# COALESCENCE OF COHESIVE PARTICLE

# RAFTS

# CAPILLARY-DRIVEN COALESCENCE OF BIDISPERSE PARTICLE RAFTS WITH TUNABLE COHESION

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Science

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2024

McMaster University MASTER OF SCIENCE (2024) Hamilton, Ontario, Canada (Physics and Astronomy)

TITLE:	Capillary-Driven Coalescence of Bidisperse Particle Rafts
	with Tunable Cohesion
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NUMBER OF PAGES:	ix, 68

### Abstract

When objects float on a liquid interface, they deform the surface under their weight. Nearby floating objects naturally clump together to minimize the energetically expensive deformation of the liquid surface through the so-called 'cheerios effect,' a consequence of capillary forces. If many particles are placed on a liquid surface they aggregate to form a particle raft, and when two particle rafts meet they can merge and form a larger structure in a manner similar to the coalescence of liquid droplets. In this thesis, we present an experiment to study the physics of particle raft coalescence using a system of microscopic, cohesive oil droplets. A bidisperse collection of oil droplets is created in a chamber filled with an aqueous solution of sodium dodecyl sulfate, a surfactant which both stabilizes the droplets and introduces a short range attractive force. The aggregate of droplets is manually separated into two nearly circular rafts then released. The process is directly observed with a camera from above as capillary forces drive the rafts to coalesce. Modifying the cohesion through the concentration of surfactant, we observe that greater cohesion impedes the progression of coalescence such that the structure ceases evolution in a more extended shape. We discuss the spatial distribution of particle rearrangements and develop a simple theory which captures the time evolution of the coalescing rafts.

# Acknowledgements

There is no way I would have made it here without the support of many. Kari, since I took your course in third year and joined your team at MesoMat, you've been relentlessly supportive, pushing me when I'm ready to push, and easing off when I need it. Thank you for the care you've shown so consistently, and for spreading your infectious passion for science. You inspire me to be a better physicist, and a kinder person. The rest of the KDV lab crew, you soften the hard days (get it), and make the good days in the lab fantastic! I feel fortunate to have had the chance to learn from and get to know you all, and I especially look forward to the next four years with this wonderful group.

I must extend a huge thank you to my dear friends and family, many of whom put up with me practicing talks for hours, and better yet, even listened to what I was saying! Your support means the world to me.

Perhaps most critically, I must acknowledge the most special four-legged girls I've ever had the privilege to adore, Daisy and Addie. You've kept me grounded on our daily morning adventures, and always remind me to smile and enjoy the ride. I love you both more than you could possibly know.

Finally, to anyone reading this whom I did not mention, you most likely made a difference in my journey, so thank you!

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# Chapter 1

# Introduction

When nearby objects float at a liquid interface, they miraculously seem to clump together. This is the so-called 'Cheerios effect' at play which arises due to an unfavourable deformation of the liquid surface caused by the floating objects that is relieved upon their aggregation [1]. A collection of many floating particles forms a raft, and when two rafts are nearby, they too will attract and begin to merge upon meeting in a process analogous to the coalescence of two drops of water on your windshield. While liquid coalescence has been studied extensively, this granular analogue of merging particle rafts has not.

In this thesis, we investigate the coalescence of particle rafts using a system of microscopic, cohesive oil droplets, in an analysis framework similar to that in the liquid coalescence literature. This particular oil droplet system is of interest as accumulations of these droplets have been shown to exhibit phenomena more akin to liquids than common granular materials despite their granular nature [2, 3]. In the presented experiment, two circular 2D rafts of oil droplets are created at an oil-water interface, and the cheerios effect drives them to coalesce. The tunable cohesive force between droplets mediates the evolution of the structure, resulting in an arrest of the relaxation process not common in liquid coalescence. Notably, the 2D geometry ensures individual droplets can be observed throughout the process for robust downstream analysis.

Chapter 1 will discuss basic concepts related to granular materials, liquids, emulsions, and the physical principles required to understand the experimental system at a base level. Chapter 2 discusses the experimental details followed by the results and analysis in Chapter 3. A simple theory is developed in Chapter 4, and finally, the thesis is summarized in Chapter 5.

#### **1.1 Granular Materials**

Fundamentally, granular materials are comprised of a collection of macroscopic rigid particles which satisfy several conditions. The particles must be sufficiently large that thermal fluctuations are not significant, and typically interact through collisions and friction. [4]. While simple mechanics governs individual particle behaviour, the collective interactions of many grains give rise to a rich array of complex behaviours in granular systems such as avalanches, jamming, force networks, and creep, all of which are the subject of intense research efforts [5–9]. These systems can display solid-like properties, able to sustain significant stresses, but can undergo failure and flow in a manner similar to liquids [4, 10]. The physics of granular media are widely involved in countless industrial processes such as in pharmaceuticals and agriculture, and underlie many natural phenomena including landslides, avalanches, and erosion [4]. Challenges arising from flow, mixing, and failures in these systems, industrial or geophysical, are frequently costly, so understanding how to manipulate and predict the behaviour of granular media is worthwhile.

Many examples of granular materials we may encounter, such as sand or powders, are made of rough grains of varying size, the complexity of which makes some aspects of modelling exceedingly difficult. As such, considering a system of reduced complexity, a collection of perfect hard spheres for example, can simplify the problem. The hard sphere consideration is central to the experiments performed in this thesis.

#### 1.1.1 Order and Disorder in Spherical Packings

With a two dimensional monolayer of monodisperse (identically sized) hard spheres, the most densely packed configuration is a triangular packing. This maximally dense configuration mimics an atomic lattice structure, and possesses rigidity to small perturbations due to the ideal topological arrangement and contact forces between neighbours [11]. For a particle to move in a dense aggregate, several of its neighbours must cooperate and move out of the way. Particles in granular media are large enough that thermal energy, the internal kinetic energy of molecules, is insufficient to agitate the system and overcome significant energy barriers. As a result, large-scale regions can form in which all particles are unable to overcome the energy barrier to rearrange, leading to clogging and jamming, interrupting flow [4, 12]. The configuration assumed by the granular system in a clogging event is a metastable state with an energy barrier which is too high for the system to overcome without external intervention. In systems of identical spherical particles, the propensity to form ordered crystalline domains increases the likelihood of clogging. To increase the mobility of the system, one can introduce a distribution of particle sizes, or a bidisperse system comprised of two unequal sized particles. Doing so creates a disordered system which relieves some of the geometric frustration present in a monodisperse collection, and particles can flow past each other more easily [4, 12]. For the experiment presented in this thesis, a bidisperse collection of athermal particles is used to enable particle rearrangements to occur with relative ease, though the barrier to flow is not fully eliminated.

#### 1.2 Fluids

Much of the physics underlying the experiments discussed in this thesis is described in the rich field of fluid dynamics. The Navier-Stokes equation is the central equation of motion underlying continuum fluid mechanics, applicable to incompressible Newtonian fluids [13]. The equation is given in Eq. 1.1 below in its three dimensional form,

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v} \cdot \nabla) \mathbf{v} = \rho \mathbf{f} - \nabla p + \eta \nabla^2 \mathbf{v}, \qquad (1.1)$$

where  $\rho$  is the fluid density, **v** is the velocity of fluid at a particular location and time, **f** is the volume force per unit mass, p is pressure, and  $\eta$  is the dynamic viscosity of the fluid. Analytically solving the Navier-Stokes equation is only possible for simple geometries or flows under constraints such as zero viscosity, or stationary flow. A useful strategy is to perform fluid experiments in a regime in which simplifying assumptions are well validated to make the problem tractable. One critical factor is the relative importance of viscous forces (shear frictional forces between neighbouring layers of fluid) and inertial forces (normal-acting forces due to the motion/intertia of the fluid). The quantity known as Reynold's number, Re, serves this purpose. The Reynold's number is defined as,

$$Re = \frac{\rho UL}{\eta},\tag{1.2}$$

where U is the characteristic velocity of the flow, and L is the spatial characteristic length. Using the below defined dimensionless variables, and dividing Eq.1.1 by  $\rho U^2/L$  we obtain a dimensionless version of the Navier-Stokes equation [13],

$$\mathbf{r}' = \frac{\mathbf{r}}{L}, \ \mathbf{v}' = \frac{\mathbf{v}}{U}, \ t' = \frac{t}{L/U}, \ p' = \frac{p - p_0}{\rho U^2}$$
$$\frac{\partial \mathbf{v}'}{\partial t'} + (\mathbf{v}' \cdot \nabla')\mathbf{v}' = -\nabla' p' + \frac{\eta}{\rho UL} \nabla'^2 \mathbf{v}'$$
(1.3)

$$\frac{\partial \mathbf{v}'}{\partial t'} + (\mathbf{v}' \cdot \nabla')\mathbf{v}' = -\nabla' p' + \frac{1}{Re} \nabla'^2 \mathbf{v}'.$$
(1.4)

The dimensionless form indicates that Re is the ratio of the non-linear inertial term,  $\rho(\mathbf{v}\cdot\nabla)\mathbf{v}$  to the linear viscous term,  $\eta\nabla^2\mathbf{v}$ . Flows characterized by high Re, dominated by the convective term are considered turbulent (characterized by the development of eddies), while low Re flows dominated by viscosity are laminar (flow appears as neighbouring parallel sheets sliding past each other). For viscous flows of relatively small L and U ( $Re \ll 1$ ), what we deem 'highly dissipative', the drag force on an object in the flow is directly proportional to the flow velocity,

$$F_{drag} \propto U \quad (Re \ll 1).$$
 (1.5)

Objects submerged in a fluid of density,  $\rho_f$  experience an upward force of buoyancy equal to the weight of the displaced fluid. For an object of volume, V this becomes,  $F_{buoy} = \rho_f V g$ . This force competes with gravity,  $F_g = \rho_o V g$  (assuming a uniform density of the object,  $\rho_o$ ), and gives a net 'apparent weight' force of,

$$\mathbf{w}_{\text{apparent}} = F_{buoy} - F_g = \rho_f V g - \rho_o V g = (\rho_f - \rho_o) V g, \qquad (1.6)$$

If the object is less dense than the fluid (e.g. oil in water), buoyancy overcomes gravity and the object floats upward.

