CONFINED
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Colloidal
DROPLETS

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The work in this thesis was carried out at the Physics of Fluids group of the Faculty of Science and Technology of the University of Twente. This thesis was financially supported by the European Research Council (ERC) Starting grant no. 678573 *NanoPacks*.

Dutch title:

Begrensde en Colloïdale Druppels

Publisher:

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P.O. Box 217, 7500 AE Enschede, The Netherlands

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ISBN: 978-90-365-5100-7

DOI: 10.3990/1.9789036551007

CONFINED AND COLLOIDAL DROPLETS

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof. Dr. Ir. A. Veldkamp,
on account of the decision of the Doctorate Board,
to be publicly defended
on Friday the 15th of January, 2021 at 14:45

by

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Introduction

In this thesis we focus on the evaporation of colloidal droplets and confined droplets. A confined droplet is a droplet that is bound by its surroundings, and therefore the interaction between the droplet and its surrounding medium is crucial. This confinement can be introduced by the presence of walls in the system, as is the case in microfluidic systems. Changing the channel geometry influences for example the droplet breakup at T-junctions in the device [1]. Another approach to change the confinement of a droplet, is to fully encapsulate it into another phase. In our case, we provide the confinement by using an elastic medium to immerse the droplet. As a result, deformations of the droplet are coupled to deformations of the gel, which introduces an elastic tension to the system. When a droplet evaporates in such a system, the presence of the gel highly influences the shape and behaviour of the droplet during its evaporation.

Colloidal droplets are droplets in which particles are suspended. Colloidal particles are typically between ~ 10 nm and several microns in size [2–4]. One of the most common cases of the evaporation of a colloidal droplet is the drying of a coffee droplet. Coffee can be seen as an colloidal suspension, as it contains coffee particles. Figure 1a shows a typical image of the final deposition pattern of the coffee particles, after the coffee drop has completely evaporated. Even though the coffee droplet had a spherical cap shape, the particles have arranged themselves predominantly in a ring at the edge of the droplet in the final stain. This is the so-called *coffee stain effect*, which is first studied by Deegan *et al.* [5]. In order to form this dense ring of particles, the contact line of the droplet must remain pinned throughout the evaporation process. This means that the base radius of the droplet is fixed and only the contact angle decreases in time. Both the roughness of the substrate can promote pinning, as well as the presence of particles inside the droplet.

Flow inside an evaporating droplet

We will model the evaporation of a sessile droplet as a diffusion-limited process. This is, the droplet maintains its closest interface saturated with vapor, which must diffuse to the unsaturated surrounding. When the diffusion equation is solved for the vapour concentration in the air surrounding the droplet, one can obtain the diffusive flux J from the drop surface. The contact angle of a sessile droplet can be anywhere between 0 and 180° , see Fig. 1b for its definition. Substrates on which a water drop displays a contact angle smaller than 90° are considered hydrophilic, for larger contact angles the substrate is classified as hydrophobic. We will focus on the solution for $\theta < 90^\circ$ (hydrophilic substrates) in the following analysis. As the evaporation-induced motion of the droplet is much slower than the diffusion time for the vapour transport [6], the quasi-steady concentration field is given by

$$\nabla^2 c = 0. \quad (1)$$

The evaporative flux J along the droplet interface is related to the gradient in vapour concentration as

$$\mathbf{J} = -D\nabla c, \quad (2)$$

with D the diffusion constant for vapour in air. The boundary conditions to solve equation 1 are (i) the substrate is impermeable for vapour, (ii) the vapour concentration just above the droplet interface equals the saturated vapour concentration c^* (iii) the vapour concentration at infinity equals c_∞ . This means that if $c^* > c_\infty$ an outward diffusive flux is present and the droplet evaporates. The full solution for the evaporative flux for a spherical cap shaped droplet is solved by Popov [7]. This solution for J is schematically depicted in Fig. 1b, using arrows to indicate its magnitude. The flux is non-uniform along the droplet surface and diverges as the contact line is approached.

The internal flow inside the droplet depends on the mode of evaporation of the droplet. If the droplet is pinned, the liquid that evaporates in the contact line region must be replenished, in order to maintain the spherical cap shape set by the surface tension of the droplet. As a result, an internal capillary flow sets up, which is directed towards the contact line. If the droplet contains particles, these particles follow this internal flow and end up at the contact line, where they form a three dimensional packing, see Fig. 2a. How these particles order themselves changes in time. Initially, when the flow velocity inside the droplet is low, particles have time to arrange themselves and a crystalline structure is obtained [8]. However, near the end of the evaporation process the flow velocity diverges. In this stage particles arrive with high velocity and as a result a disordered particle

Figure 1: Figure (a) Typical image of the stain which is left after a coffee drop has evaporated, the so-called *coffee stain*. Figure (b) shows an evaporating sessile droplet and its evaporative flux J , represented by arrows. The definition of the contact angle from the droplet θ is given as well.

arrangement appears in the particle ring. This final stage is often referred to as the *rush hour* in the life of a colloidal droplet.

In many applications a homogeneous particle distribution is needed, for example to obtain uniform coatings and prints. Therefore several methods are investigated how to tune the particle deposition, and to prevent all particles ending up in a three dimensional ring. Most of these studies rely on introducing a Marangoni flow at the interface, to change the resulting internal flow field. One example to change the flow inside an evaporating sessile drop, is the addition of salt. Salt acts as an *anti-surfactant*, as it increases the surface tension of water [3]. When such a salty drop evaporates, surface tension gradients will arise at the interface. The salt content near the contact line increases, as evaporation is the strongest in that region. As a result, the surface tension increases locally at the contact line and a Marangoni flow sets up, directed from the apex of the droplet towards the contact line. The internal flow is completely reversed as compared to the classical coffee stain case. This flow reversal has been examined both experimentally and numerically [9]. A schematic representation of the flow inside an evaporating salty droplet is shown in Fig. 2b.

Other approaches to influence the interfacial flow which arises from gradients in surface tension, are introducing thermal gradients, variations in the liquid composition or the addition of surfactants [10–14]. Tuning these control parameters, different deposition patterns as compared to the classical coffee stain ring can be obtained, and can even lead to fully suppressing the ring-shape. Whether the lack of the ring-shape is solely due to the change of the internal liquid flow, or it is due to changes in the wetting conditions or the change of physicochemical interactions when additional solvents are added, is it yet an unsolved question.

Figure 2: The evaporation of colloidal droplets, with and without the addition of salt. Figure (a) shows how particles move in the classical coffee-stain case: they all end up in a 3-dimensional packed structure near the contact line. Figure (b) shows how particles will arrive at the contact line, in the case salt is added to the droplet: they assemble into a monolayer at the droplet's interface. A schematic representation of the difference in salt concentration in the droplet is given by the different density of stars *, as well as the resulting gradient in surface tension γ .

Particle interactions

If a colloidal droplet evaporates, the movement and deposition of the particles is influenced by the flow inside the droplet. However, the particle interactions themselves are also of great importance. This includes for example the particle shape, their electrostatic repulsion and their attraction to the interface or substrate. Polystyrene particles are widely used in droplet evaporation studies. These latex microspheres are by themselves attractive [4]. Therefore, the surface of these particles needs to be functionalized in order to prevent the formation of clusters. Using charged groups, like sulphate groups, increases the electrostatic repulsion and consequently decreases the tendency to cluster. The ζ -potential, which is proportional to the electrostatic potential at the surface of the particle, is a good measure for the repulsion between particles [3]. An important factor for particle stability is the ionic strength of the solution, *i.e.* the salt concentration. Increasing the amount of salt in a solution, increases the screening of the electrostatic barrier that prevents the particles from aggregation [15]. At high salt concentrations particle solutions lose their stability and the particles aggregate. Furthermore, also the shape of particles is an important factor for their movement inside an evaporating droplet. Depending on the amount of anisotropy of the particles, different growth mechanisms of the particle deposits can be characterized [16].

Applications and aim of the project

The ability to tune the deposit of an evaporating colloidal droplet, is important for many applications. In printing and coating processes, it is crucial to prevent ring-shaped deposits in the final product. Either uniform coatings or homogeneous dried ink drops are desired [17, 18]. Another application in which controlling the particle deposit is relevant, is in chemical analysis and detection. In the case of DNA analysis the inhomogeneous deposition pattern of the molecules leads to detection problems [19].

If one wants to detect the presence of an analyte at extremely low concentrations, ultra-sensitive techniques such as Surface Enhanced Raman Spectroscopy (SERS) can be employed [20]. In SERS this ultrasensitive detection is made possible using electromagnetic enhancement, resulting from the amplification of the light generated by the excitation of localized surface plasmon resonances (LSPRs). This amplification occurs mostly in gaps, or other sharp features of plasmonic materials like golden particles with nanoscale features [21]. In order for these techniques to function, special nanostructured surfaces need to be produced for the analyte to adsorb on. The adsorption of analyte onto the nanostructures currently relies on self-assembly techniques, which means an attractive interaction between them is required. As a result the applications are limited: the variety of analytes that one can use is narrowed, or it requires to functionalize the surface or to modify the analyte. Therefore, it would be desirable to put together analyte and detector using physical means and not chemical ones.

The NanoPacks project aims to use evaporating colloidal droplets as a system to bring analyte and plasmonic agent together in a passive way for applications of high-sensitivity SERS, without relying on chemistry. Since the idea of the project is to simplify this assembly process, the plasmonic agent could be either metallic nanoparticles or metallic-coated polymer microparticles. More specifically, the aim is to obtain organized clusters or arrangements of functional particles in a reliable way that could be used as functional structures for SERS, where the analytes will also be left. This is done in several platforms in order to explore different possibilities of control and for extraction. These platforms are: (1) Droplets inside microfluidic devices, which have the advantage of the high control on size and position that microfluidic technology offers. (2) Superhydrophobic substrates, which can be more easily handled and have better optical accessibility. (3) Droplets inside gels, which would have the advantage of reducing the exposure of the liquid sample to air, either to reduce contamination or to prevent the contamination of the environment (in case, for example, of a biologically hazardous sample). (4) Pinned droplets on flat substrates, which could be manipulated to develop a monolayer network of particles.

In this thesis, we focus on the last two platforms described above: droplets inside elastic media and pinned droplets on flat substrates. The gel chosen for the first case are elastomers based on silicone oil, which are very permeable to water vapour. These gels are very accessible nowadays, they can be moulded into any desirable shape, but they have complex viscoelastic properties that will turn out to be crucial in the droplet shrinkage process. Regarding the droplets on flat substrates, we will make use of Marangoni flows to manipulate the particle organization on the substrate in a reliable way.

A guide through the thesis

In this thesis we investigate the evaporation behaviour of both confined and colloidal droplets. We also see how changing the surface tension of the droplet changes its behaviour, not only for the resulting particle deposit in the case of evaporating salty colloidal droplets, but also for the coalescence of sessile surfactant droplets.

First we focus in chapter 1 on the evaporation of a pure water droplet that is fully confined by an elastic medium. We show that the droplet undergoes 3 phases in its lifetime. Initially the droplet just shrinks isotropically and evaporation occurs pure diffusively. When the surrounding gel reaches a critical stress, a creasing instability occurs, which means the gel folds onto itself. This partially releases the stress in the elastic medium. However, as the droplet keeps evaporating, the negative pressure keeps building up inside the droplet which ultimately leads to cavitation. A stable bubble is recovered with a similar size as the initial droplet. We study both the long term evaporation process, as well as the fast dynamics of the cavitation bubble, therefore spanning 9 orders of magnitude in a single experiment. The sudden bubble growth and oscillations are described using an inertial-(visco)elastic model.

Subsequently, the evaporation of a confined colloidal droplet is investigated in chapter 2. When a droplet that contains particles, evaporates inside an elastic medium, cavitation can be stimulated earlier, thereby suppressing the creasing event completely. The chances for an early cavitation event to occur increase with particle size and particle concentration. This system of a colloidal droplet surrounded by an elastic medium serves as a simple and reliable method to measure the tensile strength of particle solutions.

Next we focus on the evaporation of salty sessile colloidal droplets in chapter 3. In previous studies the flow pattern inside this salty droplet has been examined both experimentally and numerically [9]. The internal flow is completely reversed as compared to the classical coffee stain case, as a result of surface tension gradients. In this chapter we

show that the particles in this salty droplet assemble themselves into a monolayer at the droplet's interface. In Fig. 2b a schematic representation of this flow reversal is shown, as well as the resulting particle assembly. Using laser scanning confocal microscopy we study how the particles are arranged in this monolayer. By changing the initial salt concentration of the droplet, we can tune the particle structure inside this monolayer. Thereby we can control the final deposition of the particles and even yield homogeneous deposition.

Finally we alter the surface tension of the droplets by using surfactants. In chapter 4 we show that two sessile surfactant droplets do not immediately merge, but remain in a temporary state of non-coalescence. We classify 3 regimes for this delayed coalescence, which occur for different initial contact angles and surface tensions of the droplets. Not only the surface tension difference is crucial, but also the surfactant concentration itself. This reveals that the coalescence of surfactant droplets is not purely hydrodynamically governed, but largely depends on the molecular physics of surfactant adsorption.

CHAPTER 1

TURNING DROPS INTO BUBBLES: CAVITATION BY VAPOR DIFFUSION THROUGH ELASTIC NETWORKS

Published as: **Myrthe Adriana Bruning**, Maxime Costalonga, Jacco H. Snoeijer, and Alvaro Marin, *Turning Drops into Bubbles: Cavitation by Vapor Diffusion through Elastic Networks*, *Physical Review Letters* **123**, 214501 (2019).

ABSTRACT

Some members of the vegetal kingdom can achieve surprisingly fast movements making use of a clever combination of evaporation, elasticity and cavitation. In this process, enthalpic energy is transformed into elastic energy and suddenly released in a cavitation event which produces kinetic energy. In this chapter we study this unusual energy transformation by a model system: a droplet in an elastic medium shrinks slowly by diffusion and eventually transforms into a bubble by a rapid cavitation event. The experiments reveal the cavity dynamics over the extremely disparate timescales of the process, spanning 9 orders of magnitude. We model the initial shrinkage as a classical diffusive process, while the sudden bubble growth and oscillations are described using an inertial-(visco)elastic model, in excellent agreement with the experiments. Such a model system could serve as a new paradigm for motile synthetic materials.

1.1 Introduction

Unlike animal cells, the swelling and shrinkage of plant cells are fundamental for the motion of the whole body of the plant. The key is the wall surrounding the cells: a thin but stiff wall that allows the cells to sustain large pressure differences [22]. Motion in plants often occurs over extremely separated time scales, one in the range of hours and/or days, related with tissue swelling/shrinkage and the other in the order of fractions of milliseconds, related with mechanical or thermodynamics instabilities. This fast motion typically involves the storage of elastic energy in the system and its quick (and often dramatic) release. One example of such quick release of energy is triggering by elastic instabilities, like the snapping of the Venus flytrap [23]. It can also involve more violent phenomena as cavitation, as in the fern sporangia [24]: the fern's cells shrink when they dehydrate. This induces a deformation of the sporangium, which results in accumulation of elastic energy. This energy is then quickly released in a sudden cavitation event inside several of the fern's cells, which restores the elastic energy stored in the fern and catapults the spores at large distances [24]. A synthetic analogue system was studied in the past [25] by cutting out cavities inside water-soaked hydrogels, while others have instead used a laser into hydrogels to generate a cavity, soaked it in water and then left it to dehydrate [26, 27]. In such examples, the hydrogel's high liquid affinity and rigidity yielded relatively small deformations which did not result in a significant release of mechanical energy.

In this chapter, we consider cavitation through evaporation of a drop in a soft gel [29] putting special emphasis in the cavitation and bubble expansion in the elastic medium. This system serves as a mechanical analogue of a plant cell, where the use of large elastic deformations provide an attractive route for the conversion of elastic to mechanical energy. After a slow diffusion-limited droplet shrinkage in which elastic energy is stored in the material, a rapid cavitation event follows, releasing the energy suddenly. This system allows us to monitor for the first time the whole dynamics of such complex process, from the day-long fading of the liquid droplet, to the millisecond birth and growth of the cavitation bubble. Moreover, we show that these features are accurately captured by a modified Rayleigh-Plesset equation, accounting for the viscoelastic properties of the medium.

1.2 Experimental Methods

The system under study is a single millimetric water droplet trapped in an elastic medium. The gel used is Dow Corning PDMS Sylgard184 mixed in a 1:10 ratio (curing agent:base polymer). The static shear modulus μ_0 of this gel is 0.7 MPa, as measured using a rheometer (Anton Paar MCR 502). Figure 1.1a.1 shows an image of the droplet in its initial state. A transparent containing box is filled with uncured PDMS and placed inside a chamber with

Figure 1.1: Different phases in the life of a droplet in a dry and elastic medium: (a.1) The initial water drop in a PDMS-based gel starts to shrink isotropically by evaporation. (a.2) While shrinking, the elastic medium is deformed, certain amount of elastic energy is released by creasing at the solid-liquid interface. (a.3) Eventually, enough negative elastic pressure is accumulated and a cavitation event occurs: a bubble of approximately the same size as the original liquid droplet is created. (b) The curve shows the evolution of the effective droplet radius in time and illustrates the disparity of time scales, from a day to a fraction of a millisecond. The corresponding instants for the images in the (a)-panels are also indicated. (c) A zoom of the cavity radius dynamics just after cavitation occurred at t_{cav} . A movie of the full droplet evaporation is given in the Supplementary Material [28].

a Peltier temperature control unit (dataphysics) at 70°C . After an initial pre-curing period of the gel of 15 minutes a water droplet is inserted in the center of the box, either using a micro-pipette or a tapered capillary, depending on the desired initial droplet radius R_0 . The injection of the droplet at this moment allows us to locate the droplet steadily at a given location, while the polymer structure is still not fully reticulated, avoiding the presence of an initial stress field in the PDMS. This experimental setup has been specifically designed to capture both the whole droplet shrinkage process (spanning approximately a

day) and the final cavitation event (which occurs in milliseconds) in one single experiment with good temporal and spatial resolution. To this end, we use two side view cameras, one recording at one frame per minute (Ximea MQ013MG-ON) and a high speed camera (Photron SAX-2), mounted in perpendicular direction. The high speed camera is installed to capture the dynamics of the cavitation event, at the final stage of the experiment. Image triggering is used to start recording at frame-rates in a range from 360 to 450 kfps. The duration of the full experiment varies from 3 hours to 50 hours depending on the initial drop radius R_0 (from 200 to 1000 μm).

1.3 Results

A typical experiment exhibits three stages, as shown in Fig. 1.1a. At first, the droplet shrinks isotropically due to diffusion of water vapor into the surrounding PDMS (Fig. 1.1a.1). Then, at a certain time the droplet loses its spherical shape due to an elastic instability (Fig. 1.1a.2). During evaporation of the water droplet, the droplet size decreases and elastic stress builds up at the interface with the deformed material. Eventually, such stress is partially released by the formation of surface folds, triggering the so-called *creasing instability* [30–33]. In a somewhat different setup, Milner *et al.* [29] studied the onset of creasing for droplets immersed in gels. In the present work, creases are observed below a critical radius $R/R_0 = 0.73 \pm 0.05$, in agreement with reference [29]. Finally, as the droplet further evaporates, a negative pressure builds up inside the drop due to the tensile stresses exerted on the cavity, ultimately leading to cavitation (Fig. 1.1a.3).

The final radius of the bubble is close to the initial droplet radius ($0.98 R_0$), such that plastic deformation is negligible. The bubble in our study remains stable after the cavitation event occurs. This differs from the behavior of laser-induced bubbles in air-saturated hydrogels [34], in which gas diffusion leads to further bubble growth. An example of how the radius $R(t)$ typically evolves over time is provided in Fig. 1.1b. After the creasing, the droplet is no longer spherical and we characterize its size with an effective radius using its projected area. The shrinking process is not altered substantially by the breaking of spherical symmetry, illustrated by the smoothness of $R(t)$ in Fig. 1.1b. Finally, the data captured during the cavitation event is blown up in Fig. 1.1c. A key feature of the experiment is the disparity of time scales in this single experiment, which span 9 orders of magnitude.

1.3.1 Droplet evaporation

We now proceed with a more detailed analysis of each of the stages, starting with the slow droplet shrinkage. We hypothesize that this is a diffusion-limited evaporation process in thermal equilibrium, since water and PDMS have low affinity and no convection is present

Figure 1.2: Evaporation of a water droplet in PDMS. Figure (a) shows the data for evaporation at different temperatures, in which the slope indicates the evaporation rate. Figure (b) shows the linear trend for dimensionless droplet area loss $1 - R^2/R_0^2$ as a function of $t^* = t/t_F$ for different initial radii and temperatures.

in the system. Rewriting the droplet radius R as a function of time t , this predicts $R_0^2 - R^2 = 2D\Delta c t/\rho$ [6]. Here R_0 represents the initial droplet size, ρ the density of water in its liquid phase, D the diffusivity of the water vapor in the gel and $\Delta c = c^* - c_\infty$ the concentration gradient between the interface and the far field (the last two properties are temperature dependent). Figure 1.2a shows the typical change in radius $R_0^2 - R^2$ versus time for different experimental conditions. The linear trend over a wide range of temperatures and ambient humidities (not shown here) confirms the diffusive behavior.

To quantitatively test the diffusion model, we represent the data in dimensionless form by scaling the radius as R/R_0 and time as $t^* = t/t_F = t \cdot 2D\Delta c/(\rho_w R_0^2)$. For the latter scaling, we take the diffusivity D at different temperatures from [35], while Δc is obtained by fitting the slopes in Fig. 1.2a. Following this approach we achieve a collapse of the data, shown in Fig. 1.2b with values $\Delta c = 40\text{-}50 \text{ mol/m}^3$. These are in good agreement with data from [36]. Hence, we conclude that the shrinkage of the droplet inside this elastic material is governed by a relatively simple diffusion-limited process.

1.3.2 Cavitation event

The evaporation of the water droplet eventually leads to a very rapid cavitation event, the final stage in the droplet's life, at typical values of $R/R_0 = 0.48 \pm 0.1$. The exact location of the bubble nucleation is hard to determine from the images, but it seems to occur often at the liquid - gel interface. Since cavitation occurs here due to the tensile elastic stress that builds up in the gel, we estimate it by computing the elastic energy for a spherical cavity, which can be written as $\epsilon_{el} = 4\pi\mu R_0^3 F(\xi)$. In this expression μ is the shear modulus, $\xi = R/R_0$ the scaled bubble radius, and for a neo-Hookean solid the dimensionless function is $F(\xi) = \frac{5}{6}\xi^3 - \xi^2 - \frac{1}{3} + \frac{1}{2\xi}$ [37, 38]. The minimal energy appears at $\xi = 1$, at which the elastic medium is undeformed with respect to its reference state, and a tensile elastic stress appears for $\xi < 1$. The (negative) pressure inside the cavity can then be computed using the virtual work principle $\Delta p \delta V_{cav} = \delta \epsilon_{el} + \gamma \delta A_{cav}$, where we also introduced surface tension γ , and the volume V_{cav} and area A_{cav} of the cavity/drop. Using the spherical approximation for the cavity, estimating the virtual work from δR , one obtains the pressure inside the cavity

$$p_{cav} = p_\infty + \frac{2\gamma}{R} + \frac{\mu}{\xi^2} F'(\xi), \quad (1.1)$$

where p_∞ is the atmospheric pressure far away from the droplet. Upon creasing $\xi = 0.73$, using $\mu = \mu_0$, this results in $p_{cav} = -1.3 \text{ MPa}$, this pressure can be seen as a lower bound for the pressure upon which cavitation occurs. Under extreme deformations, PDMS (1:10) is better described using the Gent model [29], which takes into account the finite extensibility of polymer chains. However, for $\xi = 0.73$ no significant difference in $F'(\xi)$ is present for the two material models.

