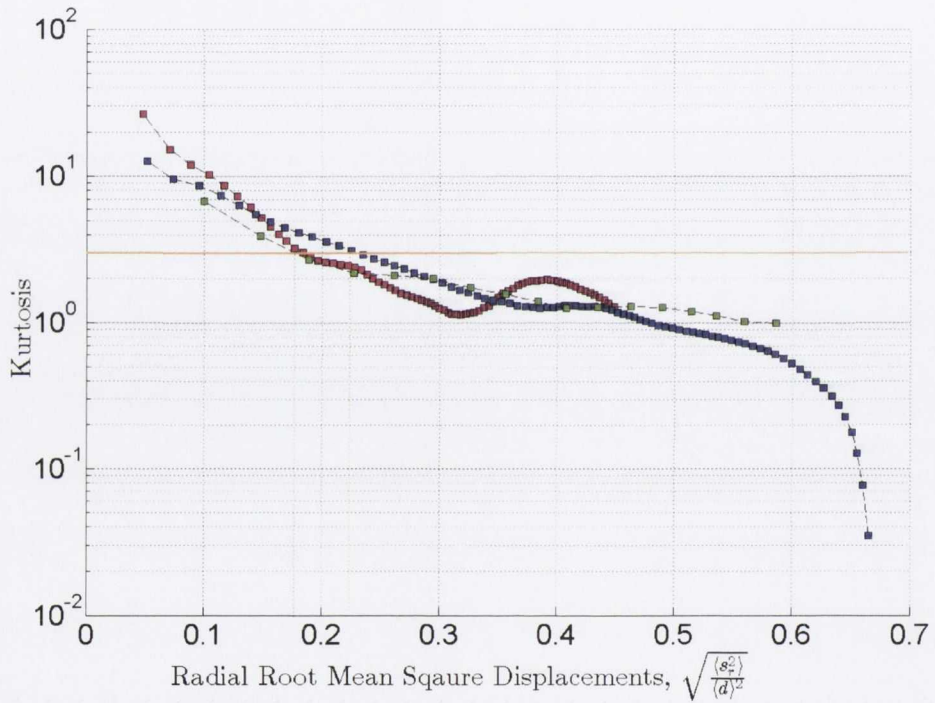


Figure 5.12: The excess kurtosis for a selection of imposed strain rates, $\dot{\gamma} = 0.05$ (red), $\dot{\gamma} = 0.1$ (blue), $\dot{\gamma} = 0.5$ (green), as a function of the root mean squared displacement. A kurtosis of 3 (orange line) corresponds to an exponential distribution which we define as the onset of diffusion. The corresponding root mean square displacement is how we define the onset of flow. Note that as the kurtosis amplifies the low frequency events noisy data can skew the kurtosis which is why we cant use it to calculate the onset of plastic flow for all samples. From this data we take the threshold to be to be $0.2 \pm 0.03d$, which agrees with 2D experiments and simulations [60, 59].

Unfortunately we cannot use the Kurtosis to measure the onset of diffusion, i.e.

the relaxation time, in all cases. Firstly the time resolution in the triangular shear measurements is larger than the time it takes for diffusive flow to begin (the relaxation time) and the mean square displacements are always in the diffusive regime. As such they will always have a kurtosis less than 3. Secondly the kurtosis is highly sensitive to noise in the tail and not all of our measurements have a well defined kurtosis. However by finding the mean square displacement corresponding to the relaxation time we do obtain from the Kurtosis we can define a mean square displacement threshold beyond which we say this system is in the diffusive regime. As shown in Figure 5.12 this threshold is $(0.2 \pm 0.03)d$. Or in terms of the mean square displacement the threshold is $(0.04 \pm 0.009)d^2$ which agrees with the experiments and simulations of Möbius *et al.* and Sexton *et al.* [59, 60]. We highlight also the similarity between this value and the Lindemann criterion used in thermodynamics to define the onset of melting in a crystal.

Now that we have this threshold we return to our mean square displacement data and obtain the relaxation time for all strain rates investigated. In Figure 5.13 we rescale the time axis for all our data by the relaxation time showing that it falls onto a single curve.

This graph confirms the linear relationship between mean square displacements and strain rate for all samples investigated. This allows us to use the relaxation time to calculate the diffusion constant. Before we do that however we present in Figure 5.14 the relaxation time as a function of strain rate, $t_r^{micro}(\dot{\gamma})$, where the strain rate has been corrected by Equation 3.25.

The black line in the slope is a power fit to the data indicating that the relaxation time goes as,

$$t_r^{micro} \propto \dot{\gamma}^{-0.86 \pm 0.15}. \quad (5.12)$$

Firstly it agrees, within error, with the relaxation time as measured in the SRFS measurements, t_r^{SRFS} . In Figure 5.15 we compare the data to the relaxation time obtained from SRFS conducted at $\phi = 0.80$. When plotted together we can see that the trends are in reasonable agreement. However, this result disagrees with what was found in the 2D experiments by Möbius *et al.* where it the relaxation

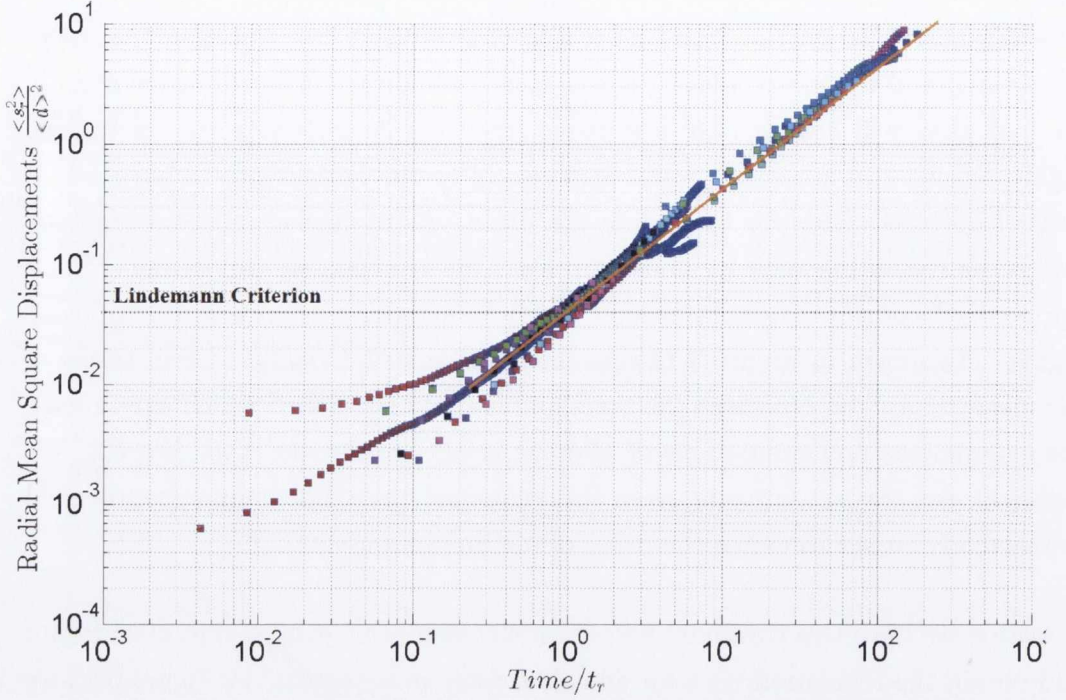


Figure 5.13: Radial mean square displacement rescaled by the relaxation time, defined by the time at which the mean square displacements cross the Lindemann criterion (dashed line). The orange line is a guide to the eye showing the linear relationship