#### **1.2.1** Interfacial Tension

Two immiscible liquids (e.g. oil and water) do not easily mix due to the inherently unfavourable enthalpic interactions between the different molecules at the interface, compared to the favourable interactions between like molecules in the bulk [14]. The solution to minimize the free energy is to drive toward a configuration with minimal interfacial area [14]. The additional energy cost per unit area of interface is characterized through the interfacial tension parameter,  $\gamma$ , which also manifests as a force per unit length. The interfacial tension between fluids is often central to the evolution of a system of interacting fluids and its equilibrium configuration.

#### **1.2.2** Laplace Pressure

A small droplet of one fluid immersed in another (like oil in water) will take on a spherical shape to minimize the surface area. From a dynamics point of view, a location of higher curvature would have a greater net surface tension force acting toward the centre of the body, shown schematically in Figure 1.1, suppressing any imbalances in curvature and ultimately equilibrating to the shape of a sphere. Energetically, interfacial area is costly, so nature finds the minimum surface area shape according to

the boundary conditions, where the sphere is the minimum area solution for a closed surface.



FIGURE 1.1: (a) Surface tension forces (per unit length) on a small curved surface element dS demonstrating the net inward force,  $\gamma_T$ , on a convex element (forces have only been shown along two edges for simplicity). (b) Imbalances in net inward surface tension for regions of higher curvature will equilibrate the shape to a sphere. Dashed box depicts a possible location for the surface element in (a).

A pressure difference exists between the inside and outside of the droplet due to the interplay between interfacial tension and curvature. Consider increasing the radius of an oil droplet in a bath of water by dR (Figure 1.2), then the total work done on the system due to pressure and capillary forces,  $\delta W$ , is given by [14],

$$\delta W = -p_o dV_o - p_w dV_w + \gamma_{ow} dA, \qquad (1.7)$$

where p is pressure, dV is change in volume, dA is change in area due to the increase in radius by dR,  $\gamma$  is the interfacial tension, and subscripts o and w refer to oil and water respectively. Given the spherical geometry, we can express the changes in volume and area according to:

$$V = \frac{4}{3}\pi R^3 \quad \Rightarrow \quad dV_o = 4\pi R^2 dR = -dV_w \tag{1.8}$$

$$A = 4\pi R^2 \quad \Rightarrow \quad dA = 8\pi R dR, \tag{1.9}$$

where  $dV_o$  is positive by virtue of the oil droplet increasing in volume, and  $dV_w$  is precisely the opposite change in volume. This allows us to rewrite Eq. 1.7 as,

$$\delta W = -p_o 4\pi R^2 dR + p_w 4\pi R^2 dR + \gamma_{ow} 8\pi R dR.$$
(1.10)

At equilibrium,  $\delta W = 0$  and rearranging the expression gives the Laplace pressure difference for a spherical droplet,

$$\Delta p = p_o - p_w = \frac{2\gamma_{ow}}{R},\tag{1.11}$$

This approach can be generalized to write the Laplace pressure under any 3 dimensional geometry as [14],

$$\Delta p = \gamma C = \gamma \left(\frac{1}{R} + \frac{1}{R'}\right),\tag{1.12}$$

where C is the curvature of the droplet, and R and R' are the two principle radii of curvature.



FIGURE 1.2: Schematic demonstrating an increase in the radius of a droplet by dR to supplement the discussion of Laplace pressure.

#### 1.2.3 Contact Angle

When a small quantity of liquid is brought into contact with a solid substrate, the inter-molecular interactions dictate whether the liquid will spread along the surface or remain in place when deposited. When the liquid's affinity for the substrate is sufficiently high it will undergo total wetting, spreading out completely on the surface, otherwise partial wetting will occur where the liquid will form a stable stationary structure. The spreading parameter, S is used to distinguish between these two wetting regimes, and is defined as the difference in energy when the substrate is dry and when it is wet per unit area [14],

$$S = \frac{E_{\rm dry}}{A} - \frac{E_{\rm wet}}{A} \tag{1.13}$$

$$S = \gamma_{s,g} - (\gamma_{s,l} + \gamma_{l,g}), \qquad (1.14)$$

where E/A is the energy per unit area of the substrate when dry and wet, as denoted by the subscripts; the subscripts, s, g and l refer to solid, gas, and liquid respectively. If the energy of the dry substrate is greater than when wet (S > 0), the liquid fully wets the substrate. Partial wetting will then occur for S < 0. If the volume of liquid is sufficiently small (capillary forces dominate over gravity), flattening due to gravity can be ignored when partial wetting occurs. In this case, the liquid forms a stable spherical cap on the substrate with a contact angle,  $\theta_E$ , between the liquid and the solid as shown in Figure 1.3. The Young-Dupré equation, which arises from a horizontal force per unit length balance at the contact line, gives the expression for deriving the contact angle [14],

$$\gamma_{l,g}\cos\theta_E = \gamma_{s,g} - \gamma_{s,l}.\tag{1.15}$$

Substituting Eq. 1.14 into Eq. 1.15 gives,

$$S = \gamma_{l,q}(\cos\theta_E - 1), \tag{1.16}$$

which is strictly negative, so  $\theta_E$  can only be defined when the spreading parameter, S < 0, and the liquid is partially wetting.



FIGURE 1.3: (a) Schematic demonstrating a spherical liquid cap partially wetting a solid substrate. The dashed box shows the zoomed area represented in panel (b). (b) Horizontal force balance at the contact line between  $\gamma_{s,l}$ ,  $\gamma_{s,g}$ , and  $\gamma_{l,g}$  which determines the contact angle,  $\theta_E$ .

The contact angle formed with the walls of a container of water with a layer of oil on top is particularly relevant to this thesis. If the container's surface has a greater affinity for water, the water will preferentially partially (or totally) spread compared to oil, and a concave up meniscus typical of water in a glass measuring cup will be achieved (see Figure 1.4a). Conversely, if the surface is hydrophobic (waterfearing) or oleophilic (oil-loving), oil will preferentially wet the surface, generating a concave down interface as shown in Figure 1.4b. This phenomenon is exploited in the experimental set-up where a hydrophobic PTFE cylinder is used to generate a concave down meniscus which gently confines buoyant particles to the centre (see Figure 2.2 in Chapter 2).



FIGURE 1.4: Demonstrating the menisci generated due to relative surface affinities in a phase separated arrangement of oil on top of water in containers with different molecular affinities. (a) A hydrophilic container in which water preferentially wets the surface, creating a concave up meniscus at the water-oil boundary. (b) A hydrophobic container in which oil preferentially wets the surface, creating a concave down meniscus at the water-oil boundary. This resulting geometry is exploited in the experiments discussed in this thesis.

#### 1.2.4 Liquid Coalescence

The coalescence of liquid bodies is a ubiquitous physical phenomenon. In nature, coalescence is central to the formation of rain drops [15], and the self-cleaning of plant leaves [16]. Coalescence is widely exploited in industrial processes such as coating sprays and inkjet printing [17]. When two bodies of liquid such as two water droplets meet, a microscopic connecting bridge or 'neck' forms between them and rapidly grows as the two droplets merge into one as depicted in Figure 1.5 [18]. This process is initially driven by the surface tension between the drops and the outer fluid through the extreme Laplace pressure at the highly curved neck region. The relative importance of viscous and inertial forces competing with the capillary forces determines the nature of the time evolution of the neck width, w. Typically, a power law relationship is described where  $w \propto t^{\alpha}$  for some positive power law exponent,

 $\alpha$ . For sufficiently viscous fluids, a viscous regime is seen at short times followed by a transition to an inertia-dominated regime with a different  $\alpha$  [18, 19], depending on the geometry and rheology of the system. The time evolution of coalescence for simple geometries has been treated by many both analytically [19–24], and through simulation [25, 26]. With the use of ultra-high speed cameras, recent experiments have succeeded in discerning the dynamics of coalescence neck growth in various systems, including droplet-droplet [18, 27], liquid lens [28], and quasi-2D systems [29]. Additionally, the coalescence of droplets within an outer viscous fluid [30], drops in confined geometries [31], and coalescence of yield-stress fluids [32] have been studied. In this thesis, we investigate an analogous coalescence process between rafts of oil droplets and attempt to quantify the neck growth in time in comparison to this body of work.