Suddenly, cavitation irrupts: a bubble appears and expands quickly, occupying almost the entire cavity previously occupied by water. Images of the early growth of such bubble are shown in Appendix 1.5.3. Two distinct stages can be observed: At early times, the bubble grows at constant velocity¹ and fills up the cavity. By tracking the bubble growth velocity

¹The growth of this early-stage bubble is linear, see Appendix 1.5.3, showing that it obeys the steady-state solution of the unconfined Rayleigh-Plesset equation [39].

Figure 1.3: Dynamics of the elastic cavity. The dynamics of the cavity growth for different initial droplet radii. Figure (a) shows the growth of the cavity for different initial droplet radii. Figure (b) displays the non-dimensionalized growth dynamics R/R_0 as a function of $t\sqrt{\mu/\rho}/R_0$ (with $\mu = 1.7 \text{ MPa}$, see text). In both figures a power law of 2/5 is displayed. The same legend applies for the two figures. The Supplementary Material [28] contains high-speed movies of the cavitation event and the subsequent cavity growth.

in that stage (v_i), see Appendix 1.5.3, we can probe the pressure of the liquid: using $v_i = 30 \text{ m/s} = \sqrt{-2\Delta P/(3\rho)}$ [39, 40], we obtain $\Delta P = -1.4 \text{ MPa}$, which is indeed consistent with the value estimated from creasing. Previous studies [29] also observed cavitation events in similar PDMS-formulation just before creasing. Although there is no general consensus regarding the critical pressure for cavitation in water, our values seem to yield somewhat lower tension as compared to other systems [41, 42]. This difference can be explained by the fact that cavitation occurs in a more heterogeneous way in the PDMS matrix, due to its hydrophobic properties and porosity. In the later stage, the bubble has reached the cavity walls and the cavity expands to almost its original size. We will continue analyzing this last stage of growth. As can be seen in Appendix 1.5.3, the cavity is initially not perfectly spherical, as a result from the creasing event prior to cavitation. Therefore an effective radius is used to analyze the growth of this cavity. Figure 1.3a shows the growth of the elastic cavity as a function of time, for several initial droplet sizes. Figure 1.3b shows the result in dimensionless form, also including smaller initial droplet sizes. For all droplet sizes we observe a power law for the growth stage, followed by (damped) oscillations and eventually a nearly static shape at $R/R_0 \approx 0.9$. A few minutes after the cavitation event, the cavity will eventually grow to $R/R_0 \approx 0.98$, practically recovering the initial droplet size. In Fig. 1.3 time is rescaled using $R_0/\sqrt{\mu/\rho}$, where $\sqrt{\mu/\rho}$ is the shear wave velocity. This appears to be the appropriate timescale for the cavity growth, showing that the dynamics emerge from an interplay between the cavity's inertia and the gel's elasticity. This is corroborated by the appearance of oscillations. However, they do not appear for all initial droplet sizes: oscillations are not observed for the smallest droplet size ($R_0 = 172 \mu\text{m}$), suggesting a transition from overdamped to underdamped oscillations.

Interestingly, all experiments performed for different initial droplet sizes yielded the same power law for the cavity growth (Fig. 1.3). This can be explained using the expression for the kinetic energy, which for an incompressible medium surrounding a spherical bubble reads $\epsilon_{kin} = 2\pi\rho R^3 \dot{R}^2$. The term ρR^3 represents the added mass of the cavity, and the same scaling should apply for cavities that are not perfectly spherical. As cavitation occurs, the elastic energy is quickly released, and assuming that the growth occurs at constant kinetic energy, we obtain $\dot{R}^2 \sim 1/R^3$, and thus $R \sim t^{2/5}$. Indeed, this is the scaling observed experimentally for all elastic cavities (Fig. 1.3). Fitting these experimental curves with $R = at^{2/5}$ gives us the prefactor a , which allows us to extract a typical value for the kinetic energy $\epsilon_{kin} \sim 0.25 \text{ mJ}$. This can be compared to the elastic energy accumulated before cavitation, 0.77 mJ in the spherical approximation, which is indeed of the same order of magnitude. The difference between these values could be attributed to several factors as the remaining liquid kinetic energy, heat release and/or experimental inaccuracies. Note that the enthalpy required for the droplet to shrink is supplied as thermal energy and is in the order of 1 J (see Appendix 1.5.2 for a more detailed calculation).

Figure 1.4: Oscillation frequency of the elastic cavity. The experimental data is shown together with the solution of the Rayleigh-Plesset equation (RP) including elasticity and viscosity (Eq. 1.3). The fitted values for the material parameters of the elastic medium, μ and η , are also given.

Consequently, only a small fraction of this energy is consumed to deform the elastic medium. The scaling $R \sim t^{2/5}$ can be also obtained as the inertially-dominated solution of the Rayleigh-Plesset equation [43]. We use here a modified Rayleigh-Plesset equation for cavities in elastic media given by:

$$\rho \left(R\ddot{R} + \frac{3}{2}\dot{R}^2 \right) = p_{cav} - p_{\infty} - \frac{2\gamma}{R} - \frac{\mu}{\xi^2} F'(\xi) - \frac{4\eta}{R} \dot{R}, \quad (1.2)$$

where we introduced an effective viscosity η of the surrounding medium [40, 44]. The use of a damping of this “viscous” form can be derived only for small deformations, where the effective viscosity can be inferred from the loss modulus as $G'' = \eta\omega$, see Appendix 1.5.1. Note that considering the static solution $\dot{R} = 0$ to this equation, we recover (1.1) for the pressure inside the cavity. Similar formulations of the Rayleigh-Plesset equation in elastic media have been previously used in the context of forced bubble oscillations [45–48].

We proceed by analyzing the cavity oscillations observed in Fig. 1.3 by considering small perturbations of the type $R(t) = R_c(1 + \epsilon e^{i\omega t})$, and linearizing (1.2), with R_c the size of the elastic cavity. This gives an expression for the oscillation frequency,

$$f \equiv \frac{\text{Re}(\omega)}{2\pi} \simeq \frac{1}{\pi} \sqrt{\frac{\mu}{\rho R_c^2} - \frac{\eta^2}{\rho^2 R_c^4}}, \quad (1.3)$$

accounting for elasticity and viscous damping. Here we omitted subdominant contributions due to the adiabatic expansion of the vapor inside the cavity, and due to surface tension, which are respectively smaller by 10^{-1} and 10^{-3} . The result (1.3) indeed predicts a transition from overdamped to underdamped oscillations, occurring at a critical drop radius $R^* = \eta/\sqrt{\mu\rho}$. In Fig. 1.4 we present our experimental measurements for the frequency, obtained by fitting $R(t)$ to exponentially damped oscillations. In this figure $f = 0$ represents the overdamped case. Given that the bubble has not yet fully recovered, we defined the cavity radius R_c as the mean of the maximum and minimum value of the first oscillation. To compare the experimental data to (1.3), we fit these data points using both the shear modulus μ and viscosity η as adjustable parameters. The values found ($\mu = 1.7$ MPa and $\eta = 8.5$ Pa·s) result in $R^* = 210$ μm . The fitted values for the shear modulus and viscosity match very well with available literature on rheological measurements of PDMS at high frequencies [49] and with our own measurements (see Appendix 1.5.1). The excellent agreement in Fig. 1.4 shows that the oscillations are quantitatively captured by a viscoelastic Rayleigh-Plesset-type model ²

1.4 Conclusion

In summary, in this chapter we have studied a cavitation process similar to that found in the cells of the fern sporangia. Our experiments capture and quantify the slow diffusive evaporation, which leads to a build-up of negative elastic pressure that eventually leads to a very fast cavitation. We provided detailed insight into the cavitation dynamics, which was accurately described by an inertial-(visco)elastic model. Understanding the mechanism by which certain plants are able to transform enthalpy into mechanical energy could lead a way to design synthetic materials able to perform similar fast motions making use of the this smart energy transformation found in nature.

²Note that in this model only viscous damping is taken into account, which can be verified by calculating the quality factors Q_η and Q_{rad} , representing viscous damping and acoustic radiation. Using expressions for both quality factors as given in [39], results in $Q_\eta = O(1)$ and $Q_{rad} = O(10)$, meaning that viscous dissipation is dominant in this system and thereby validating our approach.

Acknowledgements

The authors acknowledge fruitful discussions with Benjamin Dollet, Sascha Hilgenfeldt, Javier Rodríguez- Rodríguez, and Jens Eggers.

1.5 Appendix

1.5.1 Rheological measurements

Rheological measurements of the PDMS-gel are performed on an Anton Paar MCR 502 rheometer, in the parallel plate configuration (PP25) and gap width 0.5 mm. The gel is cured in the rheometer at 70°C for 100 minutes, afterwards the storage modulus (G') and loss modulus (G'') are monitored at different temperatures. These two moduli are measured for a wide range of ω : 10^{-2} - 10^2 rad/s, at a deformation of 0.5%. These measurements are performed at three different temperatures: -15, 20 and 70°C. Using the principle of time–temperature superposition, we are able to create one master curve at 70°C, extending the upper limit of ω above 10^5 rad/s. The results for G' and G'' as a function of ω after this superposition are shown in Fig. 1.5a.

In the measured range of ω , the storage modulus remains almost constant, whereas the loss modulus changes significantly. From the loss modulus we can calculate the viscosity, using $G'' = \eta\omega$, which is frequency dependent. The resulting curves for shear modulus μ and viscosity η are shown in Fig. 1.5b. The range of frequencies of the cavitation bubbles is 10 to 40 kHz (see Fig. 1.4), which is similar to a spread in η of 4 Pa·s. As the experimental frequency range is small, we assume a single value for η to describe the experimental measurements. Note that beyond R^* , the exact value of η has a relatively weak effect on the prediction (3).

Figure 1.5: Rheological measurements of the PDMS-gel. (a) Shows the storage modulus (G') and loss modulus (G'') at 70°C. To the measurements at different temperatures we have applied the time—temperature superposition. (b) The resulting shear modulus μ and viscosity η from the measured G' and G'' from (a).

1.5.2 Energy considerations

In this section we intend to compute the energy balance occurring in the process: from the shrinkage of the droplet to the appearance of the bubble.

When a mass of liquid evaporates, certain energy is consumed to transfer the molecules from the liquid phase to a gas phase. The energy required depends on the liquid, pressure and temperature and it is typically known as enthalpy of vaporization. The liquid phase is vaporized first by diffusion-limited evaporation, which requires the largest amount of energy, and secondly by cavitation. We will compute the enthalpy of vaporization only during the evaporation process, since this process is the one that consumes most of the liquid volume. Water at room temperature and atmospheric conditions, the enthalpy of vaporization is $\Delta H = 44$ kJ/mol and 42.5 kJ/mol at 60°C. The droplet shrinks approximately to half its initial radius before cavitation kicks in (see Fig. 1.1): $R_f/R_i \approx 0.5$. That shrinkage process requires an enthalpy of $\Delta H = 42.5$ kJ/mol $\times \Delta m/m_w$ mol = 3.9 J, where Δm is the mass of water evaporated and m_w is water's molecular weight. This energy is supplied to the system by heat transfer (note that the system is continuously heated).

Additionally, as the droplet shrinks, it deforms the elastic medium surrounding the droplet. Through this deformation, the elastic medium acquires certain amount of elastic energy, that will be ultimately released. The elastic energy is calculated using the spherical approximation:

$$\epsilon_{el} = 4\pi\mu_0 R_0^3 F(\xi), \quad (1.4)$$

where μ_0 corresponds to the static shear modulus ($\mu_0 = 0.7$ MPa). The value of ξ is taken at the moment of creasing ($\xi = 0.73$); the same ξ as used for the estimation of the cavitation pressure. This resulting pressure can be seen as a lower bound for the pressure upon which cavitation occurs. Following the same reasoning, the elastic energy calculated at $\xi = 0.73$ is the lower bound for ϵ_{el} .

Finally, we compute the kinetic energy consumed by the bubble right after the cavitation event occurs. We use the expression:

$$\epsilon_{kin} = 2\pi\rho R^3 \dot{R}^2 = 8/25 \pi\rho a^5 \quad (1.5)$$

Here we use the fact that the expansion is produced at constant kinetic energy, such that $R^3 \dot{R}^2 = \frac{4}{25} a^5$, where 'a' is obtained experimentally during the bubble expansion as $R \approx at^{2/5}$, the prefactor 'a' increases with initial droplet radius R_0 . Using a typical radius of $R_0 = 850$ μm , results in $\epsilon_{el} = 0.77$ mJ and $\epsilon_{kin} = 0.25$ mJ (with $a = 48$ mm/s^{2/5}). This energy conversion of roughly $30 \pm 10\%$ is found for all droplet sizes and is independent of cavity size.

Figure 1.6: The growth of both the full elastic cavity and the single cavitation bubble in the same experiment are shown as a function of time ($R_0=715 \mu\text{m}$). The images on top show the birth of this cavitation bubble, corresponding to the 4 points of the single bubble radius. The scale bar represents $500 \mu\text{m}$.

1.5.3 Cavitation bubble dynamics

After the cavitation event, the size of the cavity is measured as a function of time. The shape of this cavity is not spherical as can be seen in Fig. 1.6, which is due to the creasing instability which occurred prior to cavitation. The area of this cavity is used to calculate its effective radius. Not only the size of the full cavity can be measured, high speed imaging also allow us to measure the growth of the bubble generated at the cavitation event. In the very first instants ($<15 \mu\text{s}$) we can clearly measure its growing radius, see Fig. 1.6 for images of the bubble. In Fig. 1.6 we plot both the bubble and the cavity radius in time. Figure 1.7 displays the growth of different bubbles for multiple initial droplet sizes R_0 : all bubbles show a linear growth of the radius, with v close to 30 m/s . As discussed in the previous section, when the bubble *catches up* with the cavity, a small amount of liquid (water) still remains in some parts of the cavity wall. However, looking at the comparison with Rayleigh-Plesset and our calculations, it does not seem to play a major role and we can safely ignore it.

Figure 1.7: The growth of the cavitation bubble for multiple values of R_0 is shown, displaying the velocity is close to 30 m/s for each experiment.

CHAPTER 2

SOFT CAVITATION IN COLLOIDAL DROPLETS

Submitted as: **Myrthe Adriana Bruning**, Claus-Dieter Ohl, and Alvaro Marin, *Soft Cavitation in Colloidal Droplets*, Soft Matter.

ABSTRACT

When a pure droplet evaporates inside an elastic medium, two instabilities are typically observed. As the droplet shrinks, the elastic medium needs to deform and elastic tension builds up. At a critical strain, creases at the gel-droplet interface start to form. However, the droplet keeps shrinking, pulling the elastic network and therefore decreasing the pressure in the liquid phase. This drives the liquid phase into a metastable state, and leads to the second instability: the nucleation of a vapour bubble in the liquid phase by cavitation. These instabilities consistently occur in the described order whenever a pure liquid (water, in our case) is used. The presence of colloidal particles is common both in vitro and in natural environments, and they can change such phenomenology significantly by stimulating cavitation events before any creasing instability. In this work, we study the role of colloidal particle size and concentration on the early inception of cavitation in water droplets in an elastic medium. Our results in this chapter reveal an unexpected dependence with the particle size and with the size distribution of the colloidal particles. Given the simplicity and reliability of the system and preparation, the method described here could be eventually used to measure tensile strengths of particle solutions with accuracy.

2.1 Introduction

Soft materials and surfaces develop complex instabilities under dehydration, typically wrinkling and creasing [29, 50]. Such evaporation-driven instabilities are visible in our everyday life at the milk surface [51] or even in our human skin [52]. Another type of evaporation-driven instability that might occur during dehydration is cavitation, the sudden expansion of a bubble within a liquid subjected to a negative hydrostatic stress. For such instability to occur, liquid inclusions must be present within a soft (or hard) solid undergoing tension. Many examples can be found in nature. In the mineral kingdom, droughts can induce negative stresses in porous soils, giving rise to cavitation events and altering the soil structure [53, 54]. Among the examples that can be found in the plant kingdom are the xylem embolia, which are caused by cavitation events during the droughts in summer [55], and the spectacular fern sporangium [24] which exploits cavitation events within its cells to disperse its spores through the air.

In laboratory conditions, this combined phenomenon of evaporation and cavitation has been studied both for laser-generated cavities in water-soaked hydrogels [26, 27, 48] and for water droplets inside silicone-based gels [29, 56]. Interestingly, in the latter case, given the permeability of polydimethylsiloxane (PDMS) for water vapour, it has been shown [29, 56] that the evaporation of a water droplet occurs following a simple diffusion-limited process, retaining its spherical shape for most of its lifetime. However, after reducing its radius a certain critical fraction (which depends on the properties of the elastic medium), the gel-liquid interface displays a so-called creasing instability [29]. The interface folds onto itself, in order to release part of its tension which builds up during the shrinkage of the droplet. As the droplet keeps evaporating after creasing, the tension in the elastic medium keeps increasing, introducing a negative pressure inside the water droplet. As a result, the droplet suffers a cavitation event and a bubble nucleates, which eventually grows up to the same size as the initial droplet. The fast dynamics and oscillations of this bubble have been studied in detail in [56] recently. It is worth noting that the phenomenon is so reproducible, that the frequency of these oscillations could serve as a proxy of the viscoelastic properties of the surrounding gel [48].

Water in soil or inside xylem channels typically contains impurities that can alter this phenomenology significantly. By sending a shock-wave to a particle solution, Borkent *et al.* [57] confirmed experimentally that the presence of particles can trigger the formation of bubbles at lower tension levels than those predicted for pure water. Their results confirmed the crevice model for cavitation nuclei [58], which modelled and quantified the energy needed for the nucleation and growth of a bubble in a pre-existing cavity. High particle surface roughness facilitates the entrapment of gas pockets and enhances the chances of a cavitation event. Similar phenomena have been observed when studying

foaming upon beer tapping [59], which occurs when the top of a beer bottle is hit with a solid object, usually another bottle, triggering violent foaming and spoiling the subject's drink. Interestingly, foaming in beer is facilitated by cellulose fibres that take the role as cavitation nuclei [60]. Besides the roughness of the particles, also their size is an important factor, as shown by Marschall *et al.* [61]. They showed that cavitation nuclei are related to the fine scale structure of the particle surface. Critical cavities are developed, which depend on the global radii of curvature of the particle.

Interestingly, in laboratory conditions using pure liquids, cavitation occurs nearly always after creasing. But creasing instabilities have been rarely observed in natural conditions [54, 62]. Motivated by this observation, in this work, we will introduce a known concentration of well-characterized colloids inside an evaporating water droplet in elastomer gels (PDMS) and study the effect of such "controlled impurities" on the instabilities observed: creasing and cavitation. The expectation is that the presence of impurities, *i.e.* colloidal particles in our case, will always promote cavitation before any creases are developed, which would explain why creasing is never observed in nature.

2.2 Experiments

In a typical experiment, a suspension droplet injected into an elastic medium is recorded as it evaporates and manifests cavitation and/or creasing instabilities. The gel used is Dow Corning polydimethylsiloxane (PDMS) Sylgard184 mixed in a 1:10 ratio (curing agent:base polymer). The static shear modulus μ_0 of this gel is ~ 0.7 MPa. The experimental protocol involves mixing and degassing this gel and injecting the droplet after it has been cured for some time. In order to ensure similar conditions for each experiment, all of these steps follow a precisely timed protocol. After combining the curing agent and base polymer, the mixture is stirred for 2 minutes, and directly afterwards degassed in a vacuum chamber for 35 minutes. Within 5 minutes of releasing the vacuum, the gel is put in the experimental chamber. In this chamber the relative humidity is kept at 30 % and the temperature of the bottom plate is 70°C. The gel mix is poured in a transparent plastic box of dimensions 2.5 x 2.5 x 1.5 cm (width x depth x height) which is open at the top. This box is heated for 19 minutes after which the colloidal droplet will be inserted in the centre of the gel-filled box. By the time the droplet is injected, the gel is precured and the droplet stays where it is initially injected. Throughout the entire experiment the sample is heated at 70°C. A schematic overview of the set-up is given in Fig. 2.1a.

The suspension consist of milli-Q water with polystyrene colloidal particles, functionalized with sulfate groups, which makes the particles hydrophilic and conveys enough elec-

Figure 2.1: Overview of the experimental set up and typical images that are captured. (a) A schematic representation of the set up, including the humidity controlled chamber and the temperature controlled bottom plate (not to scale). The droplet size is typically $R_0 = 200\text{--}700 \mu\text{m}$ and contains different concentrations of polystyrene particles. Figures (b) and (c) are the evolution of the droplet radius as a function of time and the corresponding images, in this case for a pure water droplet. Panel c1 shows the initial (spherical) droplet, panel c2 the creasing instability and panels c3 and c4 are captured right before and after cavitation occurred. The scale bar in panel c1 represents $500 \mu\text{m}$.

trostatic repulsion between them to maintain the suspension stable with no need of additional stabilizers (microParticles GmbH, PS-FluoRed). Two different particle sizes are used for the experiments ($d_p = 0.45 \pm 0.009$ and $0.98 \pm 0.04 \mu\text{m}$) and three different particle concentrations ($c_p = 0.15, 1$ and $2.5 \text{ v-}\%$). The density of these particles is 1.05 g/cm^3 , which makes them almost neutrally buoyant. Nonetheless, the duration of the experiment (up to 25 hours) can eventually be comparable to the time required for a colloidal particle to settle at the bottom of the droplet. This is indeed the case of our larger particles, as we will discuss below. In order to prepare the suspensions, the stock solution is sonicated for 15 minutes prior to diluting. After preparing the desired volume concentration, the solution is sonicated for another five minutes to ensure no particle clusters are present. Droplets of these colloidal suspensions are injected using an Eppendorf pipette and range from 0.03 – $1.4 \mu\text{L}$ (meaning $R_0 = 200$ – $700 \mu\text{m}$). The experiments are recorded using a Ximea MQ013MG-ON and frames are captured every minute. Experiments last from 2 to 25 hours depending on the initial droplet radius R_0 . The camera is mounted outside the chamber and takes side view images of the droplet. From these recordings we can extract the (effective) droplet radius of the droplet and observe the appearance of creasing and cavitation.