time was reported to go with $\dot{\gamma}^{-0.66 \pm 0.05}$ [59]. Sexton *et al.* on the other hand, found in simulations that it went, at low and intermediate strain rates, as $\dot{\gamma}^{-1}$ and at high strain rates crossed over to $\dot{\gamma}^{-0.5}$ [60]. We have seen no such transition in our data and given the five decades of strain rate we propose that this transition does not occur in 3D experimental emulsions. For now we will proceed by taking $t_r^{micro} \propto \dot{\gamma}^{-0.86}$. Before moving on we will comment on the diffusion constant, which is a measure of the dissipative rearrangement rate. Using the definition of the diffusion constant we can calculate it using the Lindemann criterion and the relaxation time.

$$\langle s_r^2 \rangle / \langle d \rangle^2 = 2D_r t, \quad (5.13)$$

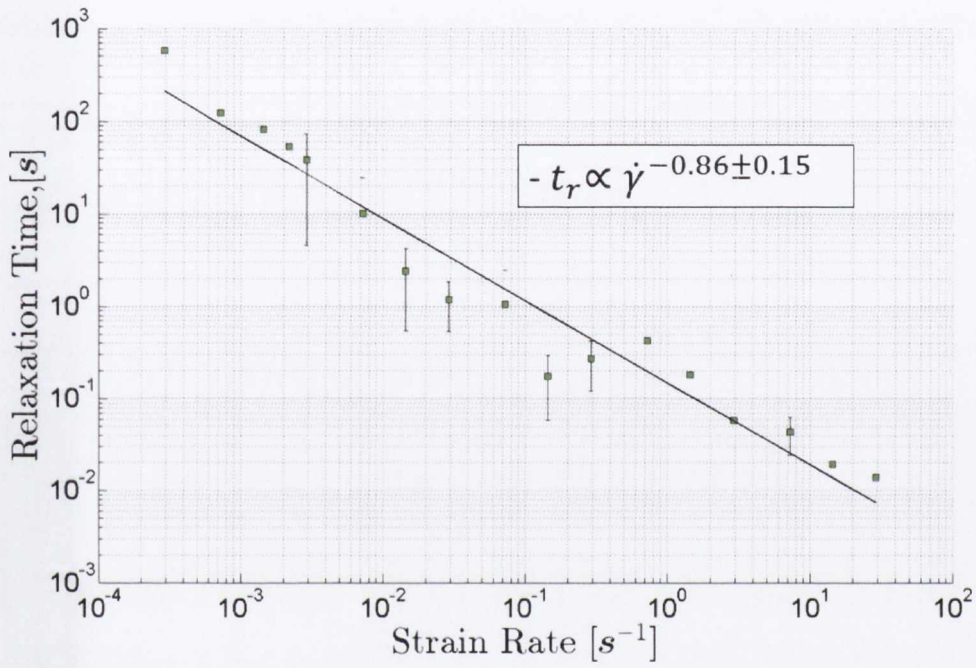


Figure 5.14: Relaxation time, as obtained from the Lindemann criterion, as a function of strain rate. Hollow symbols are from individual experiments and filled (green) the average. Black line is a fit to the data indicating that $t_r^{micro} \propto \dot{\gamma}^{-0.86 \pm 0.15}$

$$\Rightarrow D = \frac{(0.21d)^2}{2t_r^{micro}} \Rightarrow D \propto \dot{\gamma}^{0.86 \pm 0.15}, \quad (5.14)$$

Which tell us that the rate of dissipative rearrangements has a sublinear relationship with strain rate. This is a surprising result as it implies that if we shear twice as fast this does not cause the rearrangement rate to double.

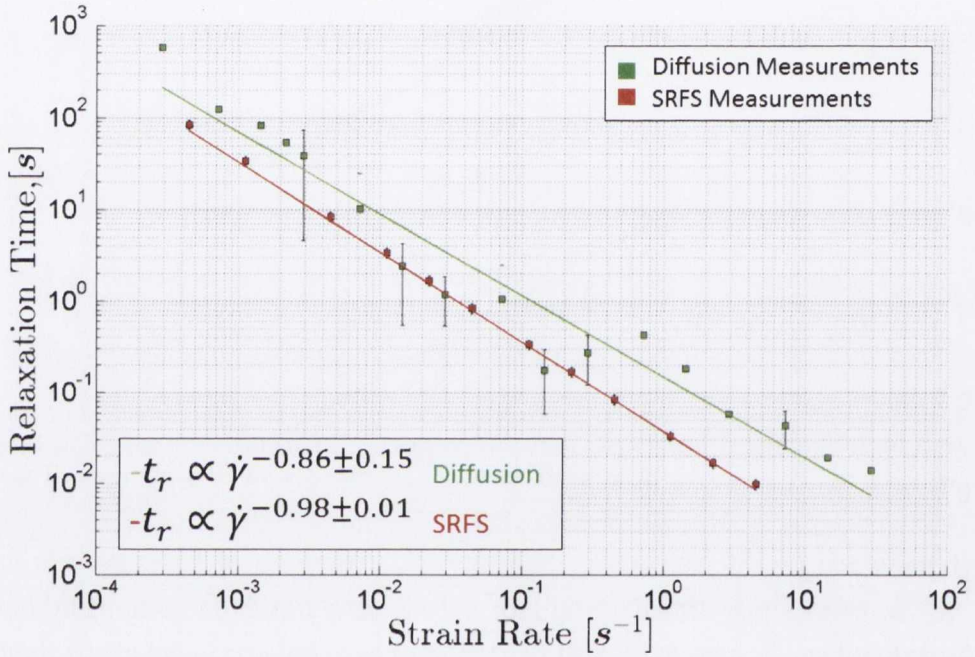


Figure 5.15: Relaxation time, as obtained from the radial Lindemann criterion (green) compared with the relaxation time obtained from SRFS measurements conducted at $\phi = 0.80$ (Black) as a function of strain rate. Hollow symbols are from individual experiments and filled (green) the average. Black line is a fit to the SRFS data indicating that $t_r^{SRFS} \propto \dot{\gamma}^{-0.98 \pm 0.01}$ while the dashed line is a fit to the microscopic data indicated that $t_r^{micro} \propto \dot{\gamma}^{-0.86 \pm 0.15}$. Note that the strain rate has been corrected using Equations 3.25 and 3.26 respectively.