FIGURE 1.5: A depiction of the coalescence of two liquid droplets. (a) The initial contact between two droplets of radius  $R_0$ . (b) A short time after contact, the neck represented with the dotted grey line forms and grows laterally as the bodies merge through an intermediate configuration in panel (c) to (d) a final equilibrium sphere of radius,  $R_f$ . For 3D spheres,  $R_f = \sqrt[3]{2} R_0$ , and for 2D disks,  $R_f = \sqrt{2} R_0$  due to volume/area conservation.

#### 1.3 Emulsions

An emulsion is a system involving droplets of one liquid, the dispersed phase, suspended in another liquid of greater volume fraction, the continuous phase. Droplets of oil dispersed in water, deemed an O/W emulsion, or the inverse, water dispersed in oil (W/O) are the most common emulsions. With no controlled techniques, emulsions made simply by agitating or mixing two components have widely variable domain sizes. When emulsions of more precise droplet sizes and polydispersities are desired, microfluidic devices are often used [33, 34]. Often these techniques involve directed flow of the continuous phase to produce droplets, and have significant variability when attempting to create a size monodisperse collection of droplets with variation on the order of  $\sim 3\%$  of the mean [33, 34]. Instead, we make use of the 'snap-off instability' to create monodisperse oil droplets of a particular size in an aqueous solution achieving an extremely narrow size distribution with only 0.5% variance [35, 36].

#### 1.3.1 Snap-off Instability

To produce droplets with the snap-off technique, we release a dispersed phase (oil in this work) out of a micropipette into a bath of the continuous phase (an aqueous solution of surfactant and sodium chloride). The micropipette must be pre-wet with the continuous phase, so once a micropipette is inserted, the dispersed phase is drawn back into the pipette to allow the continuous phase to wet the walls of the pipette tip before ejecting the dispersed phase again. As seen in the schematic in Figure 1.6, the dispersed phase begins to form a spherical droplet as it is ejected from the micropipette, and the continuous phase is drawn into the pipette near the walls. A difference in Laplace pressure between the continuous phase inside and outside the pipette causes the droplet to snap-off from the micropipette forming a spherical droplet [35]. The size of the pipette tip sets the size of the droplet, which is stable through a large range of flow rates, enabling relatively robust control over the rate of droplet production [36].



FIGURE 1.6: Side-view schematic demonstrating the snap-off instability. As oil is ejected out of a micropipette, the aqueous solution is drawn back into the pre-wet pipette, causing a spherical droplet to snap-off upon reaching a critical size due to Laplace pressure. Droplets rise upward after snap-off due to buoyancy.

#### 1.3.2 Surfactants

By definition, the two immiscible liquids which comprise an emulsion have inherently unfavourable interactions which gives rise to interfacial tension. In an O/W emulsion, the interfacial tension between the two phases is about  $\gamma_{O/W} = 5 \text{ mJ/m}^2$ which is significant enough to lead to instability over time. With no intervention, the oil droplets would favourably coalesce upon close enough contact effectively destroying the intended ensemble of droplet sizes. To increase the stability of emulsions, surfactants can be added to the solution which decrease the interfacial tension [14]. Typically these amphiphilic molecules have a hydrophobic component like a fatty acid tail which penetrates non-polar component and a hydrophilic head group which orients toward the polar liquid. In an O/W emulsion, oil droplets are coated so that the polar head groups form a shell surrounding the droplet with non-polar tails toward the inside. This shell is shown schematically in Figure 1.7. In this thesis, sodium dodecyl sulfate (SDS) is added to an O/W emulsion to stabilize the oil droplets for long times. SDS is a micelle-forming surfactant, which can self-organize into stable spherical micelles when there are free molecules which are not participating in coating the oil. These micelles are central to the depletion interaction discussed below. NaCl is added to the solution in our experiments to screen charge interactions introduced by SDS molecules.



FIGURE 1.7: A not-to-scale schematic of SDS in the experimental O/W emulsion. Individual SDS molecules are represented with a polar (or-ange) head and non-polar tail. SDS molecules coat the surface of oil droplets, reducing the interfacial tension, thereby providing stability. Free SDS molecules in solution can self-assemble into spherical micelles, as shown by the small clusters on the right of the figure, to reduce their free energy.

#### **1.3.3** Cheerios Effect

When an object floats on a liquid surface, it deforms the interface under its weight [37]. For two nearby identical objects, an attractive capillary force is created as surface tension acts to drive the objects together to minimize the extra interfacial area generated by the deformations, as shown in Figure 1.8. This phenomenon is known colloquially as the 'cheerios effect', since a milky bowl of breakfast cereal with a few floating pieces will exhibit this spontaneous clumping behaviour [1]. The 'cheerios effect' is the driving force for particle raft coalescence in the experiments discussed in this thesis.



FIGURE 1.8: (a) Schematic depicting the cheerios effect with two buoyant spheres deforming the fluid-fluid interface, feeling an attractive capillary force,  $F_{cap}$ , which drives them together as in (b) minimizing the overall excess area of the interface.

#### **1.3.4** Depletion Interaction

In this section we will consider a suspension of approximately hard spheres. The hard sphere description refers to the pairwise interaction potential between distinct particles, which for particles with diameter, D, can be written as,

$$V_{DD} = \begin{cases} 0, & r > D\\ \infty, & r \le D \end{cases}$$
(1.17)

The consequence of this potential (ignoring other interactions: ionic, van der Waals, etc.) is that particles are not deformable. The experiments described in this thesis involve an emulsion of oil droplets suspended in an aqueous solution. The oil droplets with radii on the order of tens of micromeetres have a high Laplace pressure difference (recall Eq. 1.11) and may be approximated as hard spheres.

When a collection of diffusive, small particles - *depletants* - are added to suspension of larger particles, a short-range attractive force between the large particles arises. To explain this, we consider that it is entropically favourable for the diffusing depletant particles to have the maximum possible volume to explore [38]. There is a certain volume around the large dispersed particles, like the oil droplets, from which the solutes are excluded and unable to explore. However, when the large particles come close together, there is an overlap in the excluded volumes of both particles which increases the total volume available to the solutes (see Figure 1.9). This additional volume increases the translational entropy of the depletants and therefore reduces the free energy of the system, manifesting as a cohesive force between the large droplets [39]. We can introduce this depletion interaction experimentally by adding micelles to the solution. In these experiments, SDS is used, inducing depletion interactions while also stabilizing the oil droplets against coalescence. The strength of the cohesive force increases in proportion to the concentration of micelles in the system [40],

$$F_{depletion} \propto C_m r,$$
 (1.18)

where  $C_m$  is the micellar concentration, and r is the droplet radius. Carrying out the geometric calculation, one finds that the overlapping excluded volume scales in proportion to r as reflected in the formula, rather than  $r^2$  or  $r^3$  as may be intuitively expected with dimensional arguments. The micellar concentration, and therefore the strength of cohesive forces in the system, is varied in the experiments discussed in this thesis. Previous work in our research group has verified the scaling of the depletion force with the particular oil droplet system used in this work [3].



FIGURE 1.9: Schematic representing the reduction in excluded volume when large particles are sufficiently close. Depletants are shown as small red circles, which cannot freely explore the volume within the dashed line surrounding each large particle. Compared to (a) where the depletants cannot explore the full excluded volume from each particle, the overlap of these excluded volumes in (b) shown in red enables the depletants more net volume to diffuse, increasing their translational entropy. This path to reducing free energy manifests in a cohesive force driving the large spheres together.

#### **1.3.5** Particle Rafts

Due to the cheerios effect (Section 1.3.3), many identical objects floating on a liquid surface will tend to aggregate. This forms what are often called 'particle rafts': typically quasi-2D monolayers of particles floating at a fluid-fluid interface. In nature, fire ants make impressive use of this phenomenon, forming hydrophobic ant rafts to survive floods [41]. Efforts have been made to model and verify with experiment, the kinetics of this aggregation process, including the interaction between separated particle rafts of different sizes [42, 43], but few have investigated the dynamics of the merging or 'coalescence' of particle rafts in mesoscopic systems of thousands of particles [44]. In the following chapters we discuss an experiment designed to probe this particle raft coalescence process using microscopic oil droplet rafts at an oil-water interface. Critically, these particles are athermal, frictionless, bidisperse, and experience an additional short range cohesive force via the depletion interaction, which mediates the extent to which the structure evolves.

# Chapter 2

# **Experimental Details**

This chapter details the experimental and analysis methods pertinent to this thesis. The degree of detail is intended to be such that somebody would be able to reproduce the experiments independently. Section 2.1 discusses the fabrication process for the chamber which contains the experiments, the preparation of SDS solution, and micropipettes created for droplet production. The following section describes the experimental procedure from set-up through data acquisition. Finally, Section 2.3 outlines the key procedures used to process time series images from experiments and analyze the results.

As mentioned in Chapter 1, when nearby like particles deform a fluid-fluid interface, they experience a force of attraction due to capillary forces [1]. Quasi-twodimensional aggregates of particles, also known as particle rafts, experience the same effect, but upon meeting can undergo a merging event similar to liquid coalescence. In contrast to coalescing spherical droplets, the merger of these particle rafts is closer in analogy to the coalescence of 2D patches of oil floating atop a bowl of soup. The following experiment (described in more detail throughout the chapter) was designed to observe the coalescence process of two quasi-2D rafts of oil droplets with a tunable inter-particle cohesive force.