The shrinkage of the droplet is shown in Fig. 2.1b, in which we show the radius as a function of time. Eventually, the radius shoots up to nearly the original radius. As described in [56], this final event corresponds to the nucleation of a bubble through a cavitation event. During the evaporation of the droplet the tension in the gel increases, which reduces the pressure inside the droplet. The liquid phase is then in a metastable state, sensitive to a cavitation event. Images for a typical experiment using pure water are shown in Fig. 2.1c. First a spherical droplet is injected and will start to evaporate. At some point the elastic medium creases and the droplet loses its spherical shape (see panel c2, after 14 hours from injection). From that point onwards we determine the droplet size as an effective radius using its projected area. Finally, cavitation occurs and a bubble nucleates, which eventually grows up to a similar size as the initial droplet (panel c4).

2.3 Results

2.3.1 Diffusive droplet evaporation

As shown previously in the literature [29, 56], pure water droplets evaporate inside such gels following a diffusion-limited process. In Fig. 2.2 we compare the evaporation of colloidal droplets with the evaporation of a pure water droplet. To obtain an analytical form of the droplet radius R as a function of time, we start with a mass balance of the droplet

Figure 2.2: The dimensionless droplet area loss as a function of dimensionless time while evaporating inside an elastic media for different particle sizes. The grey dotted line represents the dimensionless area at which creasing occurs for this elastic medium. The black markers represent the case of a pure water drop.

in a diffusion-limited process:

$$\rho_w \frac{dV}{dt} = -4\pi R^2 J, \quad (2.1)$$

in which ρ_w is the water density. The volume of the droplet V can be expressed as $\frac{4}{3}\pi R^3$, $J = J(R)$ represents the diffusive flux at the droplet's interface $r = R$. This flux is given by Fick's Law as

$$J = -D \frac{\partial C}{\partial r} \Big|_{r=R}, \quad (2.2)$$

which allows us to rewrite equation 2.1 to

$$\rho_w 4\pi R^2 \frac{dR}{dt} = 4\pi R^2 D \frac{\partial C}{\partial r} \Big|_{r=R}. \quad (2.3)$$

The characteristic diffusion time scale is defined as $t_D = R_0^2/D = \mathcal{O}(10^2)$ s [6], using $R_0 = 600 \mu\text{m}$ and the diffusivity of water vapor in PDMS $D = 3.3 \cdot 10^{-9} \text{ m}^2/\text{s}$ [35]. We can express the typical droplet evaporation time as $t_F = R_0^2 \rho_w / (2D \Delta c) = \mathcal{O}(10^5)$ s, which includes the density of water ($\rho_w = 998 \text{ kg/m}^3$) and the concentration gradient at the interface and the far field ($\Delta c = 33 \text{ mol/m}^3$ [36]). As the diffusion time scale t_D is much smaller than the typical evaporation time t_F , the evaporation can be assumed to follow a steady-state solution:

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \approx 0. \quad (2.4)$$

The final expression for the droplet radius reads as

$$R_0^2 - R(t)^2 = \frac{2D\Delta ct}{\rho_w}. \quad (2.5)$$

Using the expression for the typical evaporation time t_F , the final dimensionless equation for the droplet area loss in the case of steady state diffusion is given by

$$1 - \frac{R(t)^2}{R_0^2} = t/t_F. \quad (2.6)$$

In Fig. 2.2 the typical evolution of the droplet radius, using equation 2.6, is shown for different particle sizes. As a reference we also include an experiment without any particles present. From these curves we can see that the addition of particles to the droplet does not alter its evaporation: it follows the same curve as the pure water droplet. While the droplet evaporates, it shrinks. Initially this occurs in an isotropic manner and the droplet holds its spherical shape. However, at a certain ratio for R/R_0 creasing occurs and the gel starts to fold onto itself. For this type of gel $R_{crease}/R_0 = 0.71$, as observed both for pure water drops and colloidal drops. In a previous study [56], we found experimentally a ratio of 0.73 for the same type of gel. The small discrepancy could be due to small differences in composition between different batches of gel. In Fig. 2.2 the radius of creasing is highlighted with a grey dotted line ($1 - R^2/R_0^2 = 1 - 0.71^2 = 0.5$). For some curves a small bend is observed after creasing occurs, because the droplet has lost its spherical shape. At some point, a cavitation event takes place and a bubble forms. As shown in Fig. 2.2, cavitation happens after the droplet has creased, both in the case of a pure water drop and for the smallest particle size used of diameter $d_p = 0.45 \mu\text{m}$. This picture changes dramatically for the droplets containing the largest particles ($d_p = 0.98 \mu\text{m}$), a large majority of them cavitates before the interface has creased. By doing so, creasing is completely suppressed since cavitation kicks in earlier, vaporizing the liquid phase. Consequently, we will refer to this situation as *early cavitation*.

This result raises several questions as, why do small particles not show this early cavitation? Does particle concentration play a role? Since the maximum tension (negative pressure) achievable is proportional to the initial droplet size, does it play a significant role? We will try to address these questions in the following.

Figure 2.3: The evaporation process for a droplet inside an elastic medium with and without particles. These three series correspond to the evaporation curves in Fig. 2.2. In figures (a) and (b) creasing and cavitation occurs, respectively without and with (small) particles. In (c) larger particles are used and creasing is no longer observed, only the cavitation event. The first image everywhere is the initial droplet, the third image is the last image before cavitation. In all series the scale bar represents $500 \mu\text{m}$.

2.3.2 Suppressing creasing

To study this phenomenon in more detail, Fig. 2.3 shows the difference between *early cavitation* and cavitation after creasing. The three cases shown in the sequences in Fig. 2.3 correspond to the three curves shown in Fig. 2.2 with matching colours and markers. Figure 2.3a is an image sequence for the pure water experiment: first the droplet shrinks isotropically, then creasing occurs, and after some time the droplet experiences cavitation. A bubble nucleates and grows, ending up with practically the same size as the initial droplet. For more details on the cavitation dynamics we refer to [56]. In Fig. 2.3b a high concentration of small particles is added to the droplet ($d_p = 0.45 \mu\text{m}$, $c_p = 2.5 \text{ v-\%}$). Clearly the droplet is no longer transparent, and appears opaque throughout the full ex-

periment. Still, the creasing looks similar as to the case without particles and eventually also cavitation occurs. Figure 2.3c shows the situation when the particle diameter is doubled ($d_p = 0.98 \mu\text{m}$, $c_p = 2.5 \text{ v-\%}$), which also shows an opaque droplet due to the high particle concentration of that specific case. Due to their larger size, these particles start to sediment and a clear inhomogeneous particle distribution in the droplet is observed. The possible role of such an inhomogeneous particle distribution is unclear to us, but it will be nevertheless discussed below. Before creasing starts, a cavitation event occurs and the final bubble size has the same size as the initial droplet.

To analyse when creasing can be suppressed and early cavitation occurs, we performed a systematic study with different initial droplet radii, two different particle sizes and three particle concentrations. For each experiment we measure the radius at which cavitation occurs. These results are given in Fig. 2.4 for pure water droplets (2.4a) and for two different particle sizes (2.4b, 2.4c). On each subplot, for a given R_0 , every droplet evolves from the top ($R(t)/R_0 = 1$) towards the bottom of the graph, decreasing in size. The droplet will either crease when crossing the creasing radius ratio $R_{\text{crease}}/R_0 = 0.71$ (plotted as a grey dotted line), or it will go through a cavitation event before reaching the creasing line. Consequently, every point above the dotted line represents an experiment in which cavitation has occurred before creasing (early cavitation, *i.e.* $R_{\text{cav}}/R_0 > 0.71$).

In the case of pure water droplets (Fig. 2.4a) cavitation is always observed for $R_{\text{cav}}/R_0 < 0.71$, meaning that creasing occurs for every experiment. Note that we are combining in this figure results from pure water droplets taken from [56] and new measurements taken for this work. Surprisingly, the addition of a substantial amount of $0.45 \mu\text{m}$ -diameter particles does not change the process qualitatively: Almost all experiments experience creasing in a similar fashion as with pure water. A noticeable difference with pure water is that the cavitation events occur at similar radius ratios, closer to the creasing ratio, unlike the larger spread of the events for pure water.

Increasing the particle size to $d_p = 0.98 \mu\text{m}$ has a significant effect, shown in Fig. 2.4c. In this graph we show the outcome for three different volume concentrations. For the lowest volume concentration ($c_p = 0.15 \text{ v-\%}$), nothing different occurs compared to the previous results shown and the elastic medium always creases in the measured range of droplet sizes. However, increasing the particle concentration to $c_p = 1 \text{ v-\%}$, results in a completely different behaviour. For droplets with R_0 larger than a certain critical radius R^* , cavitation occurs first, suppressing creasing completely, as already introduced in Fig. 2.3c. For an even higher particle concentration ($2.5 \text{ v-\%}$), this critical radius shifts to a lower value. In summary, approximately half of the droplets containing larger particle concentrations experienced early cavitation, with a clear correlation on the initial droplet size R_0 . Using the results from Fig. 2.4 we can determine the critical radius R^* for each particle size and

Figure 2.4: The radius ratio at which cavitation occurs as a function of the initial droplet radius R_0 for different particle concentrations. Figures (a), (b) and (c) show the results for pure water droplets, $d_p = 0.45 \mu\text{m}$ and $0.98 \mu\text{m}$ respectively. The radius ratio at which creasing occurs is highlighted with a grey dashed line. The grey markers are experiments in which cavitation type B is observed, the shape of the marker represents c_p . In figure (a) the open markers are results from the current study, the closed markers are from [56]. In figure (c) also experiments are included in which salt is added to the colloidal droplet, represented by star markers.

concentration. In the case of the $0.45 \mu\text{m}$ -diameter particles, no critical radius can be extracted from the range of measured R_0 . For the case of $0.98 \mu\text{m}$ -diameter particles, an increase on the particle concentration is reflected in a decrease of R^* . We elaborate on the exact values of R^* in Fig. 2.6. Interestingly, droplets with $R_0 < R^*$ behave very similarly

(a) $R_0 = 515 \mu\text{m}$, $d_p = 0.98 \mu\text{m}$, $c_p = 2.5\text{v-\%}$

(b) $R_0 = 517 \mu\text{m}$, $d_p = 0.98 \mu\text{m}$, $c_p = 2.5\text{v-\%}$

Figure 2.5: Two types of cavitation for nearly identical initial conditions. The time scales in the upper right corner show the time after the cavitation bubble is formed. (a) Cavitation type A: a bubble is formed at the top of the droplet and then moves towards the bottom of the droplet. (b) Cavitation type B: a bubble is formed at the top of the droplet and remains at this location. The scale bars represents $500 \mu\text{m}$ and the same markers are used as in Figs. 2.4 and 2.6.

as a pure water droplet: Starting with an isotropic shrinking of the droplet, continuing with a creasing instability at the expected radius ratio and eventually cavitation kicks in. However, in the case of $R_0 > R^*$, the process turns more complex. Experiments with $0.98 \mu\text{m}$ -diameter particles have shown two different kinds of cavitation events, both shown in Fig. 2.5. In the most common type found, which we will call type A (Fig. 2.5a), a bubble is nucleated at the very top of the droplet, apparently very close to the interface, it quickly loses its spherical shape and then sinks down. From there, it grows in time until the full droplet is evaporated and a bubble with the same size as the initial droplet is obtained. Although we lack more detailed observations to support this hypothesis, it seems as if this kind of bubble nucleation occurs at the PDMS-liquid interface, and therefore the bubble loses easily its sphericity. The fact that the bubble moves downwards, in the direction of gravity, is a puzzling observation. This motion must be driven by certain convection inside the drop following the bubble nucleation, but we are uncertain of its nature. Cavitation type A can be observed before and after creasing in suspension droplets with $0.98 \mu\text{m}$ -diameter particles, and only after creasing for $0.45 \mu\text{m}$ -diameter particles and pure water. Note that the critical radius R^* , previously defined above, refers to this type of cavitation only.

Figure 2.6: Transition for suppressing creasing as a function of initial droplet radius R_0 and particle concentration, for two different particle sizes. In the colored region creasing is observed, as $R_0 < R^*$. In figure (b) non-coloured bar show the region in which $R_0 > R^*$: for these conditions creasing is suppressed and cavitation occurs early (type A cavitation). The grey markers are experiments in which type B cavitation is observed. They are shifted slightly downstairs for clarity.

The second kind of cavitation, which we will call type B (Fig. 2.5b), has several interesting features. The bubble nucleates also in the upper part of the droplet, but it seems to be formed in the liquid bulk, as it retains its spherical shape during the whole process of growth. Cavitation type B events are plotted using grey markers in all upcoming plots, from Fig. 2.4 to 2.10. It is important to stress that the difference between these two types of cavitation events is not only qualitative and visual (and therefore less objective), but also quantitative: all type B events in the presence of particles occurs before creasing. Note that a critical radius cannot be defined in this case since all cavitation type B events occur before creasing. The precise mechanism that allows the bubble to remain in place is for the moment unknown to us. In principle, by invoking symmetry, one would expect that the nucleation of a bubble at the liquid-gel interface, as seems to be the case in type A, would lead to much stronger flow than a bubble nucleating in the bulk. Another important observation from Fig. 2.4 and Fig. 2.5 is that for identical initial conditions, both types of cavitation are equally likely to occur. The experiments in Fig. 2.5a and Fig. 2.5b are performed with the same R_0 , d_p and c_p .

To summarize the observations from Fig. 2.4, we make use of the resulting values for R^* . Figure 2.6 shows the same data plotted as a phase diagram with the particle concentration c_p versus the initial droplet radius R_0 . For each set of experiments we highlight if creasing can be suppressed or not. The colored regions are regions in which creasing is observed and cavitation occurs afterwards, *i.e.* $R_0 < R^*$. The non-colored bars show the conditions in which creasing can be suppressed and cavitation occurs early. For example, in the case of $d_p = 0.98 \mu\text{m}$ and $c_p = 2.5 \text{ v-\%}$, R^* is determined from two experiments at $R_0 \approx 477 \mu\text{m}$ for which we observe creasing in one case and early cavitation in the other, so this radius represents the critical radius for this transition. In this phase space the experiments that displayed type B cavitation are also included in grey to ensure a complete overview. Once more, this figure highlights the chaotic nature of the type of cavitation events: in Fig. 2.6a we can observe events of type A and B both occurring under almost identical conditions $R_0 = 550 \mu\text{m}$ and $c_p = 2.5 \text{ v-\%}$ (for $d_p = 0.45 \mu\text{m}$); or in 2.6b, with $R_0 = 356 \mu\text{m}$ and $c_p = 1 \text{ v-\%}$ (for $d_p = 0.98 \mu\text{m}$). Opposed to this random occurrence of type B, type A cavitation never occurs for $R_0 < R^*$ and is therefore more reproducible and independent on the initial droplet radius.

Origins for the threshold to suppress creasing

Area of particles

In order to understand the origin for the observed critical radius R^* , which is a function of particles size and concentration, there are several factors to consider. Firstly, the reason for early cavitation must relate to the presence of particles in the system, as it is never observed in the case of pure water droplets (see Fig. 2.4a). The particles introduce an additional solid area into the system which might increase the amount of potential cavitation nuclei. These experiments have been categorised by their volume concentration c_p and initial droplet radius R_0 . Following this hypothesis, the area of the particles inside the droplet should be the determining parameter and not their occupied volume or their number.

In order to test this hypothesis, we calculate the total area of particles inside the droplet A_{tot} , using the volume concentration of particles, their size and the initial drop volume. The resulting phase space with c_p versus A_{tot} is shown in Fig. 2.7. Firstly, we observe that the measured range of A_{tot} is similar for the 0.45 and the $0.98 \mu\text{m}$ -diameter particles (Figs. 2.7a and b). This is not trivial, as the number of particles present in the droplet differs 1 order of magnitude: $N = \mathcal{O}(10^8)$ for $0.45 \mu\text{m}$ -diameter particles and $N = \mathcal{O}(10^7)$ for $0.98 \mu\text{m}$ -diameter particles (both for $c_p = 2.5 \text{ v-\%}$). However, when the total area of the particles is calculated, such a difference vanished, and in both cases we find A_{tot}

Figure 2.7: Transition for suppressing creasing as a function of total area of all particles, for two different particle sizes. The colored bars show for each particle concentration where creasing is observed. In figure (b) also non-coloured bar are included: for these conditions creasing is suppressed and cavitation occurs early. For low particle concentrations in (a) and (b) the transition cannot be determined from the available experiments and therefore a fading color bar is used. The grey markers are experiments in which type B cavitation is observed.

$= \mathcal{O}(10^{-4}) \text{ m}^2$. This tells us that the available area for nucleation alone is not sufficient to explain the occurrence of early cavitation only in the case of $0.98 \mu\text{m}$ -diameter particles. For the smallest particle size in our set we are nearly never able to suppress creasing, even though the total available area is even slightly larger than in the case of the larger particles.

Roughness of particles

As mentioned in both Borkent *et al.* [57] and Marschall *et al.* [61], the surface roughness of the immersed particles plays an important role in increasing the cavitation activity. Both the 0.45 and $0.98 \mu\text{m}$ -diameter particles are produced by MicroParticles GmbH, they are polystyrene particles and are functionalized with sulfate groups. To ensure that the surface roughness is similar for the two types of particles, Scanning Electron Microscopy images are made. Figure 2.8 shows the surface of the particles for different magnifications. The polystyrene particles are difficult to image perfectly due to their non-conducting character. However, these SEM images show that, on a qualitative level, there is no significant difference in the roughness of these two types of particles, that could explain the high contrasting results obtained for each of them.

Figure 2.8: Scanning Electron Microscope images from polystyrene particles (microParticles GmbH, PS-FluoRed). Figures (a) and (b) show two different magnifications for $d_p = 0.45 \mu\text{m}$. Figures (c) and (d) show two magnification levels for $d_p = 0.98 \mu\text{m}$. The scale bars in figures (a) and (c) represent 500 nm, in figures (b) and (d) 200 nm. Image courtesy Mark Smithers from the MESA+ Nanolab.

Tensile strength

To gain more insight on the influence of particles on the cavitation process inside the droplet, the tensile strength is calculated from the cavitation events in each of our experiments. We define the tensile strength of our liquid solution as the pressure deficit necessary to cause a cavitation event. In our case, we will define the pressure deficit in the droplet at the moment of the cavitation event from the experimentally obtained curves for radius versus time. We use the elastic energy for a spherical cavity inside an elastic medium, which can be written as $\epsilon_{el} = 4\pi\mu R_0^3 f(\xi)$, with μ is the shear modulus of the surrounding elastic medium (PDMS), and $\xi = R/R_0$. For a Neo-Hookean solid the dimensionless function reads $f(\xi) = \frac{5}{6}\xi^3 - \xi^2 - \frac{1}{3} + \frac{1}{2\xi}$ [37, 38]. The (negative) pressure of the droplet can be calculated using

$$P_{cav} = P_\infty + \frac{2\gamma}{R} + \frac{\mu}{\xi^2} f'(\xi), \quad (2.7)$$

where p_∞ is the atmospheric pressure far away from the droplet and γ is the surface tension of the water-PDMS interface. To calculate the critical tension for cavitation *i.e.* the

tensile strength, in the case of the evaporation of colloidal droplets, we need to separate two different cases. When the presence of particles leads to the suppression of creasing, the droplet is still spherical while cavitating. For these measurements, we can insert the exact value of R_{cav}/R_0 for ξ and calculate the corresponding tensions. For example, the experiment with $R_0 = 588 \mu\text{m}$ and $c_p = 2.5 \text{ v-\%}$ for the $0.98 \mu\text{m}$ -diameter particle. In this case $\xi = 0.76$, which results in $P_{cav} = -1 \text{ MPa}$. Therefore the critical tension in the water droplet for cavitation is $\sim 1 \text{ MPa}$ for early cavitation (type A or B). However, in experiments in which creasing occurs before cavitation, the value of ξ is not trivial. At the moment of creasing, the droplet loses its spherical shape and at the same time, the gel releases some of its build up tension. Therefore we use ξ at the moment of creasing (≈ 0.71) and the resulting pressure can be seen as a lower bound for the pressure upon which cavitation occurs. A typical value of $P_{cav} = -1.5 \text{ MPa}$ is obtained for $\xi = 0.71$, meaning that the critical tension for cavitation is $\sim 1.5 \text{ MPa}$ in the case of creasing.

In Fig. 2.9 we summarise all results for the critical tension for the performed experiments. Figure 2.9a contains the results for pure water and $d_p = 0.45 \mu\text{m}$. The critical tension for cavitation is $\sim 1.5 \text{ MPa}$ for most of the experiments, as creasing occurs always before cavitation. All experiments in which creasing takes place are given with open symbols. As creasing always occurs near $\xi = 0.71$, the spread in this data is marginal and $T_{cav} = 1.5 \text{ MPa}$. Only one experiment with $0.45 \mu\text{m}$ -diameter particles shows a tensile strength at substantially lower values than the rest, which interestingly corresponds cavitation type B, this is, with a bubble being nucleated apparently at the bulk. Figure 2.9b shows the results for $0.98 \mu\text{m}$ -diameter particles, which make a stark contrast with those of pure water and $0.45 \mu\text{m}$ -diameter particles. The main difference is the significant amount of experiments showing tensile strengths below the creasing limit. Interestingly, there is a clear inverse correlation between the particle concentration and the tensile strength T_{cav} . Also note the large spread in tensile strength in the case of early cavitation (either type A or B) in comparison to the values obtained for pure water and $0.45 \mu\text{m}$ -diameter particles in Fig. 2.9a. In Fig. 2.9b, the only two values of T_{cav} observed above the creasing limit deserve a comment: These two points correspond to very low R_0 values ($\approx 200 \mu\text{m}$). A smaller initial droplet size involves a shorter life, which becomes somewhat comparable with the gel curing time. As a result the creasing occurs at an effectively lower value of ξ , which leads to a higher T_{cav} . For larger droplets this effect becomes negligible as the time it takes to evaporate the droplet is larger, whereas the time it takes for the gel to cure remains the same.

Marschall *et al.* [61] proposed that, in the case of smooth particles, the smallest possible tensile strength of a suspension is determined by the radius of curvature of the particle. The critical tension for cavitation is determined from the stress that needs to overcome the surface tensions force of the vapour cavity with typical particle diameter d_p . This tension

Figure 2.9: The critical tension for cavitation for suspensions with different particle concentrations and sizes. The open markers highlight cases in which creasing occurs. The filled symbols represent type A cavitation, the grey markers the type B cavitation. Figure (a) shows the critical tension for $d_p = 0.45 \mu\text{m}$ and pure water, figure (b) shows the results for $d_p = 0.98 \mu\text{m}$. The coloured dotted lines show the curves for $T_{cav} = 4\sigma/d_p$, the grey dashed line the critical tension in the case of creasing.

is expressed as $T_{\text{cav}} = 4\gamma/d_p$. The surface tension of the water-air interface is temperature dependent. As the plate is kept at 70°C (corresponding to 64 mN/m [63]), but the surroundings are measured to be 40°C (70 mN/m [63]), we have used an intermediate value of 67 mN/m. However, this range of values for γ only slightly influences the resulting value for T_{cav} . Note that the presence of particles should not have any effect on the value for γ , since the solutions are surfactant-free and the particles are fully hydrophilic.