5.2.2 Measuring The Diffusion Constant as a Function of Packing Fraction

Now we explore how the microscopic dynamics are affected by the packing fraction of the system at a constant strain rate. Again we only look at the dynamics in the radial direction where the mean flow is zero. We chose an intermediate strain rate, $\dot{\gamma} = 0.1 s^{-1}$, and in steady shear conditions measure the tracer particle trajectories. We vary the packing fraction from 0.65 to 0.95. Presented in Figure 5.16 are the radial mean square displacements for all packing fractions investigated. Note we are using the same Lindemann criterion from above.

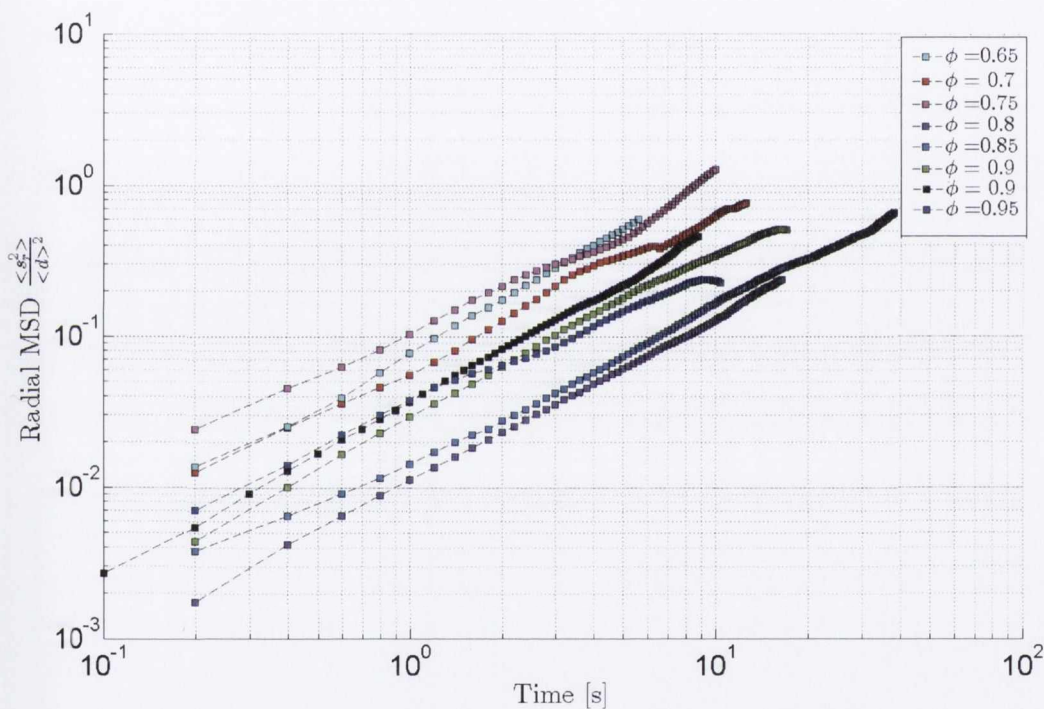


Figure 5.16: The radial mean square displacements, normalised by the average droplet diameter, as a function of time (equivalent to strain) for all packing fractions investigated. Black lines indicate, linear fits from which we get the diffusion constant. The time at which this linear equation crosses the Lindemann criterion (orange line) gives us the relaxation time for that given strain rate.

Again we, rescale the time axis with the relaxation time such that they all fall on a

single curve. The rescaled mean square displacements are presented in Figure 5.17.

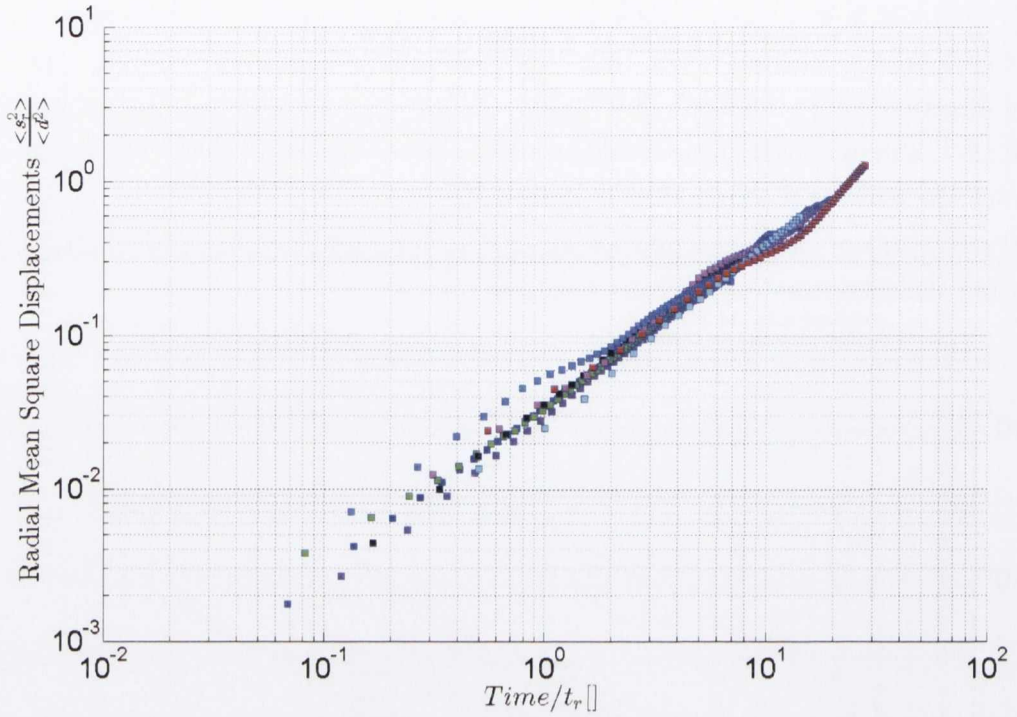


Figure 5.17: Radial mean square displacement rescaled by the relaxation time obtained from the Lindemann criterion.

We plot t_r^{micro} as a function of both ϕ and $(\phi - \phi_c)$ as shown in Figure 5.18. By fitting t_r^{micro} to $(\phi - \phi_c)$ we find a quadratic relationship. For comparison we have plotted t_r^{micro} and t_r^{SRFS} Figure 5.19.