Due to buoyancy, oil droplets (less dense than water) produced in an aqueous solution will rise until they meet a boundary. In this experiment, the interface between water and an above oil layer serves as the location where oil droplets of two distinct sizes accumulate. Two roughly circular droplet rafts of similar size were formed with a small distance between them, then released and driven together due to capillary forces. The resulting coalescence process was observed with a microscope camera from above. The dynamics of the process are mediated by the strength of the cohesive interaction between droplets which was controlled through the concentration of a surfactant in the system. The 2D nature of the system enables observation of each individual droplet throughout the process; essential for quantifying the dynamics through a downstream analysis pipeline.

#### 2.1 Chamber Design

Experimental chambers were fabricated to contain the experiments. A schematic of an un-filled chamber is given in Figure 2.1. A glass microscope slide (50 x 75 x 1 mm<sup>3</sup>) was used for the base of the chamber. Before gluing together other components, the glass slide was cleaned with Sparkleen cleaning solution, rinsed with filtered and deionized water, then dried using directed 99.9% ultra-pure nitrogen gas. 3D printed chamber walls were designed to contain the experiments. The walls divide the chamber space into two sections we will label as the 'droplet corral' (indicated in Figure 2.1) where oil droplet production will initiate, and the 'active region' where the experiment will take place. After printing, the walls are carefully cleaned with a de-burring tool to eliminate potential debris. The final solid component is a tube of PTFE (commonly known as Teflon; 1.25 inch outer diameter, 1.00 inch inner diameter) cut to  $\sim 12$  mm in length. The appropriate length of tubing was cut from a stock length by affixing it to a metal guide and using a serrated saw. The resulting piece was cleaned with a de-burring tool and precision knife to remove loose flakes of material and smooth the surface. The tube was then washed using the same process as the glass slide. Next, the PTFE tube was glued with clear silicone caulking



FIGURE 2.1: Schematic of the experimental chamber design comprised of a 50 mm x 75 mm x 1 mm glass slide, 3D printed PLA chamber walls, and a  $\sim$ 25 mm diameter PTFE tube. The 'Droplet Corral' is highlighted in blue where snap-off oil droplet production is optimized before inserting the droplet producing pipettes in the 'active region' within the PTFE tube.

inside the cavity of precisely the right shape in the chamber walls. The design of the walls is such that the tube is effectively press-fit into position, and then the junctions between the tube and the walls are carefully sealed with caulking to prevent any unwanted leakage of solution which will later fill the chamber. Critically, the tube rests on a ledge at the back of the chamber 2 mm above the glass slide which enables

a micropipette to be inserted from underneath to produce oil droplets in this 'active region.' Finally, the chamber walls with PTFE tube were affixed to the centre of the glass slide with caulking and the chamber was left for several hours to allow time for the caulking to cure.

#### 2.1.1 Solution Preparation

The chambers were to be filled about halfway with aqueous solutions of SDS and sodium chloride (NaCl). The NaCl was introduced to screen ionic interactions introduced by the polarity of the SDS molecules, and held constant at 1.5% by weight for all prepared solutions. SDS concentration was varied from 0.05% to 2.0% by weight between experiments. Solutions were well mixed and left on a shaker when not in use to prevent crystallization and ensure homogeneity. As mentioned in Chapter 1, beyond stabilizing the oil droplets against coalescence, SDS forms micelles which introduce an attractive force between oil droplets via the depletion interaction.

The concentration of micelles,  $C_m$  is directly related to the strength of the interaction.  $C_m$  is the difference in the total concentration of SDS and the critical micellar concentration, beyond which free SDS molecules self-assemble into micelles; calculated as,

$$C_m = \frac{m_{\rm SDS}/M_{\rm SDS}}{V_{\rm H_2O}} - \rm CMC_{\rm SDS}, \qquad (2.1)$$

where  $m_{\rm SDS}$  is the mass of SDS in grams,  $M_{\rm SDS}$  is the molar mass of SDS (288.372 g/mol),  $V_{\rm H_2O}$  is the volume of water in litres, and  $\rm CMC_{SDS} = 8.2$  mM is the critical micellar concentration of SDS. Experimental concentrations of SDS correspond to  $C_m$  values of 1 mM, 6 mM, 17 mM, 35 mM, 71 mM.

#### 2.1.2 Micropipettes

Producing oil droplets required the use of glass tubes, 'micropipettes' with inner diameters on the order of the desired size of the droplets. These were produced from glass capillary tubes (World Precision Instruments, USA; inner diameter 0.58 mm, outer diameter 1 mm) using a PN-31 pipette puller (Narishige, Japan). Briefly, the glass would be locally heated and then quickly pulled with a magnetic force leaving a long, tapered tip, tens of micrometers in diameter at its narrowest point. Owing to the taper, the tip of the micropipette could be broken at different spots along its length to accomplish different opening diameters. For integration with the experimental set-up, micropipettes were required to have a  $90^{\circ}$  bend 10-12 mm from the tip. For this purpose, current was passed through a 0.5 mm platinum-iridium filament (Alfa Aesar, USA) to heat it and the pipette tip was placed in contact with the filament. Guided by live feed cameras, a hook mounted on a manual translation stage was used to bend the tip over the filament. Subsequently, the thick base of the micropipette required an additional 90° bend for set-up integration, which was accomplished by locally heating the glass with the controlled flame of an alcohol burner and using the pipette's own weight to make the bend. The back end of the prepared pipette was then connected to a 10 mL syringe filled with mineral oil through plastic tubing (1/32 in inner diameter, 3/32 in outer diameter). The tubing was filled with oil until reaching the end of the pipette, and the needle was removed from the syringe to be used as an oil reservoir. For integration in the experimental set-up, vertical posts with custom made 3D printed pieces served as holders for the syring needle. The height of the holders could be manually adjusted to alter the hydrostatic pressure difference between the oil reservoir and the tip of the pipette and control the rate of oil droplet formation (see Figure 2.3). Between experiments, micropipettes would be mounted on the holders for safe storage.

The micropipettes were used to produce oil droplets through the snap-off instability technique [35] for the set-up of experiments (see Section 1.3.1). This required lowering pipettes into the filled chamber and reducing the reservoir height to allow back flow of aqueous SDS solution into the pipette wetting the internal walls. Raising the reservoir to an appropriate height would initiate droplet production via snap-off where the size of the droplet is proportional to the size of the pipette tip. This technique enables production of monodisperse oil droplets with a single pipette, so that using two pipettes with different tip diameters we can generate a bidisperse collection of droplets. For the results shown in this thesis, droplets of diameter 42  $\mu$ m and 70  $\mu$ m were used across experiments.

#### 2.2 Experimental Set-up

Initially, the chamber would be partially filled with  $\sim 7.5$  mL of SDS solution. All components of an active experiment were mounted to a mechanical breadboard (Thorlabs, USA) which rested atop a piezo-electric anti-vibration stage (Halcyonics GmbH, Germany). For illumination, an LED light sheet was placed underneath the chamber. A 3D printed chamber mount was constructed with a circular hole, 4 cm in diameter to enable light to pass through to the active region of the chamber for effective imaging. The chamber was affixed to the mount once partially filled with aqueous SDS solution, and the remaining volume of the chamber would be filled with mineral oil. The mineral oil served two purposes: prevent evaporation of water, and create the concave down oil-water interface within the PTFE tube (active region) to contain oil
droplets in a centralized region enabling viewing for extended periods.

A FLIR Blackfly BFS-U3-31S4M camera (7.07 x 5.3 mm<sup>2</sup> sensing area, 3.1 Mpx resolution) with telecentric 1x objective lens was mounted to a 3-axis translation stage viewing the chamber from above. Two 3-axis translation controllers were set-up to manipulate the position of pipettes. Unwanted microscopic air bubbles were often injected into the solution during the filling process, so time would be taken to search for and remove them from the active region before experiments. For this purpose, an empty micropipette-tube-syringe complex was fabricated to serve as a vacuum to suck out the air. Using a pipette translation stage, the 'vacuum pipette' was inserted from above the active region and used to remove air bubbles.

Once the active region was cleared of air bubbles, the droplet producing micropipettes were mounted to the two translation controllers and lowered through the oil layer to the aqueous solution of the 'droplet corral' region. Initiation of desirable snap-off production of droplets involved careful manipulation of the reservoir height and often resulted in drops larger than desired before snap-off could be achieved. The separated droplet corral section of the chamber was introduced to allow a space to optimize snap-off production without impeding the cleanliness of experiments if unwanted droplets appeared. Once droplets were being produced from both pipettes as desired, they were translated such that their tip was moved inside the active region. This was made possible by the 2 mm high gap between the glass slide and the wall separating the two chamber sections, and the L-shape of the droplet-producing pipettes. The reservoir heights were set to produce droplets at approximately the same rate for each pipette, producing roughly 4000 droplets total in 2 hours (see Figure 2.3). Once droplet production was complete, pipettes were smoothly moved back to the droplet corral region and translated up and out of the chamber.