The size of the particles is used as a typical length scale, as the vapour cavity with initial size d_p will detach from the solid surface and grow. We calculate this pressure for the two particle sizes which are studied. These theoretical bounds for the critical tension are also near 1 MPa and are given in Figs. 2.9a and 2.9b as dotted lines. The comparison of this theoretical bound with our experimental data becomes particularly interesting for the 0.98 μm -diameter particles in Fig. 2.9b. Most of the data lies in between the creasing limit and the single-particle theoretical bound represented by the dotted line. However, in Fig. 2.9a ($d_p = 0.45 \mu\text{m}$) the values for the tensile strength are larger than the theoretically predicted by the particle size. According to the predictions of Marschall *et al.* [61], the tensile strengths found correspond approximately to the radius of the particles (see Fig. 2.10) and correspond to the same order of magnitude. Therefore, we do not expect that roughness at the particles surface in the nanometric range would play a significant role as nano-crevices in our experiments.

The results shown above indicate the existence of nucleation sites smaller than the particle diameter. It would be therefore interesting to alter the length scale of the potential nucleation sites in the droplets. On the one hand, using smaller particles than $d_p = 0.45 \mu\text{m}$ would not give additional information, since the results have been quite insensitive to their presence. On the other hand, larger particles than $d_p = 0.98 \mu\text{m}$ would enhance the sedimentation of the particles to the bottom of the droplets, which involves complex additional effects. Instead, we performed series of experiments with 0.98 μm -diameter particles adding a small amount of sodium chloride to the particle solution. The presence of ions in the solution increases the screening of the electrostatic barrier that prevents the particles from aggregation [3], and therefore we expect to promote the presence of clusters, which would introduce a spread in the effective size distribution of the particles in solution. We add 10 mM NaCl to the particle solution, which is far below the saturation concentration of NaCl (roughly 6 M), and therefore we do not expect crystallisation to influence the evaporation of the droplet.

According to the argument introduced above, and in line with several references [57, 58, 61], the presence of salt promotes the formation of particle clusters, which would decrease the critical pressure for cavitation, *i.e.* T_{cav} should decrease. This is precisely the effect observed in the experiments with salt, which are shown as star markers in Fig. 2.4 and in

Figure 2.10: The tensile strength of water that contains different particle concentrations and particle sizes. The open markers highlight cases in which creasing occurs. The filled symbols represent the type A cavitation experiments, the grey markers represent type B cavitation. Experiments without any particles inside the droplet are shown as black triangles at $d_p = 0$. Also experiments containing salt are included, represented by star markers. The individual data sets at $d_p = 0.45$ and $0.98 \mu\text{m}$ are shifted slightly apart from each other, for clarity. The solid line shows the curve for $T_{cav} = 4\gamma/d_p$.

2.9b. Figure 2.4 clearly shows that the droplets containing salt and $0.98 \mu\text{m}$ -diameter particles cavitate in a very early stage (large R_{cav}/R_0), when only a small amount of elastic tension has built up in the droplet. Consequently, Fig. 2.9b shows that the critical tension for cavitation clearly decreases when compared to the situation without salt, and even reaches values below the predicted curve for $d_p = 0.98 \mu\text{m}$. This means that the typical length associated to the critical stress from the surface tension is in this case larger than the particle diameter itself. Also interesting is the fact that most of the cavitation events observed in the presence of salt are of type B. We hypothesized above that type B cavitation events seem to take place in the liquid bulk due to the presence of particles, and this observation goes in the line of our hypothesis.

2.4 Conclusions

In this chapter, we have studied how the presence of colloidal particles alters the occurrence of cavitation and creasing in a shrinking droplet under elastic tension in a PDMS gel. Surprisingly, $0.45\text{ }\mu\text{m}$ -diameter particles do not seem to influence the cavitation whatsoever, only in a marginal statistical proportion of the experiments performed. On the contrary, the influence of $0.98\text{ }\mu\text{m}$ -diameter particles is considerable. Cavitation events occur often before any creasing develops and the chances of this to occur are proportional to the particle concentration. Our main conclusion is that the onset of cavitation is largely influenced by the length scale of the particles or by their cluster size, as has been confirmed by introducing salt into the droplets to promote particle clustering. However, several questions remain open. One of the most important unanswered questions is the stark contrast between the $0.45\text{ }\mu\text{m}$ -diameter and the $0.98\text{ }\mu\text{m}$ -diameter particles; the former shows no influence from the particles and the latter does, but the influence comes from unknown length scales in between the particle diameter and the creasing limit. Furthermore, the exact origin for the existence of the critical droplet radius R^* (above which no creasing is observed) is still an open question. Several routes could be explored to gain more insight into the influence of particles on the onset of cavitation, using particles with different surface roughness or different wetting properties. This could also lead to more understanding of the two different types of cavitation which are observed. Consequently, predictions could be obtained on how the initial droplet size, particle size and/or particle concentration influence the outset of cavitation, not only in our system, but also on related systems with particle solutions under tension.

The occurrence of cavitation at the upper part of the droplet is also intriguing. Although sedimentation of particles towards the bottom of the droplet is clearly noticeable in our experiments (see for example Fig. 2.5), bubbles always nucleate at the upper part of the droplet, *i.e.* at the location of lowest particle concentration. This at first counter-intuitive observation may be explained with the ability of some particle to trap gaseous nuclei together with the long time-span of hours to build up tension. Single particles or agglomerates of particles trapping gaseous nuclei would be more buoyant than fully wetted particles with a density of $\rho = 1.05\text{ kg/m}^3$. Because the present particles' density is very close to the density of water, already a small amount of gas trapped could render them buoyant and accumulate these at the upper part of the droplet. If this would be the case, particles trapping more gas (most buoyant) would be located at the upper part of the droplet, while the rest would sediment to the droplet's lower part. This resulting stratification of buoyant particles at the top and particles without gas entrapment at the base may explain why the nucleation event occurs always on the top of the droplet.

Our experimental results show that fairly smooth particles in the nanometric range do stimulate cavitation events in evaporating droplets within an elastic matrix. This result should be independent on the nature or rheology of the matrix itself, and therefore it is an interesting conclusion both for practical applications as for rigid-walled cells exposed to such stresses [55].

In addition, our experimental system has shown to be a very reliable system to study the onset of cavitation in soft and elastic systems. The tensile strength of the solution can be measured through a rather simple preparation. By varying the elastic modulus of PDMS (e.g. mixing ratio during preparation) different regions of tensile strength can be probed. This would be of special interest for the characterization of solutions with particles that operate as sub-micrometric cavitation nucleation agents, promoting drug distribution and improving therapeutic efficacy in the body [64]. Additionally, the onset of cavitation before creasing could be an interesting advantage to introduce perfectly spherical bubbles in a controlled manner for the fabrication of soft acoustic metamaterials [65]. To conclude, we believe that the phenomena here described is a particular good example of the multifaceted puzzles that bubbles often manifest [66, 67].

CHAPTER 3

PARTICLE MONOLAYER ASSEMBLY IN EVAPORATING SALTY COLLOIDAL DROPLETS

Published as: **Myrthe Adriana Bruning**, Laura Loeffen, and Alvaro Marin, *Particle Monolayer Assembly in Evaporating Salty Colloidal Droplets*, *Physical Review Fluids* **5**, 083603 (2020).

ABSTRACT

Ring-shaped deposits can be often found after a droplet evaporates on a substrate. If the fluid in the droplet is a pure liquid and its contact line remains pinned during the process, then the mechanism behind such ring-shaped deposition is the well-known coffee-stain effect. However, adding small amounts of salt to such a droplet can change the internal flow dramatically and consequently change the deposition mechanism. Due to an increase of surface tension in the contact line region, a Marangoni flow arises which is directed from the apex of the droplet toward the contact line. As a result, particles arrive at the contact line following the liquid-air interface of the droplet. Interestingly, the deposit is also ring-shaped, as in the classical coffee-stain effect, but with a radically different morphology: particles form a monolayer along the liquid-air interface of the droplet, instead of a compact three-dimensional deposit. Using confocal microscopy, we study in this chapter particle-per-particle how the assembly of the colloidal monolayer occurs during the evaporation of droplets for different initial concentration of sodium chloride and initial particle dilution. Our results are compared with classical diffusion-limited deposition models and open up an interesting scenario of deposits via interfacial particle assembly, which can easily yield homogeneous depositions by manipulating the initial salt and particle concentration in the droplet.

3.1 Introduction

A sessile droplet containing a dilute solution of particles slowly evaporates while keeping its base radius constant. At present we have tools to predict not only where the particles will end up [5], but also the morphology and packing of the particles [8] (as long as the particle size is uniform enough). Under these conditions, a capillary flow is generated toward the droplet's rim to replenish liquid and maintain the contact line immobile. Consequently, particles follow streamlines that end at the contact line [5], forming the well-known ring-shaped stain (or coffee-stain). The ordering of the resulting three-dimensional arrangement of particles in this ring depends on the particle size and on the flow velocity, which diverges in the last stages of the droplet's life [8].

Nonetheless, small variations in the liquid composition can drastically change the system behavior and also its predictability [13]. From a fluid-dynamical perspective, the main effect of any compositional change is to induce stresses at the liquid-air interface that can influence critically the otherwise dominating coffee-stain effect. Such interfacial stresses can be also induced by thermal gradients, which may occur naturally during the evaporation process [68, 69], or may be externally induced [11, 12]. Such interfacial stresses induce an internal flow that might eventually overcome the canonical capillary flow. When this scenario occurs, *i.e.* when the coffee-stain effect is not the dominant flow, most of the streamlines close themselves and the destiny of a random particle depends on several factors: its size, shape, and density; the distance to neighboring particles, its vicinity to the liquid surface or to the solid substrate, its chemical affinity to all those, etc. In recent years, a vast literature has bloomed with studies dedicated to analyze the effect of different combinations of such parameters, with special interest in suppressing the ring-shaped stain [14, 70–72].

Interestingly, certain type of compositional changes also result in ring-shaped stains despite a substantial change in the internal flow profile: The addition of tiny amounts of NaCl to a water droplet induces an internal flow that looks as an inverted *coffee-stain* flow but also leads to a ring-shaped stain [9]. The effect is due to a solutal Marangoni flow caused by the presence of NaCl which increases the surface tension of water (as other similar chaotropic electrolytes, it effectively acts as an *antisurfactant* [73, 74]). When a droplet containing a small amount of salt evaporates, its contact line region enriches in salt content over time [75]. This induces a surface tension gradient along the droplet of the surface, and a Marangoni flow sets up directed from the apex of the droplet toward the contact line. In a recent paper, Marin *et al.* [9] showed both experimentally and numerically, that this surface flow is strong enough to overcome the bulk capillary flow. They also showed that the ring-shaped deposit originates from particles adsorbed at the liquid-air interface (from now on, droplet's surface), and convects toward the contact line region

by the surface flow. This evaporation-driven particle assembly mechanism has not been studied in detail, and it will be the focus of the current work.

In this study, making use of laser scanning confocal microscopy, we analyze the particle assembly in colloidal droplets containing small amounts of sodium chloride. Scanning a small volume of the contact line region with high spatial and temporal resolution we confirm that the assembly occurs in a monolayer parallel to the droplet's surface. Confocal microscopy allows us to reconstruct particle-per-particle the formation and growth of the particle monolayer, and investigate the influence of the initial salt molarity and particle concentration.

3.2 Experimental Methods

In a typical experiment, a sessile droplet of about 3 μL containing certain amount of sodium chloride and polystyrene colloidal particles is evaporated and simultaneously scanned with a laser scanning confocal microscope. The initial concentrations of sodium chloride ($\geq 99.5\%$ purity, BioXtra) employed are $C_0 = 5, 10$ and 50 mM (molar mass NaCl is 58.443 g/mol). This choice is made to be as far as possible from the saturation concentration in water (roughly 6 M) and high enough to be able to have sufficient particle accumulation during the time of a typical experiment (about 25 min). Experiments for each salt concentration are repeated at least 5 times.

The colloids employed are polystyrene particles, functionalized with sulfate groups to convey stability to the suspension (microParticles GmbH, PS - FluoGreen - 1.0) and died with certain green-emitting fluorescent dye (ex/em: 502 nm/518 nm). The particle diameter is chosen around 1 μm (namely $1.08 \pm 0.04 \mu\text{m}$), as a compromise to reduce sedimentation during the fairly long evaporation process (polystyrene density is 1.05 g/cm³, which makes them almost neutrally buoyant) and large enough to be visible under a confocal microscope for the magnifications employed. The polystyrene particle concentration in the droplets is 0.01 w-%. The suspensions are prepared between 0.5 and 6 h before use. Prior to the experiment the solution is sonicated for 60 s and left to reach room temperature for 4 min. A droplet from this solution of 3 μL is then gently pipetted onto a Menzel-Gläzer circular glass microscope cover slide (#1.5), previously rinsed with Milli-Q water, dried with nitrogen gas and heated at 80°C for 2.5 min for complete desiccation. This treatment ensures pinning of the droplet throughout its evaporation time. The initial contact angle of a salt water drop on this substrate is 70°.

Figure 3.1: Laser scanning confocal microscopy is employed to obtain three-dimensional information on the particle assembly. Figure (a) shows sketches of the top-view (glass-slide plane) and side-view projection of the scanned volume within the droplet, indicating length scales and axis definitions. The pink box shows the approximate location of the scanned volume respect to the droplet (not in scale). Figures (b) and (c) show projections of the scanned volume in the (x, y) -plane and the (y, z) -plane respectively. Figure (d) shows an orthogonal projection of the full scanned volume as obtained from the fluorescent channel, for $C_0 = 10 \text{ mM}$ and $t/t_{\text{evap}} = 0.8$. The dimensions of the scanned volume are included.

The evaporation experiment is performed in a controlled environment with $T = 23 \pm 1^\circ\text{C}$ and $\text{RH} = 50 \pm 1\%$ in a custom-made chamber. The humidity is controlled using a digital humidity sensor (Glyduino AM2302 DHT22), connected to an Arduino microcontroller. Depending on the outside humidity versus the target humidity, either dry or wet air is supplied into the chamber. Nitrogen gas serves as dry air, while humid air is created by bubbling gas through a water column. The flow rate of the incoming air is maintained low to avoid air convection inside the chamber, which would influence the evaporation of the droplet. The total evaporation time of the droplets is 26 ± 2.5 min.

The positions of the colloids are obtained using an inverted laser scanning confocal microscope (Nikon A1R HD) with an oil-immersed objective of 60x magnification and a numerical aperture of 1.4, which yields a resolution of $0.10 \mu\text{m}/\text{pixel}$. The total area observed in the object plane is $25 \mu\text{m}$ in width (x -axis, along the contact line) and $50 \mu\text{m}$ in depth (y -axis, toward the droplet's center). The volumetric information is obtained by scanning a total of $15 \mu\text{m}$ along the optical axis (z -axis, perpendicular to the glass slide), with steps of $0.35 \mu\text{m}$ between scanned planes, at a speed of 0.64 s per position. The humidity is manipulated to make sure that the evaporation process is slow enough to prevent blurred images during the time of a full scan (about 30 s). Also note that the step size is chosen to be smaller than the particle diameter, such that each particle appears in multiple layers of the scan for a better resolution in the particle positioning. A blue laser (488 nm) is used to excite the fluorescent particles. Both the fluorescent emission channel and the transmission channel are recorded and used for obtaining the particle positions. Three projections of the scanned volume obtained from the fluorescent channel are shown in Fig. 3.1, in which the relevant dimensions of the scanned volume and the axis definitions are included. The different projections in the figure clearly show that the particles arrange themselves into a monolayer that extends along the droplet's surface. A more detailed observation to the top-view and side-view projection (see Fig. 3.1b and c) shows that the particles in the first rows follow a somewhat irregular arrangement, not entirely following the surface. This could be due to some minor contact line motion or due to the finite roughness from the glass substrate. Nevertheless, the well-defined order of the particles and their arrangement along the droplet surface is notorious in the subsequent rows. A typical movie recorded with the confocal microscope is available in the Supplemental Material [76].

The data obtained from the confocal microscope permit to assess both the order and the growth rate of the monolayer. The former will be done using a 2D Voronoi analysis in the plane of the droplet's surface, the latter by studying the evolution of the upper *contour* of the monolayer that grows toward the center of the droplet.

Figure 3.2: Overview of the typical analysis results. Figure (a) shows the contact angle θ of the droplet as a function of time. A linear fit through this data is used to access the final evaporation time t_F , defined at $\theta = 0^\circ$. Figure (b) shows an overview of the analysis results for the same confocal scan as shown in Fig. 3.1 ($C_0 = 10$ mM NaCl and $\tilde{t} = 0.8$). The found particle positions are shown as black dots. These particles are plotted along s , which is the axis along the droplet's interface, for which the droplet contact angle θ is used. The contour of the droplet is given as the outer light blue line, and the typical detected Voronoi cells are presented. The definition of the height of the contour $h(x, t)$ is given as well.

First, the 2D Voronoi analysis requires the three-dimensional particle positions. For this we use the output from the transmission channel, as this contains the largest contrast. Using the points with maximum intensity within each layer of the scan, we determine the (x, y) -position of each particle. This is done for all layers in every full scan. As each

particle is found in multiple layers, the average of these positions is used to find the final (x, y, z) -position of this particle. At each time step the contact angle θ of the sessile droplet is obtained by fitting a plane through the detected particles, which yields a nearly linear decrease of θ versus time, as can be seen in Fig. 3.2a. A linear extrapolation is used to determine the final evaporation time t_F , defined at the point where $\theta(t = t_F) = 0^\circ$, enabling us to compare different experiments by normalizing time as $\tilde{t} = t/t_F$. Note that $t = 0$ is defined as the moment at which the droplet is deposited at the substrate, *i.e.* when the evaporation process starts. The contact angle analysis allows us to define an additional axis which we will identify as the s -axis (Fig. 3.1a), which starts at the contact line and is directed toward the droplet's symmetry axis. As shown in Fig. 3.1a, the origin of the s coordinate is the contact line of the droplet.

In Fig. 3.2b we show an example of the obtained particle positions (black dots) in the (x, s) -plane and their corresponding Voronoi cells for $C_0 = 10$ mM and $\tilde{t} = 0.8$. By definition, all points contained in a particle's Voronoi cell are closer to that particle than to any other. The regularity in the Voronoi cell's area is a quantitative sign of order in the particle array. Figure 3.2b also includes the traced upper contour of the particle array as a light blue line, obtained from the fluorescent channel of the scan. The contour is obtained from the reconstructed three-dimensional particle array and projected to the (x, s) -plane. It is represented quantitatively by the function $h(x, t)$, which can be obtained with subparticle resolution through our measurements: $h(x, t)$ is defined as the maximum height reached by particles in the array at a given position x and instant t , and therefore it yields an unique value for each x -position.

Figure 3.3: Typical results of a Voronoi cell analysis performed in the particle monolayer for different salt concentrations: (a) 5 mM, (b) 10 mM and (c) 50 mM. The colorbar represents the area of the cell A_{cell} in μm^2 .

3.3 Results

3.3.1 Voronoi analysis within particle monolayer

We perform a Voronoi cell analysis to gain insight in the level of ordering within those particles detected in the monolayer. Figure 3.3 shows the results of Voronoi analyses performed for experiments with identical initial particle concentration and increasing initial salt concentrations $C_0 = 5, 10$ and 50 mM of NaCl, all captured at the dimensionless time $\tilde{t} = 0.8$. Those cells located at the edge of the image are removed, as their size is undefined due to the absence of neighbors. Clearly the cases of 5 and 10 mM look very similar, with the same degree of order, manifested by large regions with hexagonal lattice structure. In the case of 50 mM the particle distribution is rather sparse, and the detected cells show irregular shapes. These observations are quantified using the normalized cell size A_{cell}/A_{hex} , where $A_{hex} = \frac{1}{2}\sqrt{3}D^2$ is the size of a perfect hexagonal cell (D is the particle diameter).

Figure 3.4 shows the normalized cell area plotted against the distance from the contact line s , for different C_0 . Each plot includes data from five different experiments at identical conditions. The average cell size is measured along s and all data are binned with a fixed bin of size D . The shaded region around the curve displays the standard deviation. Two important observations can be made from this figure. First, the particle ordering of the 5 and 10 mM case are almost indistinguishable, and strongly contrast with the 50 mM case. For this highest salt concentration the average cell size is larger as well as the cell size variance. Second, the particle arrays in the 5 and 10 mM cases exhibit large regions with a hexagonal structure. Near the contact line (*i.e.* for small values of s) the normalized average cell size is slightly above 1 . As can be seen in Fig. 3.1c, the particles closest to the contact line are somewhat less ordered and the packing is not entirely two-dimensional. A possible reason might be found on some marginal contact line creeping in the early stages of evaporation that disarranges the particle structure.

Salt-induced aggregation of colloidal particles at air-water interfaces has been studied for decades [77–80], often motivated as a model experiment to study diffusion-limited aggregation [81]. Note however that our particles arrange themselves at much shorter distance than in the so-called *colloidal crystalline* structures [77], which could be easily due to the presence of electrolyte in all our experiments. Our system shows, however, more analogies to those scenarios in diffusion-controlled deposition models [82, 83], especially due to the two-dimensionality of the particle monolayer. Measurements in that direction will be shown in the following section, in which we assess the growth of the monolayer as a deposition process.

Figure 3.4: The normalized average size of the Voronoi cell as a function of the distance from the contact line is shown for three different salt concentrations: (a) 5 mM, (b) 10 mM and (c) 50 mM. For each concentration, the average cell size of five experiments is used, the shaded area displays the standard deviation. All structures are analyzed at $\tilde{t} = 0.8$. The cell size is normalized with the area of a hexagonal cell, which is calculated using the particle diameter.

3.3.2 Particle monolayer growth and contour roughness

We characterize the growth of the monolayer by studying the evolution of its contour height $h(x, t)$, defined as the maximum distance of the particle structure from the contact line for each position x at every instant t . Figure 3.5 shows the evolution of the contours of the particle monolayer for different initial salt concentrations. The colorbar represents the dimensionless time of the experiment. We show contours up to $\tilde{t} = 0.8$, since final stages of evaporation yield less reliable results to compare due to depinning events. The cases of $C_0 = 5$ and 10 mM yield almost identical contours, growing fairly uniformly. For the 50 mM case however, we observe very different behavior in different positions along the contact line. Regions depleted of particles as shown in Fig. 3.5d coexist with highly populated regions as in Fig. 3.5c. The contours in both Fig 3.5c and d, but mainly the former, present prominent finger-like structures and boundant holes that are completely absent in experiments with 5 and 10 mM NaCl.