When we compare t_r^{SRFS} and t_r^{micro} it becomes more apparent that the relaxation time as measured by SRFS is linear in $\phi - \phi_c$. We argue that the t_r^{SRFS} is the most accurate trend as it has more statistics than the microscopic measurements.

5.3 The Deformation relaxation Ansatz

Now that we have obtained the relaxation time as a function of both strain rate and packing fraction we are in a position to discuss the deformation relaxation

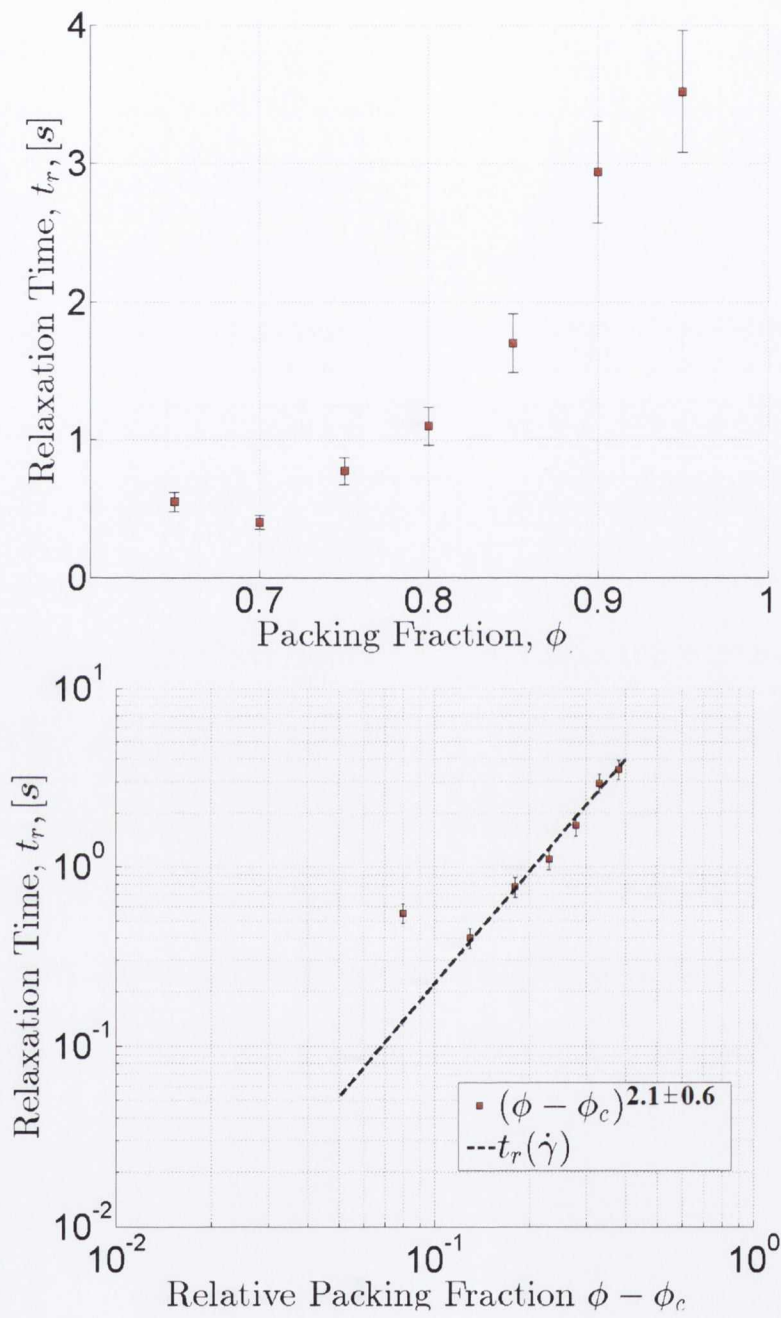


Figure 5.18: The relaxation time, as obtained from the Lindemann criterion, as a function of packing fraction and relative packing fraction.

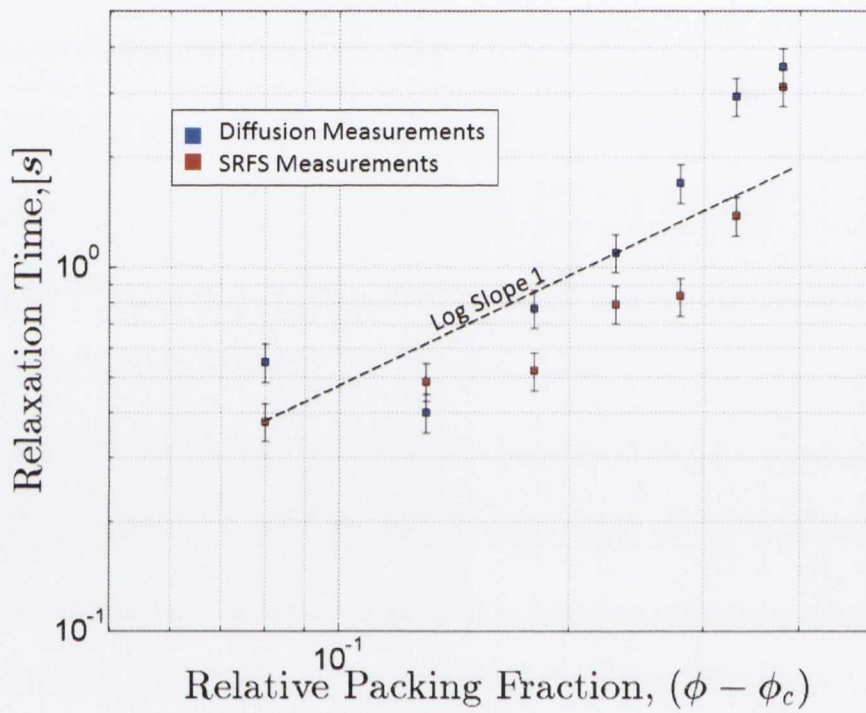


Figure 5.19: Relaxation time, as obtained from the Lindemann criterion and from SRFS, as a function of relative packing fraction at an imposed strain rate $\dot{\gamma} = 0.1s^{-1}$. The black line is log slope 1 highlighting the possible linear relationship.

ansatz. We derive the ansatz in Section 1.7 but here we will remind the reader of the final expression. It states that the viscosity, η , can be obtained from the relaxation time via,

$$\eta = G_0 t_r. \quad (5.15)$$

We can translate this into a measurement of stress using the definition of viscosity,

$$\tau = \eta \dot{\gamma} = \frac{1}{2} G_0(\dot{\gamma}) t_r(\dot{\gamma}). \quad (5.16)$$