Recall from section 1.2.3, that a concave down meniscus is generated a concave down meniscus at the oil-water interface within the PTFE tube (see Figure 1.4). The meniscus serves to guide the droplets to the centre of the chamber through the component of the effective buoyant force (difference in buoyancy minus weight) acting parallel to the interface,

$$F_{buoy,\parallel} = \frac{4}{3}\pi r^3 \Delta \rho g \sin \theta, \qquad (2.2)$$

where r is the radius of the oil droplet,  $\Delta \rho$  is the difference in density of water and oil, g is the gravitational constant (9.8 m/s<sup>2</sup>), and  $\theta$  is the local angle of the interface relative to the horizontal. As shown in Figure 2.2, the interface is steep near the edge of the active region and flattens in the centre. This geometry ensures that the parallel component of the buoyant force is only significant close to the outside, gently confining the droplets to the centre of the active region, but minimal in the centre to not interfere with the experiment.

Droplets can be mechanically manipulated by intentionally introducing a steep nearby meniscus. Glass rods (1 mm outer diameter) were pulled in the same manner as the micropipettes to generate a local meniscus and control the aggregate of droplets. The glass rods were fixed to the pipette translation controllers to be introduced from above the active region. By lowering the glass rods just below the water-oil interface to make contact and retracting slightly, a steep upward local meniscus would be generated which strongly attracts nearby droplets. The local meniscus was used to mechanically manipulate the collection of droplets. First, we ensured the bidisperse oil droplets were well-mixed to create the desired disordered system, then the rods



FIGURE 2.2: Side view schematic of the active region during droplet production. Relative sizes are not drawn to scale. The droplet-producing pipette is inserted underneath the PTFE tube to create oil droplets. Droplets rise to the oil-water boundary and move along the interface due to the parallel component of the buoyant force,  $\vec{F}_{buoy,\parallel}$ , which is proportional to the sine of the local angle of the interface with respect to the horizontal,  $\theta$ . A 1x magnification objective lens affixed to a camera captures images from a top-down perspective (see Figure 2.4).

were used to separate the aggregate into two disks of roughly equal radius,  $R_0 \approx 3$  mm. A schematic demonstrating the use of the glass rods is shown in Figure 2.3b, and a representative image is displayed in Figure 2.4a.



FIGURE 2.3: (a) A schematic of the storage position of a droplet producing pipette with connected tubing and oil reservoir. I: Detached syringe needle serving as an oil reservoir. II: 3D-printed mount fastened to a fixed post to hold syringe tip and pipette for storage. Mount can be raised and lowered to alter the flow rate during oil droplet production through the hydrostatic pressure difference driving oil out of the droplet-producing pipette (III). (b) The droplet-producing pipette in the position for droplet production with two glass rods (IV) inserted from above the active region of the chamber to generate steep menisci for mechanical manipulation of droplets. Translation controllers and chamber mount not shown for simplicity. Purple box: schematic showing the steep meniscus of the glass rods attracting nearby droplets.

Once the desired disks were prepared, the experiment was initiated by fully retracting the glass rods, leaving the two disks to interact through the attractive capillary forces (discussed in Section 1.3.3). The camera's position was adjusted to ensure the disks were fully contained in the field of view, and was set to capture images at a rate of 0.5 fps. The two disks meet and begin to merge, requiring individual particles to rearrange and break their cohesive attractive bonds to enable the rafts to progress to a more favourable configuration. A progression of the structure evolution is shown in Figure 2.4. After some time, about 10 - 20 minutes, particle rearrangements cease and the structure gets locked in a metastable configuration which does not continue to relax without additional agitation. At this point the video capture was halted and the experiment was considered complete. Glass rods could then be reintroduced to separate the structure into two circular rafts once more and another trial could be performed.

To vary the concentration of SDS micelles,  $C_m$ , a new chamber was constructed as a different aqueous solution was required and used chambers could not be restored to their initial clean state. The same droplet producing pipettes were used for all experiments such that large and small droplet sizes were identical between trials. The next section discusses the major processes used to analyze the image data acquired from the camera.



FIGURE 2.4: Images demonstrating the evolution of the structure of coalescing droplet rafts in a typical experiment. Scale bars are 500  $\mu$ m. (a) Two separated droplet rafts are held in place by the local meniscus of thin glass rods inserted from above the active region. The black dots and obscured visuals are due to the glass rods in the field of view. (b) Rafts at  $t \approx t_c$ , the time of contact. (c) An intermediate structure at t = 350 s. (d) Final metastable structure at t = 900 s.

## 2.3 Image Analysis

The time series images acquired through optical microscopy during experiments were processed and subsequently analyzed using Python. The images were cropped to only the region containing the droplet rafts to reduce computation time.

#### 2.3.1 Droplet Identification & Tracking

Each frame was analyzed to locate the position of every droplet. A representation of this droplet identification pipeline is given in Figure 2.5. This required performing an image cross-correlation between each pixel in the image and a template image of an oil droplet using the '*matchTemplate*' function from OpenCV [45]. The result of this analysis is an intensity map in which high intensity values correspond to locations which are more similar to the template image. The positions of the droplet centres were then determined from locations of local maxima of this intensity map which were above some minimum threshold. These were extracted using the 'locate' function from the Trackpy library [46].



FIGURE 2.5: Droplet template matching pipeline for locating droplet positions.(a) Cropped region of oil droplet rafts during an experiment. (b) An example large droplet template used for template matching, with radius,  $r_L \approx 35 \,\mu\text{m.}$  (c) Small droplet template with radius,  $r_S \approx 21 \,\mu\text{m.}$ (d) A magnified region of the image (orange box in (a)). (e) The intensity map resulting from template matching with a large droplet template over the region shown in (d). Bright regions correspond to a higher quality cross correlation match, and a peak finding algorithm determines droplet locations. (f) Resulting size distinguished droplet positions after comparing match quality with several templates. Large droplets are represented in blue and small droplet locations are shown in red.

To distinguish large and small droplet positions, this template matching analysis

was performed using a large and small droplet template separately. The slight differences in lighting across the field of view caused significant differences in appearance so that a single template was insufficient to consistently locate every droplet of a particular size across an entire image. Additionally, large and small droplets were similar enough that a large droplet would be incorrectly identified as small when using a small template, and holes/gaps between droplets in the structure would frequently be misidentified as droplets. Droplet identification was optimized by using multiple templates for each droplet size to account for differences in appearance from inconsistent lighting. The use of multiple templates resulted in multiple droplet identification matches at approximately the same location, and the accepted best fit match was taken to be that with the highest cross correlation intensity value. A threshold condition on the maximum pixel intensity in a tested region was used to eliminate misidentified holes. Following this template matching process, droplet positions and diameters were stored in a pandas DataFrame for downstream analysis [47].

In order to be consistent between experiments and correct for global translations and rotations of the raft system, a change of reference frame was performed such that the origin was placed at the centre of mass position or centroid of the collection of droplets in each frame, and the x-axis was directed along the major principle axis of the structure. This will be deemed the 'ideal reference frame.' The centre of mass position in the original (raw) coordinate system was calculated as,

$$\vec{r}_{\rm CoM} = \frac{\sum_i \vec{r}_i D_i}{\sum_i D_i},\tag{2.3}$$

where the position,  $r_{0,i}$ , of each droplet was weighted by its diameter,  $D_i$ , although in a well-mixed random system, this weighting would have no effect. The droplet positions relative to the centroid are then calculated simply as

$$\vec{r}_1 = \vec{r}_0 - \vec{r}_{\text{CoM}},$$
 (2.4)

where  $\vec{r_1}$  represents a droplet's coordinates relative to the centroid, and  $\vec{r_0}$  are the coordinates in the raw image frame. The major and minor principle axes were calculated from the collection of  $\vec{r_1}$  coordinates using principle component analysis, a common dimensionality reduction procedure in machine learning algorithms. In two dimensions, the eigenvectors of the covariance matrix correspond to the directions of the principle axes, where the major axis is oriented along the direction of maximum variance from the centroid (the eigenvector with greatest eigenvalue), while the orthogonal minor axis is along the direction of minimum variance. Practically, this is carried out using the *PCA* routine from the sci-kit learn python library. Relative to the centre of mass coordinate system, this enables us to account for the orientation of the two rafts relative to one another, so that rotating by an angle,  $\theta$  about the centroid according to the orientation of the major axis, the major axis will always lie along the horizontal axis, and the minor axis will lie vertically. If the eigenvector of the major axis is  $\vec{r_*} = [x_*, y_*]^T$ , the angle is calculated as,

$$\theta = \tan^{-1} \left( \frac{y_*}{x_*} \right), \tag{2.5}$$

such that  $\theta$  is the angle between the major principle axis and the horizontal. Then a clockwise rotation by  $\theta$  using a rotation matrix will fix the orientation so that the principle axis is aligned horizontally. This is accomplished by multiplying each  $\vec{r}_1 = [x_1, y_1]^T$  by the clockwise rotation matrix, R,

$$\vec{r}_f = R\vec{r}_1 = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_1\cos\theta + y_1\sin\theta \\ -x_1\sin\theta + y_1\cos\theta \end{bmatrix}.$$
 (2.6)

The final output particle positions,  $\vec{r_f}$ , are relative to the centroid (eliminating global translational motion), and relative to the mutual orientation of the rafts (eliminating global rotational motion). This ideal reference frame enables analysis of only motion resulting from the interaction of the rafts relative to one another.