Another important observation is the way in which the particles attach to the monolayer. In the case of low salt concentration (5 and 10 mM) all particles arrive one by one, as single particles, whereas for the high salt concentration (50 mM) a significant amount of the particles are already agglomerated into small clusters before attaching to the monolayer. The increase of electrolyte in solution screens the electrostatic barrier that prevents the particles from aggregation [15]. This is consistent with classical studies on salt-induced aggregation [77–80], and also explains the increase of the Voronoi cell area for 50 mM. The less packed and more intricate particle arrangement for the $C_0 = 50$ mM results in a larger area coverage (*i.e.* larger Voronoi cell area) for the same number of particles when compared with the area coverage for $C_0 = 5$ or 10 mM.

For studying the growth of the monolayer, we average along the contact line axis x to obtain $\bar{h}(t)$. Interestingly, for the cases of $C_0 = 5$ and 10 mM, the particle monolayer grows following roughly a scaling $\bar{h} \sim t^{2.5}$, the same scaling found for the particle count at intermediate stages (discussed further below). While the average contour evolution $\bar{h}$ for 50 mM is much noisier and it is difficult to draw any conclusions on its scaling. Data regarding $\bar{h}(t)$ and extended data on the particle count are shown in Appendix 3.5.1. The growth of complex interfaces was an intense topic of research after the celebrated diffusion-limited aggregation model introduced in the early 1980s by Witten and Sander [81]. In this model, particles aggregate by diffusing to a cluster and adhering to it irreversibly. The same principle for studying pattern formation was soon applied to deposition problems [82, 84, 85]: Particles arrive randomly to an interface where they will adhere irreversibly following certain rules. The growth of such interfaces was studied intensely but special interest was devoted to study the *roughness* of the formed interface for its potential reactive properties; also referred in the literature as “surface width” or “width of the active zone” [84].

Figure 3.5: Contour height $h(x, t)$ of particle monolayers along the droplet surface as a function of dimensionless time $\tilde{t}$, for three different initial salt concentrations. Figure (a) shows 5 mM, (b) 10 mM and both (c) and (d) show examples of 50 mM, as large heterogeneities are observed for different positions along the droplet's contact line. For each experiment contours are shown for $\tilde{t} = 0.35, 0.5, 0.65$, and 0.8 .

This roughness $w(t)$ is defined as the standard deviation of the contour height $h(x, t)$ at every instant t (note that we follow the nomenclature used by Family [86]). As proposed by Family & Vicsek [84, 87], the roughness $w(t)$ follows a dynamic scaling with $w \sim t^\beta$ for the initial growth, and saturating to a constant value at large times. Several deposition models were found to follow such scaling, but we will focus here in only two of them: In the simplest of them, particles appear at random x positions and they pile up on top of the previously deposited particle at that position. Since each particle is independent and does not interact with neighboring particles, this model is often referred as *Poissonian*. This simple growth model yields a roughness growth exponent $\beta = 0.5$, independent of the number of dimensions.

Another way to model the interface growth is through a so-called *ballistic* process: Particles fall down onto the substrate and stick either on the top of the column they initially fell in, or stick to a particle in the nearest neighbor columns. This reflects in a different value for the roughness growth exponent, approximately $\beta = 1/3$ (in the 2D-case) [84, 86], which can be directly obtained through the renormalization of the Kardar–Parisi–Zhang (KPZ) equation [85]. The idea that our system might follow some of these simplified growth models is very tempting. In a related experimental system, the interfacial clustering of nonspherical colloidal particles observed by Yunker *et al.* [16], the roughness has been proposed to follow universality classes that appears consistent with either KPZ [85] or KPZ with quenched disorder (KPZQ) [88] depending on the particle shape. The experimental evidence has not been entirely conclusive so far [89], but recent numerical results with patchy colloidal disks [90] suggests that a transition from KPZ to KPZQ could indeed be possible as the particle aspect ratio increases.

Looking at the results shown so far in the context of diffusion-limited deposition models, an obvious question arises on whether a similar transition of scaling or model can be measured in our colloidal deposition process. One of the main obstacles to make a direct comparison is the different definition of *time* for experiments and in the models. In order to make a fair comparison with the simulated model, we follow the same approach followed by Yunker *et al.* [16] and compare the contour roughness $w(t)$ against the average contour height $\bar{h}(t)$, instead of time, since its origin is typically ill-defined in the experiments. We have simulated the previously described deposition models introducing our empirically found incoming particle rate ($N \sim t^{2.5}$, discussed in a section below), to obtain first-hand numerical data to compare with experiments. Despite the time-dependent particle rate, the simulated *Poissonian* and *ballistic* deposition models yield roughness scalings as predicted by the Family–Vicsek dynamic scaling $w \sim \bar{h}^n$: With $n = 0.50$ for the Poissonian process and $n = 0.31$ for the ballistic, the latter also showing saturation at large $\bar{h}$ (obtained via 100 simulations using the experimentally found particle rate, see Appendix 3.5.2 for more details).

Figure 3.6: The roughness of the monolayer contours w as a function of the mean height $\bar{h}$. Figure (a) shows 5 mM, (b) 10 mM and (c) 50 mM. Different markers indicate different experiments, the black dots represent the logarithmically binned data. In order to test if the data follows Family-Vicsek dynamic scalings [84] $w \sim \bar{h}^n$, we performed weighted linear regression fits of the binned data. The exponents n found are (a) $n = 0.41 \pm 0.03$, in (b) $n = 0.47 \pm 0.05$ and in (c) $n = 0.37 \pm 0.04$.

In Fig. 3.6 the experimentally obtained values for the roughness of the contour w are given as a function of its mean height $\bar{h}$, which contains five experiments per salt concentration. Given the noisy character of the data and relatively low number of experiments per sample (five repetitions per salt concentration), it will be difficult to draw conclusions on the scaling of the data. Another drawback of the experimental data is the small range of $\bar{h}$ that can be experimentally surveyed keeping high resolution ($2 \lesssim \bar{h} \lesssim 20 \mu\text{m}$). Nonethe-

less, we have proceed to obtain power-law fits trying to reduce bias as much as possible: First, the data have been binned using variable logarithmic bin-widths (shown in Fig. 3.6). Second, the number of data points per bins has been extracted. Third, a weighted linear regression is performed on $\log w$ vs. $\log \bar{h}$ using the fraction of data points per bin as weights. Using this procedure, we obtain the following exponents: $n = 0.41 \pm 0.03$ for the 5 mM case, $n = 0.47 \pm 0.05$ for 10 mM and $n = 0.37 \pm 0.04$ for 50 mM. Other alternative data fitting strategies yield only slightly different results from these results shown here, and they can nonetheless be found in Appendix 3.5.3. Although the results are not conclusive due to the limitations described above, the obtained exponents fall in the expected trend: the lower initial salt concentration cases 5 and 10 mM develop higher roughness growth exponents (Poissonian-like), and smaller roughness growth exponent (ballistic-like) are found for the highest initial salt concentration, which shows more dendritic deposition patterns. The important role of the salt concentration in the different aggregation regimes is clear, but the detailed mechanism is more difficult to reveal. As salt concentration increases, the colloidal electrostatic repulsion is screened and particles tend to cluster throughout the whole droplet volume. This provokes preclustering of particles before reaching the monolayer, but it can also induce complex aggregation mechanisms at the monolayer, ultimately increasing lateral correlations locally (crucial for growth processes compatible with the KPZ universality class). In order to analyze such mechanisms in more detail, larger datasets and lateral correlations should be measured, which would require a very different experimental approach as the one followed here.

3.3.3 Incoming particle assembly rate

The flux of arriving particles to the monolayer is an important factor to characterize the growth of the deposit. For the classical coffee-stain flow, Deegan *et al.* [5] successfully predicted that the total number of particles deposited should scale as $N \sim \tilde{t}^{4/3}$, which is robustly found in experiments whenever this deposition mechanism dominates. In our case of salty droplets, where the deposition is dominated by an interfacial solutal Marangoni flow [9], a completely different scaling is expected to be found. Our visualization technique allows to count particle-by-particle with good resolution, and the results are shown in Fig. 3.7, where we show the total amount of particles in the monolayer N as a function of dimensionless time $\tilde{t}$. These graphs also include the relation $N \sim \tilde{t}^{4/3}$, the total particle arrival scaling in the classical coffee-stain flow [5] (grey dashed lines) as a reference. Clearly the arrival of particles is faster in the case of a salty evaporating droplet. This stresses again the very different deposition mechanism due to the change in flow pattern by the addition of small amounts of salt, and the resulting different particle arrival rate. As with previous results, $C_0 = 5$ and 10 mM show very similar results (Fig. 3.7a and c), with very high reproducibility. The particle number seems to follow approximately a scaling as

$N \sim t^{2.5}$ (similar to the scaling for $\bar{h} \sim t^{2.5}$) for most of the process, but tends to saturate as $\bar{t} \rightarrow 1$, this is shown in Appendix 3.5.1. The case of $C_0 = 50$ mM differs from the previous cases and the measurements also lack the reproducibility shown in $C_0 = 5$ and 10 mM. The lack of reproducibility was discussed previously and it is related to the presence of areas depleted of particles along the contact line, which leads to an early saturation in some of the curves in Fig. 3.7d. In addition, the higher concentration of electrolyte favors the adhesion of particles to the bottom glass substrate due to the screening of the surface charges. Consequently, from the detected particles near the substrate, we estimate that nearly 10% of the total particles do not succeed to join the particle monolayer in the 50 mM case. This is also shown in Fig. 3.7d in which many curves do not reach the same values as those in Fig. 3.7a and c.

We propose in the following a simple model to account for the particle number arriving to the monolayer. Since every particle arriving to the monolayer must have been previously adsorbed at the droplet liquid-air surface (or at least in its close vicinity), the number of particles adsorbed at the interface per unit time will give us an upper bound for the number of particles that will eventually end up in the monolayer. The particle adsorption mechanism we will consider is the simplest possible: As the droplet's surface retracts keeping a pinned contact line, it will sweep particles along with it. In other words, particles initially dispersed in the bulk will be trapped at the interface as the interface moves downward [12, 91, 92]. We will not consider any other adsorption mechanism since the particles are functionalized to be practically hydrophilic (which discards any effective diffusivity toward the interface) and their volumetric concentration in the droplet is extremely low. *Diffusiophoresis* is also discarded as a particle migration mechanism in our system since this is essentially a bulk effect that would yield a three-dimensional accumulation of particles in regions of higher salt concentration [93], and never a two-dimensional monolayer along the surface. Such interfacial particle accumulation has been reported at the same rate for experiments with fresh water [9, 12, 91], which is another strong argument against the presence of diffusiophoresis in our system.

As the droplet evaporates, assuming a homogeneous particle distribution in the bulk C_B , the decrease in droplet volume dV/dt relates to the total number of particles at the surface N_s as

$$\frac{dN_s}{dt} = -C_B \frac{dV}{dt}. \quad (3.1)$$

The evaporative flux dV/dt is obtained from the analytical solution of Popov [7]. The full differential equation for the contact angle $\theta(t)$ is solved for our experimental initial values of volume, contact angle and droplet radius. With the expected $\theta(t)$, the volume loss can easily be calculated at each instant of time. Integrating Eq. 3.1, we obtain N_s , the number

Figure 3.7: The number of particles N attaching to the monolayer as a function of dimensionless time $\tilde{t}$. Different markers indicate different experiments. Figure (a) shows the results for 5 mM, (c) 10 mM and (d) 50 mM. This number N is the total number of particles which arrive in one measurement section ($25 \mu\text{m}$ wide). The dashed grey line in these figures represents the classical coffee-stain flow where $N \sim \tilde{t}^{4/3}$ [5], using an arbitrary prefactor. The dotted light gray line in all figures shows the computed total number of particles which are captured by the droplet's surface $N_s(t)$ as a function of time. The results of the numerical solution for N (using a constant surface velocity $u_s = 1 \mu\text{m/s}$) are given with a solid black line. Figure (b) shows the same curves and experimental data as figure (a) in a linear representation and using real dimensional units.

of particles swept by the droplet's surface during the evaporation. This gives us an upper bound for the number of particles that might eventually arrive to the monolayer and it is represented in all the subfigures in Fig. 3.7 as a dotted grey line. By definition, this curve

overestimates the number of particles at the monolayer.

To compute the arrival rate of particles to the monolayer, we model the particle concentration field along the droplet surface using a simplified 1D transport equation applied to the droplet's surface

$$\frac{\partial C}{\partial t} = J(s, t) - \nabla \cdot (u_s C), \quad (3.2)$$

in which $C(s, t)$ is the particle surface concentration, $J(s, t)$ is the source term for incoming particles and $u_s(s, t)$ is the surface velocity (the advection term). Using the local volume loss, the local number of particles swept by the interface is known using Eq. 3.1. Equation 3.2 is solved numerically using a second order finite difference scheme, details on the numerical scheme and how the spatial variance of $J(s, t)$ is calculated can be found in Appendix 3.5.4. Unfortunately, we lack one of the keys to solve this problem: the surface velocity u_s . Our own measurements do not have enough time resolution to track particles reliably. In practice, we will assume a constant surface velocity comparable with velocity estimations based on our own experimental data, which are compatible with the experimental data obtained from Marin *et al.* [9] using 3D particle tracking velocimetry for different salt concentrations. The particle concentration $C(s, t)$ evaluated at the contact line $s = 0$, gives us the total number of particles accumulated at the monolayer N .

In Figs. 3.7a-d we show the result of the numerical integration of Eq. 3.2 using a constant surface velocity $u_s = 1 \mu\text{m/s}$ as a solid black line (note that we have not performed a systematic study on the optimal value of u_s). This solution for N versus t in Fig. 3.7b shows two important features: First, as expected, particles are being swept by the surface as soon as the evaporation starts, but their arrival to the monolayer is delayed in time. Figure 3.7b shows that the first particle is observed experimentally roughly 300 s after the evaporation process begins, which is well captured in the numerical solution for that particular value of u_s . Second, the curves for the number of particles at the surface $N_s(t)$ (dotted gray curve) and for the number of particles at the monolayer $N(t)$ (dark line) show a very different curvature. This curvature depends strongly on the value of the velocity u_s chosen. The solution for $N(t)$ found with $u_s = 1 \mu\text{m/s}$ matches reasonably well the trend of the experimental data and it is comparable with the values found by Marin *et al.* [9]. The curvature is related with the time taken for the particle to travel from the point in which it *collides* with the surface to the contact line. Consequently, as we increase u_s , the curve for $N(t)$ approaches the curve of particles adsorbed at the surface $N_s(t)$ (for $u_s \gtrsim 100 \mu\text{m/s}$, both curves lay on each other). Despite the limitations of the model, it supports the simple mechanism we propose for the particle assembly at the monolayer: particles are swept by the droplet's surface and consequently advected by the Marangoni flow toward the contact line where they join the monolayer.

Figure 3.8: (a) Final stains for different salt concentrations after the liquid phase has completely evaporated. The particle concentration is fixed at 0.1%w and only the initial salt concentration C_0 increases from 0 to 50 mM. (b) Final stains for different particle concentrations after the liquid phase has completely evaporated. The initial salt concentration C_0 is fixed at 50 mM and the particle concentration changes from 0.01 to 0.1%w, defined as the particle mass m_p divided by the initial droplet mass M_0 .

3.3.4 Dried particle deposits

So far we have shown detailed results on a reduced volumetric region of the droplet, carefully choosing the initial particle and salt concentration to perform the measurements accurately. In this section we analyze the dried deposit of the particles once the evaporation process is completed at a larger scale. In Fig. 3.8a we show the resulting stains for increasing salt concentration. In the absence of salt ($C_0 = 0$ mM) the well-known ring-shaped stain appears as a thin black line at the contact line. When the particles are monodisperse enough this ring-shaped stain is characterized by a highly packed deposit, manifested in a thin ring along the contact line. For the same initial number of particles, the presence of 5 mM of salt in the droplet is noticeable by an increase of the ring width. Increasing the salt concentration from 5 to 50 mM, changes the particle deposition drastically and instead of a dark ring of particles, a sparse particle network appears. As described in previous sections, this is formed by a loosely packed monolayer of particles at the droplet's surface, which collapses into the glass substrate when the evaporation process is completed.

For increasing salt concentration, the particle compaction is reduced (see section 3.3.1 and the network covers a larger area of the droplet deposit for the same initial number of particles. Salt crystals are clearly observed in the images for this range of salt concentration. These only grow in the last stage of evaporation (approximately in the last 3% of the total time for the highest salt concentration), when the deposit dries out completely and

mechanical instabilities (delamination, cracks, buckling, etc) might also occur. Since our analysis is focused on those stages in which the droplet has a well-defined shape and a stable contact line, the last deposit-drying stage has not been analyzed. Interestingly, the crystal growth does not seem to influence the final particle deposition. The colloidal structure seems to be dried and consolidated by then and the observed patterns remain almost unchanged. This can be seen in the Supplemental Material where two movies are available that show the full evaporation process for several particle concentrations and salt concentrations [76]. In Fig. 8b we have kept the initial salt concentration constant at $C_0 = 50$ mM and increased the initial particle concentration, from 0.01%w/v, yielding an almost complete coverage of the droplet contact area using an initial particle concentration of only 0.1%w/v. Consequently, simply by adding a certain amount of salt and manipulating the initial particle concentration, we can completely suppress the coffee-stain effect.

3.4 Conclusions

In this chapter we have shown that particles dispersed in an evaporating sessile drop of water with a small amount of salt (NaCl) assemble forming a monolayer that grows from the contact line and along the droplet's surface toward its center. The key ingredient is the solutal Marangoni flow generated by the presence of small amounts of salt [9], which generates a surface flow directed toward the contact line. Using laser scanning confocal microscopy we have obtained detailed information of the structure of the particle monolayer. The smallest initial salt concentrations surveyed (5 and 10 mM) yielded well-ordered and highly packed particle arrays. The largest salt concentration (50 mM) resulted in loosely packed and heterogeneous particle monolayers with areas along the contact line depleted of particles.

The roughness of this monolayer (or the *surface width*) has been analyzed using classical diffusion-limited deposition models [81, 84]. Unfortunately, the lack of enough statistics and the short range of our observation field prevents us to draw conclusions on this matter. Our attempts to fit power laws to the roughness have yielded exponents that seem to follow either Poissonian or ballistic deposition models. But larger data sets would be needed to confirm this trend. The growth of the monolayer is directly proportional to the incoming particle rate, which has been modeled using a simplified surface adsorption and advection equation with constant surface velocity. The model yields incoming particle rates that compare fairly well with that from experiments. This result supports the simple mechanism proposed for particle assembly at the monolayer: particles are swept by the droplet's surface and then advected by the solutal Marangoni flow toward the contact line.

Finally, we have analyzed the dried particle deposits on a larger scale for different initial salt and particle concentrations. As our previous results suggested, at relatively high initial particle and salt concentrations (50 mM), the particle monolayer can easily cover the whole droplet surface and results in an homogeneously and loosely packed particle array when the evaporation process is completed. This mechanism for suppressing ring-shape stains is independent of the particle shape [70] and only requires a small amount of salt in the liquid phase.

Acknowledgements

We thank Stefan Karpitschka for several fruitful discussions and comments. Pieter Berghout is acknowledged for his help on the numerical model and José Manuel Encarnación Escobar for his help using the LCSM.

3.5 Appendix

3.5.1 Monolayer growth and incoming particle rate

The relationship between the monolayer profile evolution and the incoming particle rate is not obvious *a priori*. In Fig. 3.9 we show the typical evolution of the mean height of the monolayer $\bar{h}(t)$ (Fig. 3.9a). We can see that a power law with exponent 2.5 describes the growth of the monolayer for 5 mM and 10 mM for the full time range. The case of 50 mM is more complex since, as discussed in the main text, a large percentage of particles do not reach the monolayer and are found adhered to the glass slide. This effect becomes more important as the contact angle is reduced and the particle-substrate distance reduces, and therefore the monolayer growth slows down as $\bar{t} \rightarrow 1$.

The total number of particles arriving to the monolayer is shown in Figs. 3.9b-d. We have observed the same scaling between the monolayer growth $\bar{h}(t)$ and the total number of particles $N(t)$ in our simulations of deposition models (see details further below). Therefore, the dashed black line in the plots represents the curve relation $N \sim \bar{t}^{2.5}$. This curve overlaps with the experimental data for a large part of the domain, but fails to capture the initial stages. In the next sections we describe with more details the model we have constructed to account for the incoming particle rate.

Figure 3.9: (a) The typical evolution of the mean height of the monolayer $\bar{h}(t)$ for 4 different experiments with 3 different salt concentrations. Two curves are included for the 50 mM case to highlight the variability found for this salt concentration along the contact line. The dashed black line shows $\bar{h} \sim \tilde{t}^{2.5}$. (b), (c) and (d) The number of particles N arriving at the contact line for 5 mM, 10 mM and 50 mM respectively. In all 3 figures the solid black curve represents the outcome of the model constructed to account for the incoming particles to the monolayer as presented in the main manuscript. The dashed black line shows $N \sim \tilde{t}^{2.5}$, since it is expected from simulating deposition models that $\bar{h}$ and N scale in the same way with time.

3.5.2 Simulations of Poissonian and ballistic deposition models: Interface roughness

The growth of complex interfaces was an intense topic of research in the early 1980s since it was expected that simple particle deposition models could reproduce patterns observed in nature. These deposition models were based on particles arriving randomly to an interface where they will adhere irreversibly following certain rules. The growth of such interfaces was studied intensely but special interest was devoted to study the roughness of the formed interface for its potential reactive properties. In order to verify if the growth of our particle monolayer follows any of these deposition models, we have simulated such processes using the particle rate found in our experiments ($N \sim t^{2.5}$, see Fig. 3.9a) and computed the scaling of the roughness w versus the mean height of the monolayer $\bar{h}$. In both models we will employ $L = 5000$ columns that will be filled in each iteration $t = [1, 2, \dots, t_{max}]$ by $N(t) = 0.1 \times t^{2.5}$ particles distributed randomly. Each data point shown is the averaged value of w over 100 simulations ran under the same conditions.

In the Poissonian or random deposition model *“particles simply fall until they reach the top of the column in which they were dropped or they reach the substrate. At this point they stop and become part of the aggregate”* [86]. Figure 3.10a shows w vs. $\bar{h}$ for the simulated random deposition cases with constant particle rate ($N = t$) and variable particle rate. The constant particle rate shows a robust scaling $w \sim \bar{h}^{0.5}$ for 5 decades (as expected from the results in the literature [84, 86]), while the results for the variable rate saturates to $w \sim 20$ for $\bar{h} \sim 10^3$. We assume this saturation in the random deposition occurs due to the large amount of particles being delivered in each iteration for large t . In any case, that area should not appear in our current experiments which only cover the region $2 < \bar{h} < 30$ (shaded region).