We recall from Section 5.1.1 that the shear modulus is also a function of strain rate. In previous numerical studies this value was assumed to be constant [60]. We begin by looking at the relaxation time measured at $\phi = 0.80$ as in this case we have measured the relaxation time over several decades of strain rate using both SRFS and microscopic dynamics and observed two different trends, namely, $t_r^{micro} \propto \dot{\gamma}^{-0.86}$ and $t_r^{SRFS} \propto \dot{\gamma}^{-0.97}$. We remind the reader of the empirical fit of the strain rate dependence of the shear modulus, namely, $G = G_0(a + b\dot{\gamma}^c)$. In the case of $\phi = 0.80$ the following fit parameters were found,

$$G(\dot{\gamma}) = G_0(0.98(\pm 0.02) + 0.18(\pm 0.02)\dot{\gamma}^{0.65(\pm 0.07)}) \quad (5.17)$$

In Figure 5.20 we present two calculations of the stress using the measured relaxation time. In (A) we use $t_r^{micro} = \dot{\gamma}^{-0.86}$ and in (B) we use $t_r^{SRFS} = \dot{\gamma}^{-0.97}$ and in both cases use Equation 5.17 for the shear modulus. We fit to $G_0(\dot{\gamma})t_r(\dot{\gamma})$ and leave the prefactor as an open parameter. We remind the reader that once again the strain rate was corrected using Equations ?? and ??.

It is clear from this data that when we use $t_r^{micro} = \dot{\gamma}^{-0.86}$ the deformation relaxation ansatz holds over intermediate strain rates. It fails to capture the yield stress of the system and undershoots the data at high strain rates. However given the simple nature of this ansatz, and the significant scatter in our measurements of t_r^{micro} we are satisfied with this finding, especially given that the prefactor was found to be 0.13 which is of the right order, and argue that the deformation-relaxation ansatz is a reasonable starting point from which to develop a model for flowing foams and emulsions. When we use $t_r^{SRFS} = \dot{\gamma}^{-0.97}$ it is clear that this

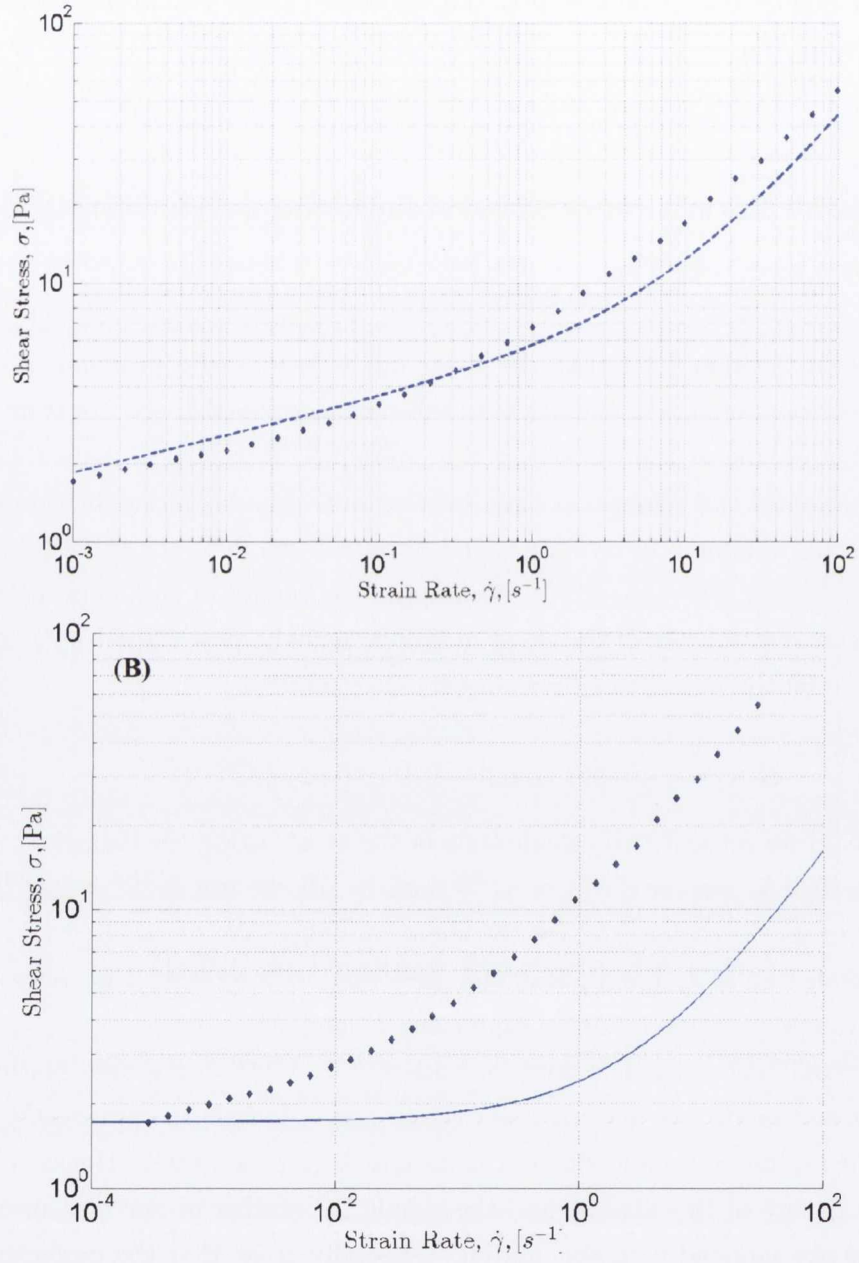


Figure 5.20: The shear stress calculated via the deformation-relaxation ansatz (dashed line) plotted with the stress obtained from flow curve measurements. In (A) we use the slope from the log fit to the data, $t_r^{micro} = \dot{\gamma}^{-0.86}$ and in (B) we use $t_r^{SRFS} = \dot{\gamma}^{-0.97}$. In both case we use $G(\dot{\gamma}) = G_0(0.98 + 0.18\dot{\gamma}^{0.65})$.

ansatz does not hold. However given that we have relaxation time measurements for several packing fractions from this method we attempt to fit the ansatz to all available packing fractions, that is, $\phi > 0.70$. This data is presented in Figure 5.21.