To investigate the nature of particle rearrangements and discern local spatial information during raft coalescence, particles were tracked between subsequent frames to obtain displacements over time. Tracking was performed using the functionality of the Trackpy library [46]. After optimizing parameters for the tracking algorithm such as the search radius (the maximum distance a single particle is estimated to move between frames), and memory (the maximum number of frames to look backward if a particle is lost in successive frames), the '*link\_df*' routine was used to give an ID to every particle in every frame. The goal was to obtain particle positions in each frame for which particle j in frame 1 was referring to the same particle throughout the time series. Spurious trajectories lasting only a few frames were discarded leaving a DataFrame which ideally contained the tracked positions of each individual particle over the course of the experiment. Displacements were determined by subtracting the positions of subsequent frames. Then, displacements were divided by the time between frames to get the average velocity of each droplet in the ideal reference frame.

#### 2.3.2 Neck Width Identification

To place these experiments in context with related literature on continuum systems, we identify the width of the 'neck' or bridge feature which forms between the two coalescing bodies when they make contact. In Chapter 4, we develop a simple theory to describe the expected evolution of the width of the neck over time. We will next describe the procedure used to identify the width of the neck in each frame. For each frame after the contact between the two rafts, the boundary of the overall structure was traced using routines from the Sci-kit Image library [48]. This involves binarizing the image, performing an edge detection on the result, and filling the holes in the resulting structure to give a closed object as shown in Figure 2.6. The coordinates of the boundary of this object can be extracted, and arranged in sequence to represent the shape as a polygon object, with which we can determine if points, lines, or other polygons lie inside, outside, or on the boundary of the object. Through this polygonal representation of the coalescing structure, the neck was defined as the smallest distance in the direction of the minor principle axis (the y-direction in the ideal reference frame) between the edges of the polygon in the neighbourhood of the centroid. The neck width in each frame was calculated by sweeping through the xdirection, finding the intersections of vertical lines with the edges of the polygon, and taking the minimum width to be the accepted value. Care was taken to ensure the line representing the width was fully contained within the shape. With the same logic, the extent of the structure along the major axis (2L in Chapter 4) was calculated for each frame.



FIGURE 2.6: (a) Unprocessed cropped image of a coalescing raft structure midway through an experiment. Scale bar is 500  $\mu$ m. (b) The result of edge detection, represented with a binarized image so that white pixels are edge locations and black are not. (c) The output after performing a hole-closing routine. (d) The identified aggregate boundary from (c), overlaid atop the unprocessed image. The results of determining the neck width, w, and structure length, 2L, are shown in the orange and purple dashed lines respectively for this frame. The coordinate axes in the ideal reference frame are displayed. y is along the minor axis direction, parallel to the neck dimension, x is orthogonal along the major axis direction. The origin is located at the centroid of the aggregate, not necessarily the position of the neck.

## Chapter 3

# Results

### 3.1 Structural Evolution

Over several trials for each experimental condition, the merging of oil droplet rafts was observed until evolution ceased (Figure 2.4 shows the typical progression of an experiment). It was found that the raft structures did not evolve to a roughly circular shape as would be expected of coalescing liquid disks. Instead, the ageing process was resisted to varying degrees depending on the cohesion strength (concentration of SDS micelles,  $C_m$ ) in the system. We observe that rafts with higher cohesion get locked in a more extended metastable configuration relative to lower cohesion rafts. This tendency can be intuitively explained as local particle rearrangements are necessary for the global structure to evolve, and stronger cohesive forces increase the energy barrier required for particles to move past each other. The athermal nature of the system, owing to the mesoscopic size of the particles, makes overcoming energy barriers unlikely once the system has settled. Figure 3.1 displays typical final morphologies for coalescing rafts under different cohesion strength conditions.



FIGURE 3.1: Representative images of the final structure of rafts with varying cohesion strengths increasing from left to right. Scale bars are 1 mm. (a)  $C_m = 1 \text{ mM}$ , (b)  $C_m = 17 \text{ mM}$ , (c)  $C_m = 71 \text{ mM}$ .

A  $C_m = 0$  condition was experimentally unrealizable since SDS is required for stabilizing the oil droplets against mutual coalescence. If we take the trend of decreasing  $C_m$  to zero, the data suggests that the structure still becomes static well before achieving the circular geometry we might expect from the continuum picture. This can be explained in part when considering the inherent geometric hindrance to rearrangements present even in frictionless packings as briefly discussed in Section 1.1.1 [11].

For the various analyses of the coalescence process, the system was typically treated starting at the first frame of observable contact between droplets in opposing rafts, which we denote,  $t = t_c$ . Recall that after a completed experiment, the aggregate of droplets was separated again into two discs to run another trial. Given the manual process of resetting the experiment and the disordered, granular nature of the system, it is unfeasible to achieve identical initial conditions. Consequently, the separated rafts are not perfect circles and may have different orientations and slightly different relative sizes between trials. As such, an average of several trials with an appropriate normalization is used to make meaningful comparisons between experimental groups.

## 3.2 Neck Width

The primary result is the time evolution of the neck as cohesion strength is varied ( $C_m = 1, 6, 17, 35, \text{ and } 71 \text{ mM}$ ). Figure 3.2a displays the results for one set of experiments at  $C_m = 17 \text{ mM}$ , while Figure 3.2b shows the results of a collection of experiments for each cohesion strength condition. We non-dimensionalize the neck width, w, by normalizing by the ideal initial radius of a raft, R, and define  $\tilde{w} = w/R$ . We assume each raft contains half the total area, and assume a circular shape so that,

$$R = \sqrt{\frac{A_{\text{Total}}}{2\pi}},\tag{3.1}$$

where  $A_{\text{Total}}$  is the total area of the raft.



FIGURE 3.2: Plots of normalized neck width,  $\tilde{w}$ , as a function of  $t - t_c$ . (a) 5 experiments at  $C_m = 17 \text{ mM}$ . The inset contours show the merging raft structure for one particular experiment at various points in its evolution. The dashed orange lines within the contours indicate the determined position of the neck. (b) Many experiments with cohesion strength conditions represented through colour as indicated by the legend.

Then, the data for several trials of one condition are averaged at each time point

relative to the time of contact,  $t - t_c$ . Since the oil droplets are discrete, time is discretized, and the edge detection contains a degree of uncertainty, the neck width makes sudden jumps between frames which is reflected in the curves from individual experiments. Figure 3.3a displays the averaged results of all trials plotted together. The final values of w from the averaged data are taken to be the equilibrium neck width,  $w_{eq}$ . These  $w_{eq}$  are plotted against  $C_m$  in Figure 3.3b. With increasing  $C_m$ , we observe a monotonic decrease in  $w_{eq}$ , and a decreased time to reach the final metastable state.

Sets of experiments within a single chamber could be completed under similar conditions as the same ensemble of droplets were reused. Between chambers however, the number of large and small droplets was not perfectly well controlled. The total number of droplets, N, had a distribution of  $4050 \pm 150$  (standard deviation) excluding the set of highest cohesion experiments for which N = 3533. Likewise, the number fraction of large droplets,  $\phi_L = 0.56 \pm 0.03$  excluding a significant outlier of 0.69 for the  $C_m = 71$  mM experiments. Both N, and  $\phi_L$  are expected to impact the coalescence process as a greater number of droplets will increase the capillary attraction between the rafts in a non-linear fashion [42], and the ratio of large to small droplets, or polydispersity, will affect the likelihood of droplet rearrangements in the system. The variation in these parameters between experiments increases the uncertainty in the presented results. Deliberate manipulation of droplet size, N and  $\phi_L$  is intended for future investigation.



FIGURE 3.3: (a) Plot of normalized neck width,  $\tilde{w}$ , as a function of  $t - t_c$  averaged across trials for each  $C_m$  experimental group. The shaded areas reflect the standard error on the mean. The final values of w are taken as  $w_{eq}$  for (b) a plot of  $w_{eq}$  vs.  $C_m$ . Error bars are standard error on the mean, marker colour is identical to previous plots depicting  $C_m$ .

The plots in Figure 3.3 quantitatively display the trends evident when comparing experimental videos by eye. Namely, the coalescence process is generally halted sooner

and at lesser neck widths for higher cohesion rafts. A more precise functional form is examined in Chapter 4, where we develop a simple theory which fits the data well.

## **3.3** Additional Analysis

#### 3.3.1 Radius of Gyration

Prior to developing the procedure for reliably determining the neck width, the radius of gyration,  $R_g$  was used as a metric for the extent of relaxation in the system. The radius of gyration is calculated here as the root mean squared displacement of droplets from the centre of mass/centroid position, weighted by the droplet diameter,

$$R_g = \sqrt{\frac{\sum_i D_i |\vec{r}_{0,i} - \vec{r}_{\rm CoM}|^2}{\sum_i D_i}} = \sqrt{\frac{\sum_i D_i |\vec{r}_{1,i}|^2}{\sum_i D_i}},$$
(3.2)

where  $\vec{r_1}$  is the position relative to the centre of mass, and  $D_i$  is the *i*<sup>th</sup> droplet diameter. More extended geometries yield a higher  $R_g$ , so as the rafts merge,  $R_g$ decreases, opposite in trend to the neck width, but capturing the same relaxation response. In Figure 3.4, the radius of gyration,  $R_g$  normalized by the radius of gyration of a circle of the same total area as the structure is shown as a function of time since contact. The neck width-based analysis is more relevant to the related literature on liquid coalescence, so the radius of gyration analysis was largely abandoned.