The ballistic deposition model is one of the models following the Family-Vicsek dynamic scaling [84], by which $w \sim t^n$ for moderate t , and it saturates to $w \sim L^m$ as $t \rightarrow L^{m/n}$. In the ballistic deposition model *“particles rain down onto the substrate following straight-line trajectories in the columns in which they were dropped until they first encounter a particle in the deposit. This can be a particle at the top of the same column, or a particle in one of the nearest-neighbor columns. At this point the particle stops and becomes a permanent part of the deposit”* [86]. The simulations of Family and Vicsek [84] yielded the values $n = 0.3$, $m = 0.42$ and interestingly, our simulations with variable incoming particle yielded identical values. In Fig. 3.10b we show a continuous horizontal black line at $w = L^{0.42} = 35.77$, and vertical dashed black line at $\bar{h} = L^{0.42/0.3} = 150854$, which confirm the Family-Vicsek scaling for w vs. $\bar{h}$ even for nonconstant particle rate. The region of $\bar{h} < 1$ shows a different scaling, which is also nicely explained by Family in another paper [94]: *“Initially, before a single layer of particles has been deposited, the diffusion process is unimportant, because it does not change the random placing of the particles on the seed particles and consequently the surface*

Figure 3.10: The interface roughness w as a function of the mean height $\bar{h}$, obtained from 100 numerical simulations of the classical deposition models: (a) random or Poissonian deposition and (b) ballistic deposition. Both are 1D systems with size $L = 5000$. The vertical shaded area represents the region of $\bar{h}$ captured experimentally. In (a) simulations are performed for a constant particle rate ($N = t$, to validate the algorithm) and for increasing particle influx as in the experiments ($N = 0.1 \times t^{2.5}$). (b) The ballistic deposition model shows larger variability in the larger values of $\bar{h}$ which is represented by the shaded region around the main curve showing the standard deviation of the 100 simulations. Interestingly, despite the variable particle rate ($N = 0.1 \times t^{2.5}$), the roughness follows the same scaling found by Family and Vicsek [94].

width varies as the square root of h ". Despite being unimportant, we decide to plot it since our experimental range covers part of that initial square root behavior. Note that if any of our experiments would follow a ballistic deposition process, it would be difficult to

Figure 3.11: Alternative fitting procedure for the roughness of the monolayer contours w as a function of the mean height $\bar{h}$. Figure (a) shows 5 mM, (b) 10 mM and (c) 50 mM. Different markers indicate different experiments. Curves for the best fit of $w \sim \bar{h}^n$ are obtained directly over the raw data (no binning) for each salt concentration: $n(5 \text{ mM}) = 0.40 \pm 0.03$, $n(10 \text{ mM}) = 0.46 \pm 0.05$ and $n(50 \text{ mM}) = 0.41 \pm 0.04$.

measure it accurately since our experimental range covers part of the transition from a this initial square root process ($\bar{h} < 1$) to the presaturation regime for $\bar{h} < L^{m/n}$. Another interesting observation is that, by limiting the simulations to a maximum number of particles equal to the number found in the experiments, we find a final mean height $\bar{h}_F$ of $26 \mu\text{m}$ for the Poissonian case and $51 \mu\text{m}$ for the ballistic case, which are both of the same order of magnitude as obtained in the experiments for low initial salt concentration and high initial salt concentration, respectively.

3.5.3 Alternative data processing $w(t)$ vs. $\bar{h}$

The experimental data for the roughness has been obtained using five datasets per salt concentration, covering a decade in $\bar{h}$. Given the stochastic nature of the data, the strategy followed processing the data to test whether $w(\bar{h})$ follows a power-law is crucial. Here we show the results of a different fitting strategy as the one shown in the main text. Instead of binning the data and perform a linear regression to $\log w$ vs $\log \bar{h}$, we perform the linear regression directly to the *raw* data. The results are shown in Fig. 3.11 for the three different initial salt concentrations. The exponents obtained from the linear regression are $n(5 \text{ mM}) = 0.40 \pm 0.03$, $n(10 \text{ mM}) = 0.46 \pm 0.05$, $n(50 \text{ mM}) = 0.41 \pm 0.04$. The trend obtained by this fit seemed counter-intuitive to us: 5 mM and 50 mM yield almost identical roughness exponent values in spite of their clear different behavior. By making a linear regression without any filtering, it seems that the fit has taken too much weight from those rogue data points laying in the tails of the probability distribution. However, we decided not to apply any criterion for defining outliers that would be removed from the dataset. Instead, to remove any bias from our side, we choose to perform a logarithmic binning, followed by a weighted linear regression using the number of points per bin as weights. This strategy has resulted in more coherent values that have been shown in the main text.

3.5.4 Transport equation for incoming particles along the droplet surface

To obtain a more accurate prediction of the incoming particle rate, we model the particle distribution at the interface of the droplet by solving numerically a simplified interfacial transport equation for the particle concentration $C(s, t)$. The mechanism proposed is the simplest possible: particles are captured by the droplet surface as the contact angle decreases (source term $J(s, t)$) and advected along the surface due to the Marangoni flow at an unknown velocity $u(s, t)$ until they arrive at the monolayer, located at the contact line. This transport equation reads

$$\frac{\partial C}{\partial t} = J(s, t) - \nabla \cdot (uC) = J(s, t) - u \frac{\partial C}{\partial s} - C \frac{\partial u}{\partial s}. \quad (3.3)$$

Given the lack of experimental data or theoretical or numerical solutions on $u(s, t)$, we decide to use a constant value based on our own observations and comparable to those found by Marin *et al.* [9]. The amount of particles trapped by the droplet surface per unit time and area is represented by $J(s, t)$, which acts as a source term in this equation. Equation 3.3 is solved in 1D along the interface (for $0 \leq s \leq L(t)$) as the system is axisymmetric around the apex of the droplet. The assumptions which are made in order to solve this equation are (1) an initial homogeneous particle distribution in the bulk of the droplet, represented by the bulk concentration C_B . (2) The particles are captured at the surface

Figure 3.12: A schematic representation is given to show how the change in local volume is implemented into the numerical code. In this schematic the number of grid points is 20. The two spherical caps represent $t = 0$ s (blue) and t is 100s (green), with respectively $\theta = 70$ and 65 degrees. The grid points at $t = 100$ are equally spaced along the arc, and the corresponding points at the spherical cap of $t = 0$ are shown.

due to the surface area decrease during the evaporation while keeping a constant base radius. Under such conditions, $J(s, t)$ can be obtained directly using the model developed by Popov [7]: we solve the differential equation for $\theta(t)$ for our experimental conditions: $R_i = 1.3$ mm, $\theta_i = 70^\circ$ and $c_s = 2.08 \cdot 10^{-2}$ kg/m³ [6]. Solving this equation for θ using a forward Euler method, and combining these two assumptions we can write the change of particles captured at the interface as

$$\frac{dN_s}{dt} = -C_B \frac{dV}{dt}, \quad (3.4)$$

with $C_B = 1.5 \cdot 10^6$ (# number part/m³), using our initial particle concentration of 0.01 %w. To implement the spatial dependence of the influx of particles we discretize the system into smaller volumes. A schematic of this discretization is shown in Fig. 3.12. As locally the volume of the evaporated compartment changes along s , a different number of particles will be swept by the moving interface. We use Eq. 3.4 to convert this local volume loss into a number of particles. When we also take the area of the local segment into account, we can calculate the local particle flux $J(s)$ for each time step. The value of J increases for increasing s , which means it is the largest near the apex of the droplet. This is to be expected, since the apex is the only point in the droplet surface following a direct

downward motion (same direction as gravity) and consequently it has the highest downward velocity.

When we implement all geometrical equations to describe the spherical cap shape at every time step, combined with the fact that our numerical domain shrinks in time (L is a function of time, with $L(t_F) = R_i$), we can solve Eq. 3.3 and obtain the particle concentration $C(s, t)$. The boundary conditions which are used to solve this equation are $C(0, t) = 0$ and an outflux (Neumann) condition at $C(L, t)$. From the solution of the concentration field we can extract a number of particles which is located at the contact line, *i.e.* at the end of the domain ($s = L$). We also take into account that our experimental measurement section is only $25 \mu\text{m}$ wide by introducing a correction $\phi = 2\pi R_i / 25 \mu\text{m}$, in order to compare this numerical solution to the experimentally obtained values.

CHAPTER 4

DELAYED COALESCENCE OF SURFACTANT CONTAINING SESSILE DROPLETS

Published as: **Myrthe Adriana Bruning**, Maxime Costalonga, Stefan Karpitschka, and Jacco H. Snoeijer, *Delayed Coalescence of Surfactant Containing Sessile Droplets*, *Physical Review Fluids* **3**, 073605 (2018).

ABSTRACT

When two sessile drops of the same liquid touch, they merge into one drop, driven by capillarity. However, the coalescence can be delayed, or even completely stalled for a substantial period of time, when the two drops have different surface tensions, despite being perfectly miscible. A temporary state of non-coalescence arises, during which the drops move on their substrate, only connected by a thin neck between them. Existing literature covers pure liquids and mixtures with low surface activities. In this chapter, we focus on the case of large surface activities, using aqueous surfactant solutions with varying concentrations. It is shown that the coalescence behavior can be classified into three regimes that occur for different surface tensions and contact angles of the droplets at initial contact. However, not all phenomenology can be predicted from surface tension contrast or contact angles alone, but strongly depends on the surfactant concentrations as well. This reveals that the merging process is not solely governed by hydrodynamics and geometry, but also depends on the molecular physics of surface adsorption.

4.1 Introduction

The coalescence and interaction of sessile droplets has been the subject of intensive study in scientific literature [95–103], not least motivated by its relevance for industrial processes such as ink-jet printing or surface processing. These studies have revealed intriguing and frequently counterintuitive physics behind this ubiquitous process. When two droplets of the same liquid touch, a liquid bridge forms in between them. Capillary forces promote filling of this bridge and the droplets merge into a single liquid body. In contrast, sessile drops of two different but miscible liquids do not always merge instantaneously after contact [102–104]. Under certain conditions the height of the liquid bridge connecting the two droplets does not grow, but remains very thin as compared to the droplets. Connected by a thin liquid neck, the droplets move over the substrate without merging. The droplet with the lower surface tension chases the other droplet, and only significantly later, the drops will merge. From a free-energy perspective, this is very surprising, as the total free energy of the two miscible drops is certainly lowered by merging into a single droplet.

The mechanism behind this “delayed coalescence” has been identified as a competition between capillary and Marangoni flows [102, 103]. The difference in surface tension between the two drops causes a Marangoni flow which drains the liquid bridge between the drops. If this flow is strong enough, it compensates the capillary flows that fill this neck. It also causes a motion of the neck toward the droplet with the higher surface tension. Studies have addressed the coalescence behavior of drops of pure organic liquids on completely [103] and partially wetted substrates [104], and of aqueous solutions of liquids with low surface activity [101, 102, 105]. It was found that the coalescence behavior is determined by two key parameters, the surface tension contrast between the droplets, and their (mean) contact angles in the moment when they initially touch. Experiments on non-surface active, non-volatile liquids have revealed a single sharp boundary between the regimes of immediate coalescence and delayed coalescence, where delayed coalescence was observed for small contact angles and/or large surface tension differences. Other control parameters like the droplet volume did not show any significant influence on the coalescence behavior [101–105].

In this chapter we investigate the coalescence behavior of spreading drops of surfactant solutions. This is relevant e.g. in ink-jet printing processes: typical inks are highly complex formulations that almost always contain surfactants. Precisely controlling the coalescence of printed droplets is of key importance for the quality of the final print. It is well known that the physico-chemical behavior of surfactant solutions can be significantly different from “simple” mixtures of liquids with low surface activity. The surface tension of surfactant solutions is a highly nonlinear function of concentration, and the kinetics of ad-

sorption and desorption to interfaces play an important role for dynamical processes [106]. One pronounced feature of spreading surfactant solutions, which is of relevance here, is the frequently observed fingering instability of spreading fronts. This instability develops when drops of surfactant solutions are placed on thin films of water [107], or when they spread in a high humidity environment [108]. Instead of the regular spreading behavior with a smooth circular spreading front, fingers will grow out of the front, leading to irregular patterns and complex dynamics [106, 108–112]. Therefore, also a different coalescence behavior could be anticipated.

Here we present a systematic experimental study of the coalescence behavior of sessile drops of surfactant solutions, showing how the coalescence process is altered in the presence of surfactant induced Marangoni flows. We discover three distinct modes on non-coalescence and a dependence on surfactant concentration that cannot be described by the surface tension difference alone.

The chapter is organised in the following way. In section 4.2 we describe the experimental methods by which we studied the coalescence behavior of surfactant drops. In section 4.3.1 we report our observations of different coalescence regimes, section 4.3.2 focuses on the motion of the drops in the delayed coalescence state, and in section 4.3.3 we report on the duration of this state. In section 4.4 we discuss and conclude our results.

4.2 Experimental Methods

The principle of the experimental procedure is to simultaneously deposit two droplets of surfactant solutions of various concentrations at some initial distance onto a substrate (Fig. 4.1). The droplets spread over the substrate until they eventually touch. The (dynamic) solid-liquid-vapor contact angle in that moment can therefore be controlled by adjusting the initial distance between the drops. As liquids we used solutions of Sodium Dodecyl Sulfate solutions (SDS, Sigma Aldrich, purity 98% p.a., used as supplied) in MilliQ water (MilliPore Q-Pod, resistivity 18 M Ω cm) at various concentrations ranging from 0.1 c^* to 10 c^* , where $c^* = 8.1$ mM is the critical micellar concentration at which the surface tension of the solution saturates [113]. The surface tensions of the solutions are measured by the pendant drop method; analysis is performed with an open-source code [114]. Our experimental set-up is depicted on Fig. 4.1a. Two 5 μ L pendant droplets of SDS solutions with surface tensions γ_1 and γ_2 ($\gamma_1 < \gamma_2$) are created at tips of 0.9 mm-diameter needles using a volume-controlled syringe pump. The reproducibility of the volume of the deposited droplets was within 10%. To ensure a smooth deposition on the substrate, the substrate is lifted by a motorized stage to collect the droplets. This results in spreading droplets with base radius $R \sim 3$ mm, comparable to the capillary length (which decreases from 3 mm for pure water drops, to 2 mm for SDS-drops at $c = c^*$). As substrates we

Figure 4.1: (a) Cross-sectional sketch of the experimental set-up, defining the parameters θ_i and γ_i . (b) and (c) show typical images obtained from side and top view cameras, respectively. In both images the scale bar represents 3 mm. The left droplet is pure water, the right droplet contains SDS. Note that in the top view the needle visible in the image is no longer in contact with the droplets.

used standard glass microscope slides (Menzel-Gläser, 26 x 76 mm) which were cleaned by immersing them in piranha solution (hydrogen peroxide 30 % with sulfuric acid, volume fractions 1:3, respectively), rinsing, and sonicating them thoroughly with MilliQ water afterwards (10 minutes at 25 °C, Elmasonic P). This consistently yielded completely wetted surfaces on which the spreading of pure water droplets precisely followed Tanner's law. The spreading and coalescence behavior was monitored by simultaneously recording side and top view with digital cameras that were triggered synchronously at 150 frames/s with a pulse generator (BNC model 575). The contact angles were measured optically using the side-view recordings (PCO-1200s camera, Zeiss 60 mm macro lens) as shown in Fig. 4.1b. An example of top-view recordings (Ximea XiQM013MG-ON camera, Sigma 50 mm macro lens) is shown in Fig. 4.1c, featuring a typical case of delayed coalescence at $t = 0.2$ s after initial contact.

Controlling the ambient relative humidity, RH , is critical to our experiments. Depending on RH , fingering instabilities, similar to those reported e.g. by Marmur and Lelah [107], can arise during the spreading of our SDS solutions. Consequently, all experiments are performed in a closed chamber, where relative humidity is maintained at a constant value by a home built apparatus, using a feedback loop to control the RH . The RH is constantly monitored with a sensor inside the chamber. When the measured RH is lower than the

Figure 4.2: The spreading behavior for a single SDS droplet, depending on relative humidity and surfactant concentration (normalized with the critical micelle concentration c^*). Blue circles represent the stable circular spreading, see upper image (RH = 55% and $0.3 c^*$). Green diamonds depict the fingering case, shown in the bottom image (RH = 55% and $1 c^*$). Both images are taken 1.5 s after droplet deposition. The scale bar represents 5 mm. The dashed line between the regimes is intended as a guide to the eye.

target value, humid air (generated by bubbling through water in a gas wash bottle) is gently injected into the chamber. Conversely, dry nitrogen gas is injected to lower RH. In Fig. 4.2 we report our observations regarding the occurrence of fingering instabilities with respect to c and RH for the spreading of single SDS solution droplets on hydrophilic glass slides. Fingering was not observed at very low or very high surfactant concentrations. It appears for intermediate concentrations at humidities larger than 40%. The range of concentration for which fingering was observed increases with relative humidity, as has also been reported by Cachile and Cazabat in the case of non-ionic surfactants [112]. Frank and Garoff showed that for surfaces with a repulsive head-surface interaction, fingering of the surfactant solution may occur in a wide range of ambient humidities [115]. This effect depends strongly on the properties of the substrate surface, like charges, dipole moment, and polarizability. Thus we attribute the differences in observations to the different nature and treatment of the surfaces. For low ambient humidities RH = 30% and concentrations ranging from $0.1c^*$ to $5c^*$, we observe stable spreading that follows Tanner's law. Therefore, all coalescence experiments that we will present in the following were performed at RH = 30% in order to avoid this instability and initiate the coalescence process with well-defined drop geometries.

4.3 Results

4.3.1 Coalescence regimes

Figure 4.3: Coalescence behavior for a surfactant drop (droplet 1) and a pure water drop (droplet 2), $\gamma_2 > \gamma_1$. Three regimes are observed for different contact angles: (a) precursor-mediated interactions, (b) fingering regime and (c) stable delayed coalescence. $t = 0$ refers to the moment the droplets touch. In each series the upper drop consists of pure water and the bottom drop is the surfactant solution, in all cases $\Delta\gamma = 13 \text{ mN/m}$. The colors match the colors used in Fig. 4.4, In all series the scale bar represents 3 mm.

There are three main control parameters in our experiments which control the coalescence behavior. These are the mean contact angle at which the two droplets meet, $\bar{\theta} = (\theta_1 + \theta_2)/2$, their surface tension difference $\Delta\gamma = \gamma_2 - \gamma_1$, and the surfactant concentrations c_1 and c_2 . In all experiments that we performed, a state of delayed coalescence is observed, provided that the two drops are not from the same solution (*i.e.* $\Delta\gamma \neq 0$), even for the smallest tested $\Delta\gamma \sim 2 \text{ mN/m}$. In all cases with $\Delta\gamma \neq 0$, we observed three different modes of delayed coalescence. In contrast to previous observations with non-surface active miscible liquids [102–104], different behaviors could be observed depending on the surfactant concentrations, even with identical $\bar{\theta}$ and $\Delta\gamma$. Therefore we split the

coalescence experiments into two main groups: (i) experiments where only one droplet initially contained surfactant, while the other one was pure water, and (ii) those where both droplets were prepared from surfactant solutions.

We begin with a description of case (i), the coalescence behavior of an SDS containing droplet (drop 1) with a pure water droplet (drop 2), *i.e.* initially $c_2 = 0$ and $\gamma_2 = 72$ mN/m. Thus the surfactant concentration $c_1 < c^*$ of drop 1 and the surface tension difference between the drops are not independent, and we will representatively use $\Delta\gamma$ in the following. Depending on $\Delta\gamma$ and $\bar{\theta}$, three distinct regimes are observed. A time series of top view images for each regime is shown in Fig. 4.3. See Supplemental Material for a movie of each regime [116].

At low contact angles (Fig. 4.3a, $\bar{\theta} = 3^\circ$), the lower surface tension drop (drop 1, containing SDS) is attracted toward the higher surface tension drop (pure water, drop 2), while the water drop is pushed away from the SDS drop. However, an apparent gap separates the two drops, and the macroscopic liquid bodies remain separated. In this configuration, the droplets travel together on the substrate without coalescing. For volatile binary mixtures, interaction at a distance had previously been attributed to Marangoni flows induced by evaporation and condensation and are termed vapor-mediated interaction [101,117]. This could explain the response of the surfactant droplet because water vapor is enriched in the interstitial region. However, the response of the pure water droplet can not result from water evaporation or condensation alone. Water vapor does not affect the surface tension of pure water, and volumetric or thermal consequences of evaporation or condensation have a much weaker impact on the spreading of a one-component liquid [118] than what is observed here. On the other hand, SDS is essentially non-volatile. This suggests the importance of a wetting precursor in the transport phenomena between the two droplets. The presence of the precursor around the spreading surfactant is also described in [108, 115].

Increasing the mean contact angle $\bar{\theta}$ reduces and finally removes this gap between the droplets, so that they spread into macroscopic contact. Fig. 4.3b shows an experiment at $\bar{\theta} = 7^\circ$. A fingering instability occurs in the connecting region, which is reminiscent of the fingering instability observed when a droplet of surfactant solution is deposited onto a film of water [107, 109]. At the same time, the water drop is being propelled away from the SDS drop, frequently travelling distances that exceed the footprint size of the two droplets. It is interesting to note also that the dynamics of this regime is quite different from the previous case at lower $\bar{\theta}$: the water droplet moves ~ 100 times faster as compared to the precursor-/vapor-mediated interaction.

Finally, at even higher contact angles, the fingering instability disappears, and a smooth, stable, and moving neck separates the droplet, similar to delayed coalescence for non-

Figure 4.4: Phase diagram of the coalescence behavior of a water drop and a SDS-drop. Both the surface tension difference $\Delta\gamma$ and contact angle are varied. Blue squares: vapor-/precursor mediated interaction, light green diamonds: fingering instability, dark green triangles: stable delayed coalescence. The color regions are intended as a guide to the eye. The insets show zooms of the top view of the contact region between the two drops, with scale bars of 3 mm.

surface active liquids. Fig. 4.3c shows an experiment at $\bar{\theta} = 10^\circ$, in which the front between the two droplets remains smooth. The water droplet advances, set into motion by the Marangoni flow due to the lower surface tension of the SDS-droplet. At the same time, the SDS droplet flattens into a film. The overall process lasts for several tens of seconds.