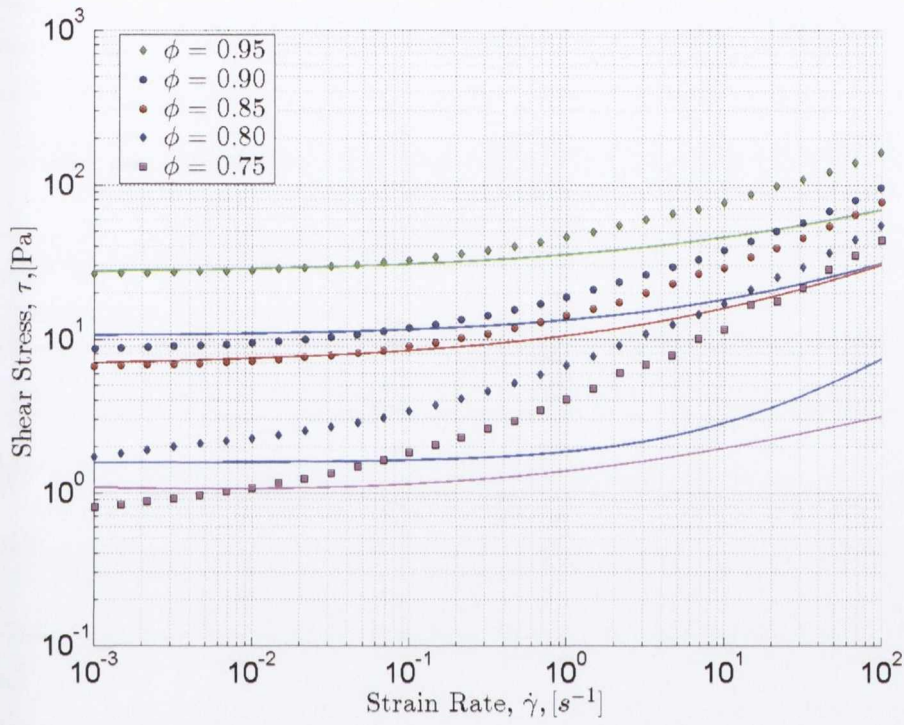


Figure 5.21: The shear stress calculated via the deformation-relaxation ansatz (solid line) plotted with the stress obtained from flow curve measurements using the relaxation time and shear modulus obtained from rescaled strain rate frequency superposition data. This data shows that the deformation relaxation ansatz does not hold when we use the relaxation time obtained from SRFS measurements

It is clear from this graph that the deformation-relaxation ansatz does not hold when we consider the relaxation time as obtained from SRFS measurements. The prefactor in all these cases was greater than one which also adds doubt to this ansatz.

5.3.1 The non-Equilibrium Stokes-Einstein Relation

We will close this section with a brief comment about the non-equilibrium Stokes-Einstein relation as this has been explored in 2D experiments and simulations in the past and found to be valid for foams [59, 62]. We remind the reader that the non-equilibrium Stokes-Einstein relation states that the elastic energy fluctuations in a flowing foam or emulsion can be described by the product of the viscosity, which we calculated using the deformation-relaxation ansatz, and the diffusion constant which we obtained via our microscopic measurements of the relaxation time. So we have,

$$\langle \delta E \rangle = \eta D \langle d \rangle = G_0(\dot{\gamma}) t_r(\dot{\gamma}) D(\dot{\gamma}) \langle d \rangle \quad (5.18)$$

Since $D = \frac{(0.2\langle d \rangle)^2}{t_r}$, the strain rate dependence cancels out and we are left with the prefactors from Equation 5.13 giving us,

$$\langle \delta E \rangle = G_0(\dot{\gamma}) \frac{(0.21\langle d \rangle)^2}{2} \langle d \rangle. \quad (5.19)$$

We now take $G_0(\dot{\gamma})$ from our SRFS measurements (Figure 5.1.1) and plot Equation 5.19 in terms of the surface energy of a bubble in Figure 5.22.

While the shear rate dependence is in contrast with what was found in the 2D experiments, the plateau value is of the same order of magnitude as what was found by Möbius *et al.* who reported $\langle \delta E \rangle \approx 7 \times 10^{-3} \sigma \langle d \rangle^2$ for a 2D foam [59]. As we have argued in Section 5.1.1 G_0 is not strain rate independent in our system and varies as a result of timescales of the surfactant kinetics. In the experiments conducted by Möbius *et al.* they did not go to high strain rates and the strain rate dependence of G_0 was not found [59]. On a side note they also used a commercial detergent to stabilise their foam and as such it is difficult to obtain information about surfactant kinetics as commercial detergent constitutes several different surfactants. In recent years there has been a push within the community to use established surfactant recipes as it allows different research groups to effectively compare their experiments with others [54].

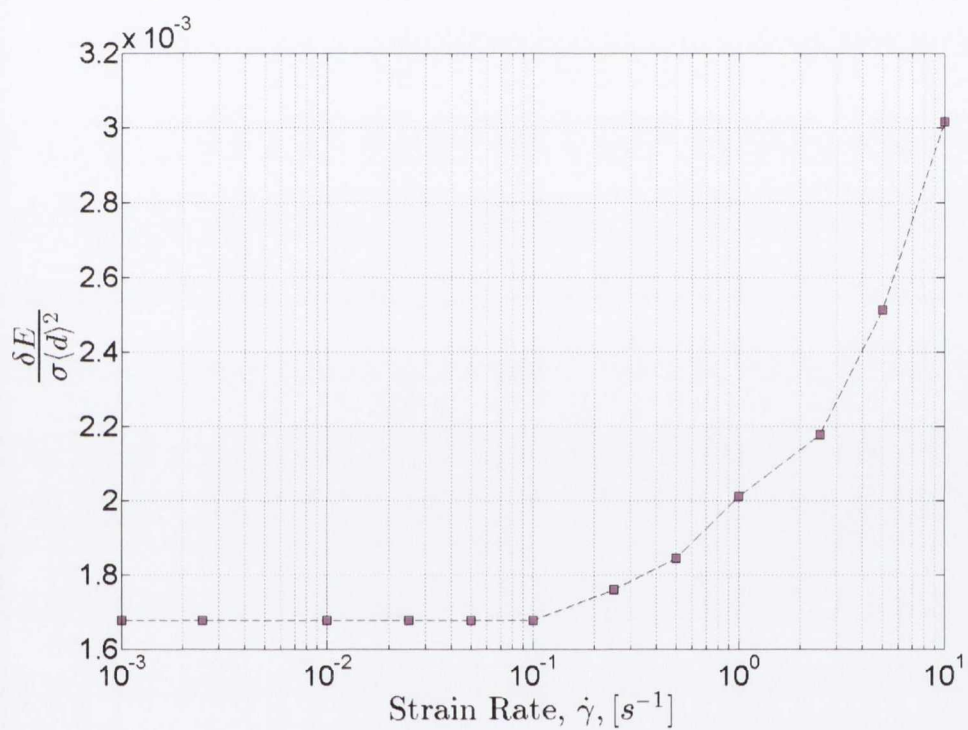


Figure 5.22: The elastic energy fluctuations in a flowing foam calculated using Equation 5.19 and normalised by the surface energy of a bubble.

5.4 The Yield Strain

We will close this chapter with a discussion of the yield strain. We are now in possession of 3 different measurements of the yield strain, namely, the oscillatory yield strain obtained from the rescaling strain sweep data (Figure 4.2). We also argue, on dimensional grounds, that the product of the strain rate and relaxation time should equal a yield strain, that is,

$$\gamma_y = t_r \dot{\gamma}. \quad (5.20)$$

This provides us with two more measurements of the yield strain (5.19) which we call γ_y^{micro} and γ_y^{SRFS} . In Figure 5.23 we present these yield strain measurements as well as comparing our results with the microscopically measured yield strain in the work of Knowlton *et al.* (Figure 2.10)[105]).