FIGURE 3.4: (a) Plot of normalized radius of gyration as a function of  $t - t_c$  averaged across trials for each  $C_m$  experimental group. The shaded areas reflect the standard error on the mean. (b) An example of the radius of gyration depicted geometrically on top of an experimental image. The scale bar is 1 mm.

#### 3.3.2 Voronoi Tessellation

It is possible that the density of the particle raft increases with time as the system settles to a more preferred configuration, and the local density change is most significant in a certain feature the structure (e.g. the neck, bulk, or perimeter). The Voronoi tessellation is a tiling of space constructed by connecting the perpendicular bisectors of the lines connecting particles centres to their nearest neighbours. The area of a particle's Voronoi cell can give a measure of local density, so it may serve as a useful metric for investigating the spatial distribution of density in the aggregate over time. The visualization is shown for one frame below in Figure 3.5, however it did not yield the resolution that was required to probe density changes in the structure over time. The lack of resolution was due to the sensitivity to particle size, the time resolution, and limited precision of particle positions. If treated equally, small particles are more likely to skew toward large Voronoi areas relative to their size since neighbouring large droplets will bias the area to be larger, and vice versa. Analyzing each droplet size individually was not fruitful.



FIGURE 3.5: (a) Voronoi tessellation of a particle raft in one frame, with colour representing the area of each Voronoi cell. The Red line on the colour bar marks the average Voronoi area. (b) A zoomed section of image shown in (a) to enhance detail.

#### 3.3.3 Particle Velocities

Tracking particles throughout an experiment enables extraction of their displacements and therefore velocities frame to frame. A visualization of the flow can be made using vector arrows to denote the direction and magnitude of each particle's velocity, which is given for one frame in Figure 3.6. Interestingly, particles near the centre of the neck slow early on, while particles toward the outside of the neck (highly curved region of the perimeter) see significant motion along the minor axis (y-direction) as they move to vacant spaces extending the neck as the bulk of the lobes move in toward the centre of mass. Motion along the direction of the neck can be quantified through the y component of the velocity in each frame (in the ideal reference frame), which we expect to decrease as we move away from the neck. Figure 3.7 displays the average magnitude of  $v_y$  of droplets binned according to their *x*-position. Colour is used to show the progression of time, where Figure 3.7a shows the data for 3 times throughout an experiment, and 3.7b displays the data for all frames at once..



FIGURE 3.6: Particle velocities visualized at one instant in the ideal reference frame. Horizontal and vertical axes depict position in the ideal reference frame in pixels. Colour indicates magnitude of velocity according to the colour bar.



FIGURE 3.7:  $|v_y|$  plotted against x for a particular experiment ( $C_m = 6 \text{ mM}$ ), with colour representing different time points. Individual data points are the mean  $|v_y|$  of particles binned by x-position, with bin widths of twice the large droplet diameter ( $\sim 140 \ \mu\text{m}$ ). (a) Data for 3 times, early, intermediate, and late as given in the legend. (b) Data for each frame of the experiment overlaid with time represented according to the colour bar.

From Figure 3.7, we see that as time progresses (moving from yellow through green and blue to purple), the average  $|v_y|$  diminishes and the structural evolution slows as expected. Additionally, the greatest values of  $|v_y|$  are generally located near the neck (close to x = 0), and decrease for particles further away, suggesting the neighbourhood of the neck is the most actively rearranging region throughout the coalescence process.

## **3.3.4** $D_{min}^2$

A quantity termed  $D_{min}^2$  characterizes the relative non-affine motion of particles to their neighbours [49]. Keim and Arriata [50] give a detailed description of  $D_{min}^2$ , supplementing the original discussion by Falk and Langer [49]. Falk and Langer [49] define  $D_{min}^2$  as the minimum mean square difference between the actual displacements of neighbours relative to a central particle, and the relative displacements they would have under a uniform strain.  $D^2$  between time  $t - \Delta t$  and time t is then defined to be,

$$D^{2}(t,\Delta t) = \sum_{n} \sum_{i} \left[ r_{n}^{i}(t) - r_{0}^{i}(t) - \sum_{j} (\delta_{ij} + \epsilon_{ij}) \left( r_{n}^{j}(t - \Delta t) - r_{0}^{j}(t - \Delta t) \right) \right]^{2},$$
(3.3)

where *n* runs over particles within the interaction range of the reference molecule (n = 0), and *i* and *j* indices denote spatial coordinates.  $r_n^i(t)$  represents the *i*<sup>th</sup> component of the position of the *n*<sup>th</sup> molecule at time *t*, and  $\delta_{ij}$  is the Kronecker delta [49]. Minimizing  $D^2$  requires calculating the uniform strain field,  $\epsilon_{ij}$  which minimizes this quantity. This minimization is accomplished through the following,

$$X_{ij} = \sum_{n} \left( r_n^i(t) - r_0^i(t) \right) \times \left( r_n^j(t - \Delta t) - r_0^j(t - \Delta t) \right),$$
(3.4)

$$Y_{ij} = \sum_{n} \left( r_n^i(t - \Delta t) - r_0^i(t - \Delta t) \right) \times \left( r_n^j(t - \Delta t) - r_0^j(t - \Delta t) \right), \quad (3.5)$$

$$\epsilon_{ij} = \sum_{k} X_{ik} Y_{jk}^{-1} - \delta_{ij}. \tag{3.6}$$

The resultant minimum value of  $D^2(t, \Delta t)$  from this procedure represents the local deviation from affine deformation from time  $t - \Delta t$  to time t and is denoted  $D^2_{min}$ . Effective analysis of  $D^2_{min}$  relies heavily on robust and precise particle position tracking, which the experimental set-up did not consistently achieve, hence it was not pursued in great length. Qualitatively,  $D^2_{min}$  gives a result very similar to the  $v_y$  analysis, but the signal is not as strong. Figure 3.8b shows results similar to that of  $v_y$ , using  $D^2_{min}$ normalized by the square of the large droplet diameter. Note that a large  $D^2_{min}$  is associated with regions containing more active rearrangements.



FIGURE 3.8: (a)  $D_{min}^2$  (normalized by large droplet diameter) between subsequent frames visualized for each particle with colour for a particular experimental frame. (b) The same analysis depicted in Figure 3.7b, but with  $D_{min}^2$  on the vertical axis. Time since contact is represented through colour according to the colour bar.

From Figure 3.8, we see more active rearrangements (greater  $D_{min}^2$ ) earlier and closer to the neck region. This analysis gives a detailed picture of the mechanism underlying the particle raft coalescence process through the spatial distribution of particle rearrangements.

## Chapter 4

# Theory

In this chapter we outline a simple theory based on the dominant forces in the system. The system is comprised of two initially separated particle rafts of  $\sim 2000$  cohesive, bidisperse oil droplets, which deform the water-oil interface due to buoyancy. The resulting deformation is energetically costly resulting in capillary forces which tend to drive the system toward a state of minimal interface deformation. In a continuum system this would yield a circular equilibrium shape following the coalescence of two disks. In contrast, within this granular system there are competing forces which arrest this relaxation process, namely geometric frustration, and inter-particle cohesion, as discussed in Chapter 1.

## 4.1 Geometric Description and Assumptions

Figure 4.1 illustrates the geometric parametrization used in the analysis. We begin with two rafts of the same radius, R, and take t = 0 to be the time of contact,  $t_c$ , between the two merging rafts. We take the x-axis to be along the major principle axis (the direction parallel to the line connecting the centroids of the original separated rafts), and y to be the perpendicular minor principle axis direction. Additionally, we set the centre of mass to be the origin. We then define the neck width, w(t), to be the vertical distance between the edges of the structure at x = 0 as a function of time, where w(t = 0) = 0. The extent of the structure along y = 0 is 2L(t), where 2L(t = 0) = 4R. We define non-dimensionalized quantities,  $\tilde{w}(t) = w(t)/R$ ,



FIGURE 4.1: Schematic of an intermediate state during particle raft coalescence, showing the neck width, w, and extent along the major principle axis, 2L. The left lobe is distinguished as the blue patterned area. v is the average velocity of the droplets in the left lobe.

and  $\tilde{L}(t) = L(t)/R$ , for this analysis. Finally, we turn our attention to the portion of the raft for which x < 0 and consider the velocity, v, to be the average horizontal component of the velocity of all particles on that half (effectively the velocity of the centre of mass of the left lobe). Under these geometric conditions, we have,

$$v = -Q\frac{dL}{dt}, \quad \rightarrow \quad \tilde{v} = -Q\frac{dL}{dt},$$

$$(4.1)$$

with the constant, Q > 0, and  $\tilde{v} = v/R$ . We next make an assumption about the relationship between  $\tilde{L}$  and  $\tilde{w}$  as follows. Beyond a short window after contact,

 $\Delta \widetilde{L} \propto \Delta \widetilde{w}$  with a negative proportionality constant (as  $\widetilde{L}$  shrinks,  $\widetilde{w}$  grows). We get,

$$\widetilde{L}(\widetilde{w}) = -G\widetilde{w} + H,\tag{4.2}$$

for positive G and H. Combining Eq. 4.2 and 4.1, we get,

$$\widetilde{v} = -Q\frac{d\widetilde{L}}{dt} = -Q\frac{d}{dt}\left(-G\widetilde{w} + H\right) = QG\frac{d\widetilde{w}}{dt} = K\frac{d\widetilde{w}}{dt},\tag{4.3}$$

where K = QG. The plot of  $2\tilde{L}$  vs.  $\tilde{w}$  shown in Figure 4.2 demonstrates the  $\tilde{L} = -G\tilde{w} + H$  relationship assumed earlier, supporting the validity of our assumption.