We construct a phase diagram of these regimes in Fig. 4.4, by repeating the coalescence experiments for various $\Delta\gamma$ (adjusted by the SDS concentrations in droplet 1) and $\bar{\theta}$. It appears that vapor-/precursor-mediated interactions occur only for contact angles below 3° , regardless the surface tension difference between the droplets (blue squares). It occurs already at the lowest concentration $c_2 = 0.05$ mM we used, but was absent for two pure water droplets. At higher contact angles, there is no gap between the drops, but fingers appear, and the motion of the water droplet is much faster (light green diamonds). These changes clearly appear within a fraction of a degree of $\bar{\theta}$, rendering a sharp transition from vapor-/precursor-mediated interaction to the fingering regime. Increasing the contact angle further, fingering eventually disappears and a smooth front between the drops appears. The transition to this mode is not sharp: as $\bar{\theta}$ increases, fingers are first removed from the center of the connecting front, but still appear on its sides, until they gradually disappear completely. Dark green triangles indicate experiments for which no

Figure 4.5: Phase diagram of two coalescing droplets of different SDS concentrations, the same legend as Figure 4.4 applies for the regimes. Several concentration couples are used to obtain series at $\Delta\gamma = 10$ mN/m and 20 mN/m. From left to right we move to higher concentrations. The table specifies the concentrations, in terms of the critical micelle concentration c^* . The open symbols at 20 mN/m represent the water-SDS case from Figure 4.4, included for comparison.

fingering in the centre was visible any more. This transition depends on $\Delta\gamma$, and fingering occurs on a wider range of contact angles as $\Delta\gamma$ increases. This trend is consistent with previous observations for surfactant droplets spreading on water films. There, higher surface tension differences were required to observe the instability on thicker films [106]. In the present case, the contact angle adopts a role reminiscent of the film thickness.

Next we consider case (ii), the coalescence behavior of two droplets of surfactant solutions. Interestingly, if SDS is initially present also in the second droplet, the boundary between fingering and stable delayed coalescence is strongly altered, whereas vapor-/precursor-mediated chasing appears as before. Fig. 4.5 shows how this affects the phase diagram. We prepared droplet pairs with two values of $\Delta\gamma = 10, 20$ mN/m, using several different surfactant concentrations to realize each $\Delta\gamma$. The corresponding results for case (i) and $\Delta\gamma = 20$ mN/m are indicated in this figure as well for comparison.

From Fig. 4.5 it is clearly visible that the surfactant concentration has a strong impact on the coalescence behavior, even at identical $\Delta\gamma$. A slight amount of surfactant in the previously pure water droplet reduces the range of the fingering instability with respect to $\bar{\theta}$. For $\Delta\gamma = 10$ mN/m, it is even possible to completely avoid the fingering destabilisation, in contrast to case (i) where it was always observed except for $\Delta\gamma = 2$ mN/m. However,

increasing the mean surfactant concentration further, expands the range of the fingering instability. Also, increasing c beyond c^* for one droplet (series (c) and (d) at $\Delta\gamma = 10$ mN/m in Fig. 4.5), yet keeping the same c in the other droplet, expands the fingering regime. These effects show that, for surfactant solutions, the physics on a molecular scale have a direct influence on the macroscopic hydrodynamics of the coalescence process.

4.3.2 Front velocity

Next we focus on the characteristics of the motion of the neck between droplets during stable delayed coalescence (dark green region in Fig. 4.4). As the two droplets meet, the higher surface tension droplet (droplet 2) “pulls” on the lower surface tension drop (droplet 1), with a clearly distinguishable front (the “neck”) separating them. After the neck has formed, it travels with a certain velocity v_F (see Fig. 4.3a). This velocity is not constant over time. It reaches its maximum value almost instantaneously (below the temporal resolution of our imaging system) after initial contact and continuously decays thereafter. In the following we focus here on the initial (maximum) velocities.

We non-dimensionalize v_F with the capillary velocity and obtain the capillary number $Ca = \eta v_F / \bar{\gamma}$, with $\bar{\gamma} = (\gamma_1 + \gamma_2)/2$. Fig. 4.6a shows that Ca initially increases with $\Delta\gamma$, but saturates at $\Delta\gamma/\gamma_1 \sim 0.2$, for all mean contact angles $\bar{\theta}$ we explored ($4^\circ \leq \bar{\theta} \leq 16^\circ$). This is consistent with previous observations on non-surface active liquids [102], although in the SDS case, higher $\Delta\gamma$ are required for velocity saturation. Also consistent with [102], experiments with pure water vs. SDS solution (case (i), open symbols on Fig. 4.6a), and those with two surfactant-containing droplets (case (ii), filled symbols on Fig. 4.6a) yield identical v_F , provided that the surface tension difference remains the same. This indicates that the initial front velocity is determined only by $\bar{\theta}$ and $\Delta\gamma$, and not by the molecular interactions of the surfactant molecules.

In Fig. 4.6b we plot the saturated values of Ca as a function of $\bar{\theta}$. In this regime, all data, irrespective of $\Delta\gamma$ and c , collapses onto a single master curve. This is similar to the case of miscible liquids of low surface activities reported previously [102] and suggests that the driving mechanism for the motion of the neck is the Marangoni flow. However, the values of Ca for the case of surfactant solutions studied here differs from those of previously reported experiments on simple non-polar liquids [103]. The experimental results for various combinations of room-temperature liquid alkanes (see [103] for a detailed description of these experiments) are included here as well.

Both datasets show a saturation of Ca with respect to $\Delta\gamma$, but the saturated values of Ca are significantly different. For small $\bar{\theta}$, the front between droplets of different alkanes moves by about an order of magnitude slower than for aqueous SDS solutions. Also the trend of Ca with respect to $\bar{\theta}$ is different for both cases: aqueous surfactant solutions are

Figure 4.6: The capillary number of the front of the moving drop (droplet 2) versus reduced surface tension difference $\Delta\gamma/\gamma_1$ ($\gamma_1 < \gamma_2$) and contact angle, for the delayed coalescence regime. (a) The open symbols represent the coalescence of a water and SDS-droplet, closed symbols represent two SDS-droplets. The colorbar shows the contact angle in degrees and the dotted lines serve as a guide for the eye to see the trend for Ca for $\theta = 6, 10$ and 14° . In (b) the black series are water-SDS and the blue series are the SDS-SDS case, including the best fit as a green line. The second part of the legend shows the results for delayed coalescence of different alkane pairs from [103], inserted for comparison.

best fitted by $Ca \sim \bar{\theta}^{1.6}$, the alkane data by $Ca \sim \bar{\theta}^{2.4}$. The main difference between both cases are the relevant transport phenomena: in the case of surfactants, surface advection and diffusion presumably becomes important in addition to bulk advection and diffusion. Also, changes in surface tension depend on the ad- and desorption kinetics of the surfactant molecules, which are much slower as compared to the almost instantaneous equilibrium of alkane mixtures. Last but not least, electrostatic interactions could play an important role for an ionic surfactant like SDS. Either of these effects could have an impact on the height profile and the local composition of the liquids, and thus also on the front velocities.

4.3.3 Duration of delayed coalescence state

In the previous section we have shown that the initial neck velocities during delayed coalescence depend only on $\Delta\gamma$ and $\bar{\theta}$, but show no explicit dependence on the concentrations. However, the dynamics at later times differ dramatically. Fig. 4.7 shows a direct comparison between two experiments with nearly identical $\Delta\gamma$ and $\bar{\theta}$, but with different SDS concentrations. The case of pure water against SDS ($c_1 = 0.3 c^*$) is shown in Fig. 4.7a, while in Fig. 4.7b, both droplets contain SDS ($c_1 = 0.6 c^*$ and $c_2 = 0.3 c^*$). While the initial front velocities are comparable for both cases, the lifetime of the delayed coalescence is significantly different. In case (a), pure water against SDS solution, the motion of the neck and water drop away from the SDS drop is sustained for a long time. The SDS drop flattens into a film, covering the trace of the water droplet. The neck typically remains stable until the SDS droplet has drained completely, which may take up to the order of a minute. The water droplet may travel distances that are an order of magnitude larger than the initial droplet radius. Duration and distance increase with the initial $\Delta\gamma$. In case (b) however, with two SDS droplets, the duration of delayed coalescence is much shorter, even though $\Delta\gamma$ and the initial neck velocities are the same as in case (a). At $t \sim 0.1 - 0.3$ s, the neck motion has stopped and even starts to recede. Then the neck gradually disappears and the drops merge, visible by the decaying contrast between the two drops. In the Supplemental Material we provide the corresponding movies from Fig. 4.7 [116].

To rationalize the difference in the duration of the delayed coalescence state in the two cases, we consider the surfactant coverage of the front (downstream) droplet, which has the higher surface tension (droplet 2), see Fig. 4.8. The advection onto an initially surfactant-free surface is maintained for a long time. The surfactant that is advected from droplet 1 has an empty surface to cover and an empty bulk liquid to desorb into. This process is schematically depicted in Fig. 4.8a. In the case of coalescence between two SDS containing droplets, both surfaces are initially covered by surfactant in equilibrium with the re-

Figure 4.7: Image sequences for two experiments with approximately the same surface tension difference: (a) shows the coalescence of a pure water droplet with an SDS solution droplet ($0.3 c^*$), with $\Delta\gamma = 13 \text{ mN/m}$, whereas (b) shows the coalescence between two SDS solutions droplets (droplet 1: $0.6 c^*$ and droplet 2: $0.3 c^*$), with $\Delta\gamma = 10 \text{ mN/m}$. In both cases (a) and (b), $\bar{\theta} = 8^\circ$. The time at which the images are taken are labeled below (the same for a and b). The black dashed line indicates the position of the front separating the two droplets, at $t = 0.25 \text{ s}$. In case b) the front does not move any more after $t \sim 0.1 - 0.3 \text{ s}$. The scale bars represent 5 mm .

spective bulk concentration (see Fig. 4.8b). Even though the bulk concentration of droplet 2 is rather low in our experiments (at lowest $0.1 c^*$), the surface coverage is already $2/3$ in terms of its saturation value [119]. We propose that in the case of two SDS droplets, Marangoni convection will rapidly compress the downstream surface and lower its surface tension until coverage reaches saturation. This could be described as a traffic jam-like situation on the surface of droplet 2, since surfactant desorption occurs on much slower timescales [120]. Similarly, the upstream surface expands and its surface tension dynamically increases as long as adsorption is comparably slow.

As a consequence, the surface tension contrast would decrease rapidly, and the associated Marangoni flow ceases and the drops merge. A corroboration of this hypothesis would require an independent measurement of the desorption kinetics of SDS where surface and bulk are far from equilibrium. While substantial literature exists on adsorption kinetics [120, 121], desorption rates of SDS have not been directly measured. The only available data were inferred indirectly by fitting kinetic models to adsorption measurements close to equilibrium. These timescales lie beyond tens of seconds [120], but the correct values for our case might differ to some extent. Nonetheless, with the proposed mechanism of

Figure 4.8: Mechanism of lifetime difference between case (a) and (b) explained. Figures (a) and (b) show the difference in surfactant coverage. Figure (b) shows the accumulation of surfactants at the surface of droplet 2 in a schematic way. In all images the size of the surfactant molecules is exaggerated as well as the number of surfactants at the interface as compared to the bulk.

advective surface compression, we can robustly estimate the time required to reach saturation, by comparing the typically observed surface velocities to the droplet diameter. With a front velocity $v_F \sim 50$ mm/s and a droplet footprint radius $R \approx 5$ mm, this gives $\tau = R/v_F = 0.1$ s. Since advection and desorption timescales differ by orders of magnitude, this suggests that the surface reacts mostly elastically. The advective timescale also agrees well with the experimental observation in Fig. 4.7, where we noted that τ must be 0.1 - 0.2 s. Furthermore, we also observed a decrease of τ with contact angle in our experiments. This matches the fact that the front velocity increases with contact angle which would lead to a faster saturation of the surface coverage.

4.4 Discussion & Conclusion

This experimental study shows that the coalescence of sessile surfactant droplets exhibits a rich phenomenology. Depending on the mean contact angle of the drops and their surface tension difference, we observed 3 different regimes of delayed coalescence: precursor-mediated interaction for droplets with small contact angles, a fingering regime for intermediate contact angles and a strong surface tension contrast between the droplets, and stable delayed coalescence for larger contact angles and weaker surface tension contrast. We also show that the concentration of surfactant alters the lifetime of delayed coalescence.

For small dynamical contact angles, we observed a regime where the droplets interact at a distance, without a visible, macroscopic contact of their liquid bodies. Importantly, this interaction is bi-directional: not only is the SDS-containing droplet attracted toward the water droplet, but also the pure water droplet is repelled by the SDS containing droplet. This excludes a pure vapor mediated process [101] since SDS is virtually non-volatile. Most likely, SDS transport is precursor mediated. Accordingly, the macroscopic response of the second contact line offers a novel way to probe the properties of ultra-thin wetting precursors.

We have also investigated the dynamics of a moving neck in the situation of stable direct drop-drop contact. The velocity of the moving neck saturates at $\Delta\gamma/\gamma_1 \sim 0.2$, and does not depend on surfactant concentration. This saturation was also observed in delayed coalescence of miscible liquids with low surface activity [102]. However, for the duration of this delayed coalescence state, the concentration of surfactant in the two drops plays an important role. The movement of the neck stops much faster and coalescence proceeds, if both drops initially contain surfactant, as compared to the case where one drop initially consists of pure water. We propose that this direct influence of concentration is due to the advective accumulation of surfactant caused by the Marangoni flow, since the timescale of desorption is much slower than the timescale of advection, and the surface reacts mostly elastically to its compression or expansion. The accumulation reduces the surface tension differences between the two drops, the associated Marangoni flow decreases, and the movement stops. The timescale of advective accumulation until saturation can be estimated and matches well with the experimentally observed lifetime.

We limited this study to equally sized droplets (within experimental accuracy), therefore capillary pressures in the main droplet bodies are considered identical. Previous experiments on liquids with low surface activities have shown that the phenomenology does not change if the drop sizes are different [105]. Different drop sizes would cause different capillary pressures in the main droplet bodies, which would drive an additional capillary flow. However, this difference in capillary pressure remains small as compared to the large negative capillary pressure in the neck region, due to the strongly curved interface there. Whether this is also the case for the more complicated surfactant case remains open.

In this chapter we presented an overview of the basic phenomenology observed in coalescence of sessile surfactant droplets which opens up many possible directions for future investigations. The multi-scale nature and the coupling between bulk and surface terms render it an interesting problem for numerical modelling, to see, for instance, whether a

velocity saturation or a coverage saturation would be observed with a minimal model like lubrication theory. Clearly, future experimental work should involve different types of surfactants, exploring the influence of charge and steric interactions, and tuning adsorption and desorption timescales. Also the wetting behavior depends on surface and surfactant properties [115], so different combinations should be tested in the future. Importantly, dynamic surface-compression or subphase-exchange experiments could provide directly measured calibrations of adsorption kinetics.

In conclusion, in this chapter we have shown how surface active molecules not only alter surface tension, they also change the relevant physical processes at the interface, giving molecular processes an important and directly measurable influence on macroscopic dynamics. There is a coupling between hydrodynamics and physico-chemical processes, such as adsorption/desorption kinetics or electrostatic interactions that give rise to a complicated surface rheology; surface tension depends on the dynamical expansion or contraction of the local surface area, and hydrodynamic boundary conditions can no longer be described by simple linear constitutive equations.

CHAPTER 5

PERSPECTIVE

ABSTRACT

In this thesis we have studied the evaporation of confined (chapters 1 & 2) and colloidal droplets (chapters 2 & 3). The confinement is introduced by fully encapsulating the droplet with an elastic medium. Furthermore we have showed the importance of additives like salt (chapter 3) and surfactants (chapter 4), on respectively the particle assembly or coalescence behaviour. This research was done in the light of the *NanoPacks*-project, in which we aim to use evaporating droplets as a system to prepare samples for ultrasensitive detection techniques such as Surface Enhanced Raman Spectroscopy (SERS). In this perspective chapter, we pose various questions that originate from our results. Furthermore we elaborate on the applicability of the investigated systems as possible pathways for SERS sample preparation.

5.1 Create motion using drops inside gel

In chapter 1 we study the evaporation of a droplet inside an elastic medium. We propose that this system could serve as a new approach for motile synthetic materials. Therefore, a preliminary study to transform the evaporation of a droplet inside an elastic medium into motion has been performed. A 3D-printed supporting backbone is designed, onto which several chambers are created in which droplets are injected. This backbone is 4.5 cm long, 0.5 cm in depth and 0.5 cm in height. The thickness of the printed surfaces is 0.5 mm. The chambers in this supporting structure are filled with almost fully cured PDMS. The entire system is then heated at 70° for the duration of the experiment. Images of such a system are shown in Fig. 5.1. Initially all droplets shrink simultaneously. During this evaporation phase the (initial straight) bone deforms and obtains a curled shape. When one of the droplets cavitates (Figs. 5.1b and c), there is a small but visible relaxation from the structure of the bone. This deformation is highlighted in Fig. 5.1d. A microliter droplet is able to move a centimetre sized object. This means that in principle it is possible to use the coupling between evaporation and elasticity as a method to move a larger system. However, the moment at which cavitation occurs in each chamber is completely independent from other cavitation events. Therefore the resulting relaxation per cavitation event is small. To study this coupling of cavitation events in a more basic system, two droplets are injected very close to each other in the same box of PDMS, see Fig. 5.2. The distance between these droplets is only one droplet diameter. But also in this situation, the cavitation of one droplet does not trigger the cavitation of the other. Hence it is worth taking a closer look at the properties of the elastic medium. PDMS has a very high stiffness and viscosity. The high shear modulus of PDMS, $\mu = \mathcal{O}(1)$ MPa, results in a high elastic tension in the gel, when the droplet shrinks. The high viscosity prevents triggering subsequent cavitation events. Using less viscous gels would enable a domino-effect between the different droplets, and one cavitation event could trigger others. This would result in a violent and quick release of all the build-up energy, like in the Fern Sporangium [24]. In order to increase the movement of the structure, not only the properties of the gel need to be taken into account. Also the design of the bone itself, its dimensions and material, need to be optimised. For example, the supply of heat to fasten the evaporation should not deform the structure of the bone as well.

One solution to decrease the waiting time for cavitation, would be to use colloidal droplets instead. Using colloidal droplets inside an elastic medium, decreases the deformation needed to induce cavitation. As we show in chapter 2, the addition of particles to a droplet, makes the droplet more vulnerable for cavitation. This cavitation event can take place even before the creasing instability occurs.

Figure 5.1: Reconstructing a moving bone using droplets inside an elastic medium. Figure (a) shows the initial nearly flat structure of the bone, in which all droplets still need to cavitate. The bone is 4.5 cm long and 0.5 cm in depth. Figures (b) and (c) are taken directly afterwards each other ($\Delta t = 2$ min). The blue circle in (b) highlights the droplet that has cavitated in figure (c). Figure (d) overlays the contour of the three images, in order to visualize the deformation of the bone resulting from the single cavitation event; it partly relaxes. Grey is the initial shape of the structure, light blue is the contour of figure (b), and green represents figure (c). The arrow indicates the movement of the structure after a cavitation event. The system is heated at 70° throughout the entire experiment.

Figure 5.2: The evaporation of two water droplets in close proximity inside PDMS. The system is heated at 70° and kept at RH = 30 %. The initial droplet radii are $R_0 \sim 330 \mu\text{m}$. The scale bar represents $500 \mu\text{m}$.

5.2 Acoustic metamaterials

Ultrasound imaging is widely used as a medical imaging technique. The advantages of using ultrasound as a tool for imaging are amongst others the fact that it is a less invasive and more energy-efficient diagnostic tool. In this technique low-energy acoustic waves are used, which ensures a relatively safe diagnostic procedure. However, at the same time these low-energy waves introduce difficulties for penetrating thick layers of (human) tissue. One solution is to use lower frequencies in order to increase the penetration depth, but this is at the expense of the obtained resolution of the image. Another challenge in ultrasound imaging is caused by the presence of bones or metal pieces, as they distort or completely block the acoustic signal.

In order to deal with these challenges, the shape of the acoustic wave needs to be controlled. This can be done using acoustic metamaterials: materials that are specially designed artificial materials [122]. Acoustic metamaterials can be designed to focus acoustic waves to increase their penetrability or to allow waves through obstacles [123, 124]. The existing metamaterials based in soft matter (liquid, colloids, gels, etc.) are most promising as they are versatile and can achieve a large amount of properties in a wide frequency range [65]. Assembling these soft metamaterials (based on droplets, bubbles or particles) with high precision is a challenge. So far mixtures are used, which results in limited control on the final properties of the material. Especially the microscopic size of the components forming the material, which is required for manipulation of ultrasound waves, creates a limitation.

Figure 5.3: The evaporation of a pure water droplet encapsulated inside a very soft elastic medium (CY52-276). The system is heated at 60° and kept at $\text{RH} = 30\%$. The initial droplet radius is $R_0 = 195\ \mu\text{m}$. The scale bar represents $200\ \mu\text{m}$.

In chapter 1 we show how we can turn a droplet into a bubble, when it evaporates in an elastic medium. This control of the resulting bubble size and position is a promising tool for the fabrication of acoustic metamaterials. These bubbles trapped inside gel behave as sound scatterers on a microscopic level, with a well-defined resonant frequency. In an infinite (non-elastic) medium, this frequency is the so-called Minnaert resonance frequency. For a typical ultrasound frequency of $1\ \text{MHz}$, bubbles of $d = 5\ \mu\text{m}$ are required. However, if one uses bubbles trapped in an elastic medium, the visco-elastic properties of this medium are crucial for the frequency range that can be achieved. Equation 1.2 in chapter 1 shows the interplay between the stiffness and viscosity of the gel. For small bubbles the viscosity becomes dominant, and can even fully suppress the bubbles oscillations. The maximum frequency which can be obtained for bubbles trapped inside PDMS is $\sim 40\ \text{kHz}$ (see Fig. 1.4 in chapter 1), which is the in the lower limit for use in ultrasound imaging. Therefore, gels need to be selected in which the stiffness is still large, but the damping is minimised (*i.e.* low viscosity).

If such gels are found, the next step would be to evaporate small droplets inside gel, in order to create these small bubbles and achieve high frequencies. This poses some practical challenges. Using heat-curing gels is not trivial, as the time it takes to cure the gel is significantly larger than the lifetime of such a small droplet. Solutions could entail the use of UV-curing gels, which ensures a fully cured gel before the droplet has evaporated completely.

Using droplets inside an elastic medium is a versatile tool which has the potential to create acoustic metamaterials with a broad range of acoustic properties. Tuning the properties of the gel, determines whether cavitation occurs and a bubble is created. Also particles could be added to the system, which will introduce a solid phase into the elastic medium. The final material which contains either droplets, bubbles or particles, would allow for improvement of the acoustic imaging by ultradamping or superlensing [65, 125].

Figure 5.4: The evaporation of a colloidal droplet in a very soft elastic medium (CY52-276). Polystyrene particles with $d_p = 0.52 \mu\text{m}$ and $c_p = 0.005 \text{ v-\%}$ are suspended in water. The system is heated at 80° and kept at $\text{RH} = 30 \%$. The initial droplet radius is $R_0 = 120 \mu\text{m}$. The scale bar represents $100 \mu\text{m}$.