Based on the empirical equations of Mason *et al.* [78] one would expect the yield strain to have the following functional form.

$$\tau_y = G_0 \gamma_y \Rightarrow \gamma_y = \frac{\tau_y}{G_0} \propto \frac{(\phi - \phi_c)^2}{\phi(\phi - \phi_c)} = \frac{\phi - \phi_c}{\phi}. \quad (5.21)$$

As such we attempted to fit this to our measurements of the yield strain. We found from the amplitude sweeps the yield strain went as,

$$\gamma_y \propto \frac{(\phi - 0.64)}{\phi}, \quad (5.22)$$

Which is not surprising as $\frac{\tau_y}{G_0}$ took the same form (See figure 4.16). γ_y^{SRFS} took the same form,

$$\gamma_y^{SRFS} \propto \frac{(\phi - 0.57)}{\phi}, \quad (5.23)$$

but required us to use $\phi_c = 0.57$. Note that for both fits $\phi = 0.95$ was excluded for reasons explained above. It is interesting that both fits required different packing fractions. This may be due to a possible strain rate dependent influence of the yielding of adhesive emulsion below ϕ_{RCP} as unlike SFRS in amplitude sweeps the strain rate varies. When we looked at γ_y^{micro} we found the best fit to be

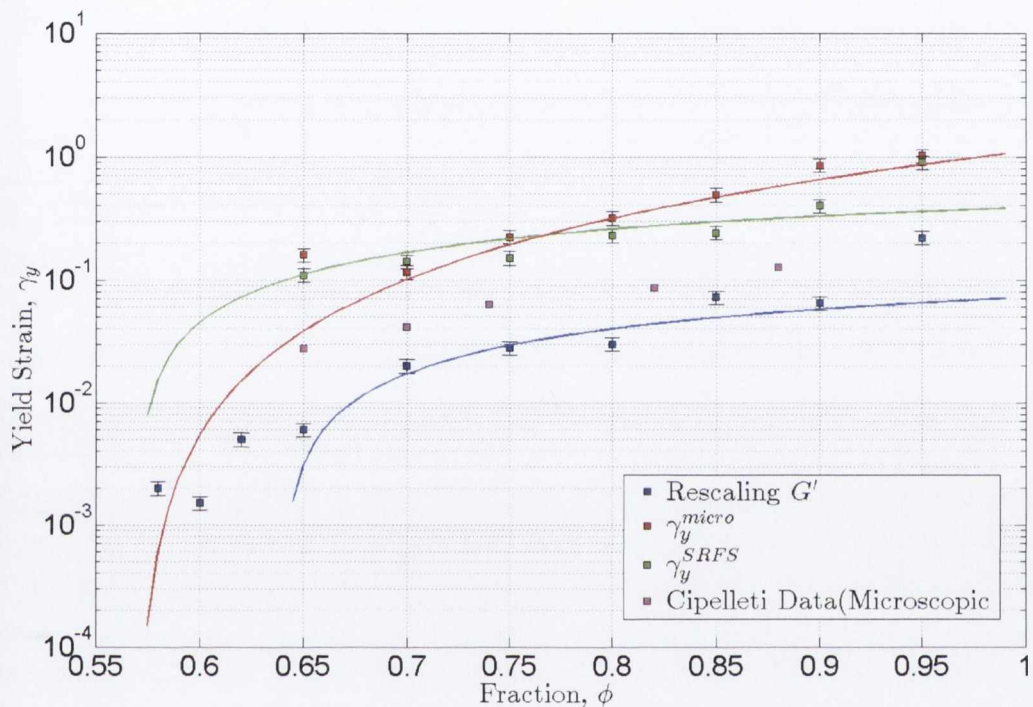


Figure 5.23: Yield strain as a function of packing fraction for various different definitions of the yield strain: strain rescale factors of the storage modulus (blue), γ_y^{micro} (red) and γ_y^{SRFS} (green). The pink data is from Knowlton *et al.* where they look microscopically at the sharp increases in mean square displacements in dense emulsions during oscillatory measurements [105]. The solid lines are fits to our data: $\gamma_y^{micro} \propto (\phi - 0.57)^2$ (red), $\gamma_y^{SRFS} \propto \frac{(\phi - 0.57)}{\phi}$ (green) and the oscillatory yield strain is fit to $\propto \frac{(\phi - 0.64)}{\phi}$ (blue).

$$\gamma_y^{micro} \propto (\phi - 0.57)^2. \quad (5.24)$$

It is not surprising that this does not follow the same trend as this was measured in steady shear and Equation 5.21 was derived from empirical fits to oscillatory data. We conclude from this that there exist two yield strains “dynamic” and “static” that correspond to the steady shear and oscillatory measurements respectively.

5.5 Conclusion

In summary we have measured the relaxation time as a function of strain rate and packing fraction using two complementary methods, strain rate frequency superposition and microscopic droplet dynamics.

With regard to the strain rate dependence of the relaxation time we found a discrepancy between the two methods. That is $t_r^{micro} \propto \dot{\gamma}^{-0.86 \pm 0.015}$ (Figure 5.14) which was in agreement within error with $t_r^{SRFS} \propto \dot{\gamma}^{-0.97 \pm 0.015}$ (Figure 5.5) but contrasted the work of Möbius *et al.*[59]. While t_r^{SRFS} agreed with what was found in the literature for both repulsive and attractive emulsions we still favour the trend found by the microscopic measurements as we have used this relationship to validate the Deformation-Relaxation Ansatz. We also found a discrepancy between the two measurements of the relaxation time with regard to $(\phi - \phi_c)$, namely, $t_r^{micro} \propto (\phi - \phi_c)^2$ and $t_r^{SRFS} \propto (\phi - \phi_c)^1$ (Figure 5.19). Here we argue that the linear relationship is the most accurate as $t_r^{SRFS}(\phi)$ has much more statistics than $t_r^{micro}(\phi)$.