FIGURE 4.2: Plot of  $2\widetilde{L}$  vs.  $\widetilde{w}$  for a representative experiment. The trend line is a guide to demonstrate the roughly linear relationship.

#### 4.2 Relevant Forces

Next, we consider the forces acting only on the left lobe of the structure as a function of  $\tilde{w}$ . We consider that the capillary forces must diminish as the structure evolves in time and eventually vanish when there is no energetic benefit to reducing the perimeter of the merged raft. Defining  $\tilde{w}_*$  as the neck width at which the capillary force vanishes, we assume the capillary force varies linearly in  $\tilde{w} - \tilde{w}_*$  and exclude higher order terms. Note that  $\tilde{w} \leq \tilde{w}_*$ . Then for the capillary force,  $F_{cap}$ , we take,

$$F_{cap} = -B(\widetilde{w} - \widetilde{w}_*), \tag{4.4}$$

where the coefficient B has units of force, and B > 0 for the force to be diminishing with increasing  $\tilde{w}$ . As we will see, this simple approximation works well at capturing the time evolution of the neck width. Note that Eq. 4.4 suggests the force at  $\tilde{w} = 0$ is  $B\tilde{w}_*$ .

We next consider the competing forces in the system which impede the progression of the structure. The short range cohesive force between particles contributes to the repulsive contact force between the left and right lobes of the structure. A greater number of contacting droplets between the lobes should result in a greater resultant force. Thus, we assume a repulsive force which scales with the number of contacts, proportional to  $\tilde{w}$ , and with the strength of the cohesive attraction, proportional to  $C_m$ . Additionally, there is an effective repulsion,  $F_{geom}$ , due to the geometric hindrance to particle rearrangements, which also scales linearly with  $\tilde{w}$ . The inclusion of the term for geometric effects is guided by the data which suggests that at  $C_m = 0$ , the neck width of the equilibrium structure,  $w_{eq} \neq \tilde{w}_*$ , where  $w_{eq} = \tilde{w}(t = \infty)$ . For the magnitude of the repulsive force,  $F_{rep}$ , we get,

$$F_{rep} = [D(C_m) + F_{geom}] \widetilde{w}, \qquad (4.5)$$

where D, and  $F_{geom}$  are positive constants with units such that each term has dimensions of force. Finally, we consider that this low Re system has a drag force,  $F_{drag}$ , proportional to v and acting in the opposite direction of motion (discussed in Section 1.2). The magnitude of the drag force can be expressed as,

$$F_{drag} = J\widetilde{v},\tag{4.6}$$

where J is a constant with J > 0. The experiments hold the size of the rafts, droplet size ratio, and absolute droplet size roughly constant, so the dependence on these parameters is ignored, though we expect they would have a significant impact on the dynamics.

### 4.3 Neck Width Evolution

The net horizontal force at a given neck width and  $C_m$  under these assumptions is thus,

$$F_{net} = F_{cap} - F_{rep} - F_{drag}$$

$$F_{net} = -B(\widetilde{w} - \widetilde{w}_*) - [D(C_m)\widetilde{w} + F_{geom}] - J\widetilde{v}$$

$$F_{net}(\widetilde{w}, C_m) = -[B + F_{geom} + D(C_m)]\widetilde{w} + B\widetilde{w}_* - J\widetilde{v}.$$
(4.7)

Notice this suggests an equilibrium neck width,  $w_{eq}$ , when  $F_{net} = 0$ , and  $\tilde{v} = 0$  of,

$$w_{eq} = \frac{B\widetilde{w}_*}{B + F_{geom} + D(C_m)}.$$
(4.8)

To proceed, we claim that this is a quasi-stationary flow process, such that at any moment the acceleration of either lobe of the structure is sufficiently small to claim  $F_{net} \approx 0$ . Recalling Eq. 4.3, we have,

$$F_{net} = 0 = -[B + F_{geom} + D(C_m)]\widetilde{w} + B\widetilde{w}_* - J\widetilde{v}$$

$$J\widetilde{v} = JK\frac{d\widetilde{w}}{dt} = -[B + F_{geom} + D(C_m)]\widetilde{w} + B\widetilde{w}_*$$

$$M\frac{d\widetilde{w}}{dt} = -[B + F_{geom} + D(C_m)]\widetilde{w} + B\widetilde{w}_*$$

$$\frac{d\widetilde{w}}{dt} = -\left(\frac{B + F_{geom} + D(C_m)}{M}\right)\widetilde{w} + \left(\frac{B\widetilde{w}_*}{M}\right) = -\alpha\widetilde{w} + \beta,$$
(4.9)
$$(4.9)$$

where M = JK, and for simplicity the coefficients have been combined into  $\alpha$  and  $\beta$ , both positive constants. Integrating the differential equation of Eq. 4.10 with separation of variables, we get,

$$\int \frac{d\widetilde{w}}{-\alpha \widetilde{w} + \beta} = \int dt$$
  
$$\frac{-1}{\alpha} \ln|-\alpha \widetilde{w} + \beta| = t + C_0$$
  
$$-\alpha \widetilde{w} + \beta = C_1 e^{-\alpha t}$$
  
$$\widetilde{w}(t) = C_2 e^{-\alpha t} + \frac{\beta}{\alpha}.$$
 (4.11)

Using the initial condition,  $\widetilde{w}(t=0) = 0$  gives  $C_2 = -\frac{\beta}{\alpha}$ , yielding,

$$\widetilde{w}(t) = \frac{\beta}{\alpha} \left( 1 - e^{-\alpha t} \right). \tag{4.12}$$

Eq. 4.12 suggests the neck width asymptotically approaches,

$$w_{eq} = \frac{\beta}{\alpha} = \frac{B\widetilde{w}_*}{B + F_{qeom} + D(C_m)}.$$
(4.13)

Additionally, the time constant of exponential decay is  $1/\alpha$  which decreases for increasing  $C_m$ . Figure 4.3 displays the results of fitting Eq. 4.12 to the data, which captures the behaviour well considering the stochasticity of droplet rearrangements. The manual procedure of selecting the contact frame coupled with the time resolution of the data result in a non-zero average neck width at t = 0, so the curves are shifted horizontally so that their best fit curve passes through the origin.



FIGURE 4.3: Fitting Eq. 4.12 to the  $\tilde{w}$  vs. t data from Figure 3.3. Curves are horizontally shifted according to the best fit profiles to force the initial condition, w(t = 0) = 0.



FIGURE 4.4: Fitting  $w_{eq} = \frac{\beta}{\alpha}$  vs.  $C_m$ . The dashed line is Eq. 4.13 with best fit parameters. Error bars are standard error on the mean.

Using the experimental data for  $w_{eq}$  vs.  $C_m$  shown in Figure 3.3b, we can fit the data according to Eq. 4.13 to yield the plot in Figure 4.4. The trend of equilibrium neck width versus  $C_m$  is well captured by the theory.

This functional form is not typical of the neck width time evolution of coalescing continuum liquids which see characteristic power law behaviour for short times. However, the granular and athermal characteristics of the system, and the presence of interactions (cohesive pressure and geometric effects) which halt structural evolution, make this system fundamentally unique from continuum Newtonian fluid systems.

## Chapter 5

# Conclusion

Following a background discussion of the relevant physics of granular materials, fluids, and their intersection, we outlined an experimental procedure where the coalescence of 2D rafts of cohesive oil droplets was observed. The strength of cohesion between droplets was varied and its effect on the time evolution of the neck was captured. We developed a simple model which captures the structural evolution in this granular system, and find that it differs from the typical continuum coalescence literature. The project is intended to be extended with an investigation of the effect of droplet size, number, and polydispersity on the particle raft coalescence process.

Our unique experimental system has several features which enable us to supplement novel findings to the body of experimental research on granular systems. The ability to achieve monodispersity with an extremely small size variation relative to conventional microfluidics systems is one primary feature. We are able to finely tune the degree of disorder in the system through the number ratio of large to small droplets, spanning from perfectly crystalline monodisperse systems, to evenly distributed bidisperse ensembles. This level of control is rare in the research area, and allows to directly address questions about the effect of disorder on the behaviour of granular systems. Furthermore, the ability to control the strength of inter-particle cohesion in the system admits careful exploration of an uncommon regime of granular physics. Using a two-dimensional monolayer of particles permits tracking each individual constituent particle throughout an experiment which cannot be achieved in three-dimensional systems. Knowledge of all particle positions makes possible a broad spectrum of analyses which enable us to precisely characterize many aspects of the system's behaviour. The described features of our system of cohesive, monodisperse oil droplets make it fruitful for performing experiments under well-controlled conditions to strengthen the scientific community's understanding of granular media.
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