5.3 Clustering particles inside an elastic medium

Let us return to the original application of clustering particles and analyte inside an elastic medium: to serve as an easy way of sample preparation for Surface Enhanced Raman Spectroscopy. For clustering particles inside an elastic medium, the cavitation event is an unwanted phenomena as it prevents the particles and analyte to come close to each other. Therefore we explored the possibility of using softer gels, in order to reduce the build up of elastic tension. Evaporation experiments have been performed using CY 52-276, with $\mu = \mathcal{O}(1) \text{ kPa}$, which makes this gel 1000 times less stiff as compared to PDMS. Indeed, if we evaporate a pure water droplet inside this soft gel, we do not observe a cavitation event (Fig. 5.3). In this system the droplet also evaporates initially isotropically, until the creasing instability. After this creasing occurred, the droplet lost its sphericity but keeps decreasing in size until it is fully evaporated. After the droplet disappeared, only a small deformation in the gel remains visible, along the axis of the first and major crease. In the soft gel, the elastic tension should still increase as the droplet approaches $R/R_0 \rightarrow 0$, but adhesion of the gel onto itself as a result of creasing might prevent cavitation to happen. Therefore using softer gels to evaporate colloidal droplets, could potentially lead to clustering of the particles, as cavitation is prevented. However, as we see in Fig. 5.4, the creasing instability itself also prevents the particles to cluster. As this gel is relatively soft and sticky, particles are expelled from the droplet and remain in the gel. Even though cavitation is suppressed, now creasing hinders particle clustering.

Concluding, in order to cluster particles from an evaporating colloidal droplet inside an elastic medium, the properties of the surrounding gel are crucial. One must be able to prevent cavitation, as well as influence the crease formation. We need to be able to decouple the evaporation of the droplet and the curing of the gel. One possible solution is

to cure the gel only after the droplet has evaporated. As heat-curing gels also (slowly) cure at room temperature, a solution could be to use UV-curing gels. In that case the sample can be heated to promote fast evaporation of the droplet, without accelerating the curing of the elastic medium. In this situation the colloidal droplet evaporates in a viscous but non-elastic medium, and no elastic stresses will build up during its shrinking. Therefore no creasing and cavitation will occur, and the particles will have the opportunity to cluster. Afterwards the surrounding medium can be cured, in order to serve as a protection for the cluster with analyte inside.

5.4 SERS templates using salty evaporating droplets

Another potential system that is explored for sample preparation for SERS, is the addition of salt to an evaporating sessile droplet. As a result of introducing salt to such a system, particles do no longer arrange themselves into a thick ring along the contact line, but form a monolayer along the interface of the droplet. Details of this monolayer formation can be found in chapter 3. The final deposit of the particles is therefore much more spread out and seems a promising way to enhance the applicability of evaporating sessile droplets for SERS. If one would add gold nanoparticles and the analyte to an evaporating salty droplet containing micron-sized polystyrene particles, a nanostructured landscape of the gold particles will be deposited on the substrate. The polystyrene particles serve as a template onto which the nanoparticles and analyte are embedded.

Experiments are performed in which a microliter-sized salty colloidal droplet is evaporated, containing both micron-sized polystyrene particles and gold nanoparticles. Using Scanning Electron Microscopy allows us to locate the position of the nanoparticles within this deposit, see Fig. 5.5. Clearly, the nanoparticles are nicely embedded into the deposit of the polystyrene particles. This is mostly visible in Figs. 5.5c and d in which the same location is imaged twice, using different signals to highlight either the position of the polystyrene particles or the golden nanoparticles. The nanoparticles are nicely spread around the polystyrene particles and have embedded themselves into the template formed by the micron-sized particles. This is a promising observation for the applicability for SERS.

Figure 5.5: The final particle deposit of a salty sessile droplet (10 mM NaCl) containing both micronsized polystyrene particles ($d_p = 1 \mu\text{m}$ and $c_p = 0.1 \text{ v-\%}$) and gold nanoparticles ($d_p = 20 \mu\text{m}$ and $c_p = 0.025 \text{ v-\%}$). The initial droplet volume is $2 \mu\text{L}$. Figure (a) shows a microscope image from the final particle deposit (scale bar is 1 mm). Figures (b)-(d) are obtained using Scanning Electron Microscopy (SEM). Figure (b) is a zoom of the deposit near the contact line region (scale bar is $50 \mu\text{m}$). Figures (c) and (d) capture the same region but either highlight the position of the polystyrene particles or the gold nanoparticles. In both images the scale bar represents $2 \mu\text{m}$. Image courtesy Mark Smithers from the MESA+ Nanolab.

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Summary

In this thesis the evaporation of confined and colloidal droplets has been examined in different configurations and systems. The confinement is achieved by fully immersing the droplet in an elastic medium. When the droplet evaporates, it also deforms the surrounding elastic gel. As the droplet decreases in size during evaporation, the tension in the gel increases. Therefore the gel tries to release its tension by folding onto itself, the so-called creasing instability. However, as the droplet keeps shrinking, the pressure inside the liquid keeps decreasing until cavitation occurs inside the droplet. A bubble nucleates and grows up to nearly the same size as the initial droplet. In chapter 1 we investigated the evaporation and cavitation dynamics in large detail for pure water drops. The frequency of the oscillating cavitation bubble could be related to the visco-elastic properties of the surrounding elastic medium. Insights in this conversion of enthalpy (evaporation) into mechanical energy (sudden release of the build up elastic tension), could open new ways of designing motile synthetic materials.

When in such a confined system, colloidal droplets are evaporated instead of pure water droplets, the creasing instability can be fully suppressed. In chapter 2 we show that in the presence of particles, cavitation events occur often before any creasing develops. The chances for an early cavitation event to occur increase with particle concentration. The length scale of the particle is of great influence for this early onset of cavitation. When salt is added to such a colloidal droplet, particles tend to cluster and thereby cavitation occurs even earlier, proving that an increased the length scale of the particle is important for this phenomenon to occur. This system of introducing a colloidal droplet into an elastic medium serves as a simple and reliable method to measure the tensile strength of particle solutions.

Salt cannot only be used to influence the interaction between particles, but also serves as an *anti-surfactant* as it increases the surface tension of water. When a (pinned) salty sessile droplet evaporates, the salt content near the contact line increases. As a result a Marangoni flow arises which is directed from the apex of the droplet towards the contact line. When particles are added to such a system, their assembly during evaporation is completely different as compared to a colloidal droplet without any salt. In the latter case, particles arrive at the contact line via the bulk of the droplet and form a three dimensional packing near the contact line. In the case of a salty droplet, particles follow the surface flow and arrive at the contact line via the droplet's interface. In chapter 3 we show that, as a result, particles arrange themselves into a monolayer at the liquid-air interface. Confocal microscopy allows us to observe the particle-per-particle formation and structure of this monolayer. By changing the salt concentration inside the droplet, we can alter the structure of the monolayer. Low initial salt concentrations (5 and 10 mM NaCl), result in well-ordered and highly packed particle arrays. For higher salt concentrations (50 mM), loosely packed and heterogeneous particle monolayers are observed. The formation of this monolayer also alters the final particle deposit. High salt concentrations and large particle numbers lead to monolayers which easily cover the whole droplet surface. After the droplet has completely evaporated, this leads to an homogeneously distributed final particle deposition.

Finally, not only the addition of salt introduces surface flows, also the presence of surfactants can induces these Marangoni flows. In chapter 4 we show that if two sessile surfactant droplets meet, they do not immediately coalesce. Instead, they remain in a temporary state of non-coalescence. The coalescence behaviour can be classified into three regimes that occur for different surface tension differences and initial contact angle of the droplets. However, the surface tensions difference is not the determining factor alone, also the actual surfactant concentration matters. This reveals that the merging process is not solely governed by hydrodynamics and geometry, but also depends on the molecular physics of surface adsorption.

Samenvatting

In dit proefschrift is de verdamping van begrensde en colloïdale druppels in verschillende configuraties en systemen onderzocht. De druppel wordt begrensd door de druppel volledig te omringen met een elastisch medium. Wanneer de druppel verdampt, vervormt deze ook de omringende gel. Naarmate de druppel tijdens de verdamping kleiner wordt, neemt de spanning in de gel toe. Daarom probeert de gel de opgebouwde spanning te verminderen door op zichzelf te vouwen, de zogenaamde vouwinstabiliteit (*creasing*). Na dit vouwen blijft de druppel kleiner worden, en neemt de druk in de vloeistof steeds verder af, totdat cavitatie optreedt. Er vormt zich een bubbel die uitgroeit tot bijna dezelfde grootte als de oorspronkelijke druppel. In hoofdstuk 1 hebben we in detail de verdampings- en cavitatiedynamiek onderzocht voor pure waterdruppels. De frequentie van de oscillerende cavitatiebel houdt verband met de visco-elastische eigenschappen van het omringende medium. Inzichten in deze omzetting van enthalpie (verdamping) in mechanische energie (het plotseling loslaten van de opgebouwde elastische spanning), zorgen voor nieuwe manieren om beweeglijke synthetische materialen te ontwerpen.

Wanneer in een dergelijk systeem colloïdale druppels worden verdampt in plaats van pure waterdruppels, kan *creasing* volledig worden onderdrukt. In hoofdstuk 2 laten we zien dat in de aanwezigheid van deeltjes, cavitatie vaak al optreedt voordat er vouwen ontstaan. De kans op zo'n vroege cavitatie neemt toe met de concentratie deeltjes. Ook de lengteschaal van het deeltje is van grote invloed. Wanneer zout aan zo'n colloïdale druppel wordt toegevoegd, zullen deeltjes clusteren en daardoor treedt cavitatie zelfs nog eerder op. Dit bewijst dat het vergroten van de lengteschaal van het deeltje belangrijk is om dit fenomeen te laten optreden. Dit systeem van het introduceren van een colloïdale druppel in een elastisch medium, dient als een eenvoudige en betrouwbare methode om de treksterkte van zulke oplossingen te meten.

Zout kan niet alleen worden gebruikt om de interactie tussen deeltjes te beïnvloeden, maar dient ook als een *anti-surfactant* omdat het de oppervlaktespanning van water verhoogt. Wanneer een zoute druppel verdampt op een substraat, met een vaststaande contactlijn, neemt het zoutgehalte dichtbij de contactlijn toe. Hierdoor ontstaat er een Marangonistroom vanaf de top van de druppel naar de contactlijn. Wanneer deeltjes aan zo'n systeem worden toegevoegd, is de manier waarop zij elkaar ontmoeten tijdens de verdamping compleet anders dan bij een colloïdale druppel zonder zout. In het laatste geval komen deeltjes via de bulk van de druppel bij de contactlijn aan en vormen daar een driedimensionale pakking. In het geval van een zoute druppel volgen de deeltjes de oppervlaktestroom en komen ze via het oppervlak van de druppel bij de contactlijn aan. In hoofdstuk 3 laten we zien dat als gevolg daarvan deeltjes een monolaag aan het vloeistof-lucht grensvlak vormen. Met confocale microscopie kunnen we de vorming en de structuur van deze monolaag deeltje per deeltje observeren. Door de zoutconcentratie in de druppel te veranderen, kunnen we de structuur van de monolaag veranderen. Lage initiële zoutconcentraties (5 en 10 mM NaCl) resulteren in goed geordende en dicht op elkaar gepakte verzameling deeltjes. Voor hogere zoutconcentraties (50 mM) zien we dat de deeltjes een losser gepakte en meer heterogene monolaag vormen. De vorming van deze monolaag verandert ook de uiteindelijke deeltjesafzetting. Hoge zoutconcentraties en grote aantallen deeltjes leiden tot monolagen die gemakkelijk het hele druppeloppervlak bedekken. Nadat de druppel volledig is verdampt, leidt dit uiteindelijk tot een homogeen verdeelde verdeling van deeltjes op het substraat.

Ten slotte veroorzaakt niet alleen de toevoeging van zout oppervlaktestromen in een druppel, ook de aanwezigheid van oppervlakte actieve stoffen (*surfactants*) leiden tot Marangonistromen. In hoofdstuk 4 laten we zien dat als twee druppels met oppervlakte-actieve stoffen elkaar ontmoeten, ze niet onmiddellijk samenvloeien. In plaats daarvan blijven ze in een tijdelijke staat van niet-coalescentie. Het coalescentie-gedrag kan worden ingedeeld in drie regimes die optreden afhankelijk van de verschillen in oppervlaktespanning en de initiële contacthoek van de druppels. Het verschil tussen de oppervlaktespanning alleen is echter niet de bepalende factor, ook de daadwerkelijke surfactant concentratie is belangrijk. Dit laat zien dat het samenvloeingsproces niet alleen wordt bepaald door hydrodynamica en geometrie, maar ook afhankelijk is van de moleculaire fysica van oppervlakte-adsorptie.

Acknowledgements

My first introduction with the Physics of Fluids Group was already during my premaster for the Applied Physics master. In one of these courses, I experimentally studied the coalescence of sessile droplets. This immediately intrigued me, and I am sure the decision for doing experimental research related to fluids was made back then.

Two years after this course I started my master thesis in this group. In this time, Jacco and Detlef proposed many PhD-projects to me. One of them being the experimental *NanoPacks* project of Alvaro Marin. Of course I knew Alvaro by name from the famous coffee-stain experiments published some years earlier. The idea of having an outstanding experimentalist as my main supervisor, really appealed to me. *Alvaro*, when you first explained the project to me, I was directly enthusiastic and I liked the several routes we could follow in the project. And I must say, I never regretted choosing this project and this supervisor. Spending the days together in the lab (listening to some good old Americana), discussing all the interesting experiments, together with the 100% involvement you always showed. Also your critical eye for detail in figures and movies has resulted in for example the Poster Award in Durham at the Droplets 2019 Conference. Thank you Alvaro for your guidance, your dedication and your passion for science the last four years. It is a true honour to be your first PhD-student in Enschede to graduate.

I would also like to thank *Detlef* for stimulating me to pursue a master at the Physics of Fluids Group and to stay for a PhD-project as well. When I discussed my transition from my bachelor in Chemical Engineering to the Fluids master, you were really cooperative and made the transition very smoothly. Later on, when convincing me to also do a PhD in your group, you gave me several projects to choose from. I am happy that you also found the project of Alvaro in your drawer.

Furthermore, my time in this group would not have been the same without *Jacco*. In my master, I really enjoyed the courses you taught and I have learned tremendously from them. Afterwards I continued with my master thesis with you. Initially, I spend most time in the lab with Maxime. But after some preliminary results were gained, the discussions we had were really fruitful and made this master project a successful one. When I was

handed out the Shell Master thesis award, I was in the USA for the APS-conference. Thank you for travelling to The Hague (KHMW) and stepping in for me. During my PhD we still stayed in contact, as the surfactant study still needed to be finished for publication. Also in my first project with Alvaro (droplets inside an elastic medium), we worked together, which resulted in a nice publication (even though we had to fight that one referee a lot haha).

My last two scientific teachers in POF were Stefan and Maxime. *Stefan*, your dedication in the surfactant study was a real inspiration. I still cannot wrap my head around the fact that someone can be an excellent experimentalist, theoretician and numericist... But yet, you manage to be all of that. Thanks for your guidance in my master thesis, but also in the four years afterwards. *Maxime*, your level of enthusiasm is unique. When you started your postdoc in POF, you all of a sudden had to deal with a master student as well, with a subject you had no prior experience in. However, the speed at which you managed to get your hands on the subject was impressive. Besides that, your love for fabricating set-ups and Arduino circuits is still felt at POF. I am happy that we also continued our collaboration. Additionally I want to thank *Claus-Dieter* for his input in the study of cavitating colloidal droplets, also *Benjamin* for your enthusiasm and the fruitful discussions we had. Thank you *Laura* for all your hard work during your master thesis, our work resulted in a nice publication.

I would like to thank the group of girls that always made going to the office great; Carola, Maaïke, Jessica, Anja, Liz, Diana and Ambre. I am proud of us, we went running together frequently, even though we all had our own speed and challenges. It was always a good motivation to go together. Also the dinners we had together, were very nice. *Carola*, it was a real pleasure to have you as my NanoPacks-buddy, lab-buddy and officemate. I am happy we connected both on a scientific and personal level. *Maaïke*, you are always there for me, and I really appreciate all you have done for me. Discussing together in the lab, playing lots of beach volleyball (with those tall boys Bram and Pieter), organising the Bata, as well as playing music together; we did it all. *Jessica*, your spontaneous character really brightens up every situation, and thank you for all the good talks. *Anja*, it is such a pity I was never able to join your epic birthday parties. First my trip to New-Zealand, then Corona entered the picture. I am sure that I will be there next time! *Liz*, we spend a lot of time together in POF. We were the best talk buddies, walk buddies and tea buddies. I was very happy that our offices were located next to each other, so there was always time for a small talk. *Diana*, I was really happy when you came back from your time in Germany. It's really fun to have you back in the lab. Finally someone that understands my PDMS-struggles... *Ambre*, you arrived in POF when Corona just started. As a result we did not see each other a lot initially. It's impressive how you managed to arrange everything in these tough times to start at a new place. However, when the lab opened a bit more, we hang

out a lot. I really enjoyed discussing with you and I cannot thank you enough for all the times you offered me some (badly needed) chocolate.

I want to thank my office mates from The Best Office ME 214-C, *Peter, Carola and Mikhail*, later succeeded by *Pim Waasdorp*, and my own successor *Ambre*. As we were all experimentalists, the office could sometimes be almost completely empty. But those days when we were all analysing data or writing, were the best days. I remember people entering our office to check what was going on... Apparently our laughter was audible throughout all corridors. Also there was never a shortage of chocolate (thank you Carola, Mikhail and Ambre), or oranges (thank you Peter).

The trips before or after APS are of course part of the most unforgettable experiences during my time as a PhD student. Liz, together we saw so many beautiful National Parks as we drove from Denver to Las Vegas. Thank you for driving all the way! Maaïke and Jessica, aka the APSisters, our tour from Washington to Atlanta was amazing. Visiting the world of Dolly Parton and boiling all the water ourselves to heat up the jacuzzi, are memories I will definitely never forget. *Pim Bullee* and *Michiel* (also my lunch walk buddy), I really enjoyed our trip to Seattle. I was never so excited in my life as when all of a sudden a raccoon appeared, when we were just relaxing in the jacuzzi.

I want to thank everyone I have met in POF. Especially, *Rianne, Marise, Hanneke, Ruben, Yaxing, Guillaume, Dominik, Jelle, José, Ricardo, Marvin, Utkarsh, Álvaro Moreno, Mathieu and Jiaming*, also *Joanita, Gert-Wim, Bas, Martin* and *Dennis*. Some of you helped me out in the lab often, others I played lots of sport with, others I used to hike with every lunch break. Thank you all!

Het succes van een lang traject, zoals een promotieproject, hangt niet alleen samen met de ondersteuning die je op professioneel vlak ontvangt. Net zo belangrijk, of al dan niet belangrijker, is je sociale kring daaromheen. Ik wil daarom graag *Laura, Marijn, Lara, Fleur* en *Marjolein* bedanken. We zien elkaar nog steeds na onze gezamenlijke middelbare school-tijd, en dat is voor mij heel waardevol. Het blijft bijzonder dat het nog altijd zo fijn is om samen te zijn, ondanks een wisselende frequentie van elkaar zien. *Anna* en *Marije*, in de bachelor ST hebben we veel samen gedaan. Marije, jij was mijn vaste labpartner tijdens alle labvakken. Was je niet verbaasd toen ik een experimenteel onderzoek ging doen voor m'n PhD? *Maaïke, Randy* en *Vivian*, ik heb jullie via Musilon en Harambee ontmoet. Ik denk nog steeds met veel plezier terug aan onze spelletjesmiddagen en de trip naar Schotland. Die is zeker voor herhaling vatbaar! *Maura*, we hebben elkaar leren kennen tijdens het afstuderen bij POF. De maanden samen in het lab staan, daarna onze grote reis naar Zuid-Amerika en vervolgens allebei kiezen voor een PhD in Enschede. Ik ben blij dat we zoveel samen hebben kunnen doen.

Verder wil ik graag mijn familie bedanken. Ten eerste natuurlijk mijn ouders. *Papa* en *mama*, jullie hebben allebei vroeger Scheikundige Technologie gestudeerd, kennelijk valt de appel dus niet ver van de boom. Toen ik voor mijn master wilde switchen naar Natuurkunde, heb ik daar veel support voor gehad. Ook stonden jullie volledig achter mijn besluit om een PhD te doen, bedankt voor al deze steun. *Papa*, het was fijn om iemand dichtbij me te hebben die de wetenschappelijke wereld zo goed kent. Met elk type vraagstuk (hoe deel je een PhD goed in, hoe om te gaan met lastige referees) kon ik bij jou terecht. Verder heb je al vanaf jongs af aan mijn nieuwsgierigheid getriggerd, bijvoorbeeld door aan tafel te vragen: *Je cola is aan het bubbelen, betekent dat dus dat cola kookt op kamertemperatuur?* Ik weet zeker dat dit mijn onderzoekende instelling heeft gevormd. *Mama*, bedankt voor al je steun de afgelopen jaren. Je welbekende 'praatje voor de klets' start standaard met '*schikt het?*', het antwoord is meestal ja. Fijn dat je altijd zo betrokken bent in alle aspecten van mijn leven. Daarnaast wil ik graag *Pieter van Wijchen* en *Jetty* bedanken. Jullie zijn er altijd voor mij geweest en ik prijs me zeer gelukkig dat jullie zo'n grote rol in mijn leven spelen. *Aster* en *Nora*, bedankt dat jullie deze dag naast mij willen staan als paranimf. En nee, dat betekent helaas niet dat je je als elf mag verkleden, haha. Ik vind het fijn hoe close we met z'n drieën zijn, ik kan altijd alles met jullie delen. Maar meestal liggen we gewoon samen in een deuk. Kennelijk kan iedereen horen dat we zussen zijn door ons typische gegiebel. Verder wil ik graag *Oma Ans* en *Oma Annie* bedanken, het is bijzonder hoe jullie beiden altijd zo vol interesse en enthousiasme zijn, ik bewonder jullie erg. Peetouders *Jacqueline*, *Marinus* en ook *Iris* en *Milo*, bedankt voor alle mooie tijden samen. Ik koester warme herinneringen aan de vakanties samen, met alle spelletjes en liedjes. Daarnaast wil ik *Christie*, *Marijke*, *Noémi* en al mijn andere familieleden bedanken. Graag wil ik ook mijn dank uitspreken naar de *familie Berghout*, ik voel me vanaf het begin zeer welkom in de familie. In het bijzonder wil ik *Ma* en *Leendert* bedanken voor jullie warmte en interesse.

Tenslotte de allerbelangrijkste persoon. Lieve *Pieter*, ik ben ongelofelijk blij dat ik jou heb leren kennen. We hebben het zo ontzettend goed samen, je maakt me erg gelukkig. Ook is het uniek dat we elkaars onderzoek tot op zeer grote hoogte konden begrijpen. Het feit dat we nu ook nog op dezelfde dag ons werk gaan verdedigen, is helemaal de kers op de taart. Bedankt dat je er altijd voor me bent en al mijn gestress met je mooie lach kan doorstaan. Je zorgt er echt voor dat ik het beste uit mezelf haal. Nu samen op een naar een nieuw leven in het westen van het land. *Pieter*, ik hou van je.