With regard to the yield strain we again found different regimes,

$$\gamma_y^{micro} \propto (\phi - 0.57)^2. \quad (5.25)$$

$$\gamma_y^{SRFS} \propto \frac{(\phi - 0.57)}{\phi}, \quad (5.26)$$

And suggest that there exist two yield strains “dynamic” and “static” that cor-

respond to the steady shear and oscillatory measurements respectively. We also remind the reader that we do not understand slip dynamics in oscillatory measurement and this may also be a contributing factor. As γ_y^{SRFS} fits well to Equation 5.21 which is based on the ratio of well established empirical trends and that we define it as $\gamma_y^{SRFS} = \dot{\gamma} t_r^{SRFS}$ We are now in a position to refine our understanding of t_r^{SRFS} . Equation 5.5 now becomes,

$$t_r(\dot{\gamma}, \phi) \propto \frac{(\phi - \phi_c)}{\phi} \dot{\gamma}^{-0.97 \pm 0.015} \approx \frac{(\phi - \phi_c)}{\phi \dot{\gamma}} \quad (5.27)$$

With regard to the flow transition described by Sexton *et al* using bubble model simulation[?] we found no evidence of droplets being confined to lanes at high strain rates, that is the radial diffusion constant does not plateau (a plateau in the radial diffusion constant would signify an eradication of radial diffusion and hence “lanening”). It is possible that we have not implemented high enough strain rates to achieve laneing motion. A Couette Cell would be required to measure diffusion at higher strain rate as above $\dot{\gamma} = 100s^{-1}$ the emulsion is expelled from the parallel plate geometry.

Another important finding reported in this chapter was strain rate dependent shear modulus which we argue arises out of surfactant kinematics that can occur in systems with surfactant concentration above the CMC. We used the non-linear relationship between the shear modulus and strain rate to validate the deformation relaxation ansatz. Following from that we used the non-equilibrium Stokes-Einstein relation to obtain an energy scale in our system which was consistent with what was found in 2D experiments.

Chapter 6

Conclusions and Outlook

*“All things are impermanent, with
mindfulness strive on.”*

-Siddhārtha Gautama

6.1 Conclusions

We set out to explore the relaxation time of densely packing adhesive emulsions. We approached this investigation using two complementary methods. We inferred the relaxation time microscopically from dynamics on the droplet scale and macroscopically from strain rate frequency superposition measurements. Before we discussed these findings we presented the results obtained from conventional rheological techniques, namely amplitude sweeps and flow curves. We found in our system that elasticity existed below ϕ_{RCP} and we found our critical packing fraction to be $\phi_c = 0.57 \pm 0.015$ (Figure 4.3).

Before we discussed the steady shear rheology we presented data obtained from microscopically measuring the local strain rate which showed that despite the presence of sandpaper there was significant slip in our system yielding a local strain rate of $\dot{\gamma}_{local} = (0.29 \pm 0.03)\dot{\gamma}_G$ in steady flow and $\dot{\gamma}_{local} = (0.45 \pm 0.05)\dot{\gamma}_G$ in oscillatory flow (See Figure 3.24). We used these values to correct for our imposed strain rates during analysis.

When we reviewed all of our macroscopic measurements we found that above ϕ_{RCP} our data adhered to the well established trends. Our yield stress went as $(\phi - \phi_{RCP})^2$ (See Figure 4.16) and when we manually rescaled our flow curves by τ_y and $\dot{\gamma}_c$ we found that our data adhered to that of Parades *et al.* for $\phi > \phi_{RCP}$ (See Figure 4.13 and 4.14). From this we concluded that despite exhibiting elasticity below ϕ_{RCP} adhesive emulsion exhibit different yielding mechanisms below this point. We did not attempt to model these mechanisms but observed that the relationship between the yield stress and packing fraction was shallower below ϕ_{RCP} than it was above it. With regard to the Herschel-Bulkley equation we found that the Herschel-Bulkley exponent, n , decreased linearly with packing fraction and to the best of our knowledge this has not been explicitly stated in the literature from experimental investigations (See Figure 4.11).

When we discussed the relaxation time as a function of strain rate we found that the two approaches produced the same results within error. When measured microscopically we found that $t_r^{micro} \propto \dot{\gamma}^{-0.85 \pm 0.15}$ (Figure 5.14) which was disagreed with the work of Möbius *et al.* but confirmed what we found in the strain rate frequency superposition measurements which gave $t_r^{SRFS} \propto \dot{\gamma}^{-0.97 \pm 0.015}$ (Figure 5.15). The reason we proposed for the discrepancy between the 2D and 3D experiments was that the confining geometry used in the 2D experiments imposes an additional drag which is not present in the 3D experiments.

In our strain rate frequency superposition measurements we also found that the storage modulus varied with the strain rate, but only after some packing fraction independent critical strain rate (See Figure 5.1.1). We attributed this to surfactant kinetics that relate to the lifetime of micelles in solutions containing surfactant concentrations above the CMC. This was a significant finding because to the best of our knowledge it is the first time it has been reported for adhesive emulsions. It was also significant because it affects the stress versus strain rate relation deduced from the deformation-relaxation ansatz (See Figure 5.20).

We used this result to calculate the energy fluctuations within our system via the

Stokes-Einstein relation and found it to be in agreement with the 2D experiments of Möbius *et al.* with the exception of a weak strain rate dependence (See figure 5.22). Unfortunately we were not able to proceed further, as they did in their experiments, and relate this energy fluctuation to the change in bubble shape during shear. In order obtain this information one would need a confocal microscopic and a fluorescent continuous phase to observe the change in droplet shape during shear.

Finally, we observed that t_r^{SRFS} and t_r^{micro} did not yield a conclusive functional form but owing to the larger number of statistics obtained from the SRFS method we propose the following relationship between the relaxation time and packing fraction (See Figures 5.14 and 5.23).

$$t_r \propto (\phi - \phi_c)/\phi, \quad (6.1)$$

6.2 Outlook

Based on the conclusions outline above we would recommend introducing into the field the following investigations.

6.2.1 Relaxation Time at Low Strain Rates

As we could not confidently confirm the existence of two regimes in $t_r^{micro(\dot{\gamma})}$ (Figure 5.14) we would suggest measurements of the particle dynamics at low strain rates using a larger quantity of points per decade. As this crossover has been shown in simulations [60] we think that it is worth exploring $t_r^{micro(\dot{\gamma})}$ for strain rates lower than what we investigated in this work, that is, $\dot{\gamma} < 0.001s^{-1}$. This would be feasible in emulsions as Ostwald ripening happens at very slow timescales.

6.2.2 Relaxation Time at High Strain Rates

As we did not observe the transition to Laminar flow that was observed in simulations at high strain rates we also suggest conducting diffusion measurements at strain rates exceeding $\dot{\gamma} = 100s^{-1}$. This would need to be performed in a Couette

geometry as the parallel plate geometry used in this work does not allow for these strain rates. if the existence of this transition cannot be established experimentally we would suggests revisiting the bubble model to uncover an artefact that may cause "laneing" at high strain rates.

6.2.3 Micelle Kinetics

Finally we would also suggest conducting SRFS on emulsions comprised of different surfactants with different micellar time constants. If the onset of the strain rate dependence of G_0 corresponds to this time then it will confirm our hypothesis regarding the surfactant adsorption on stretched films.

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