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Producing tubes of a droplet in an emulsion with surface particles at the interface

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Preface

This thesis presents experimental results that were obtained through experiments done at the Department of Physics at the Norwegian University of Science and Technology (NTNU), Trondheim.

The goal of the work in connection with this thesis was to investigate the physics behind emulsions through obtaining tubes of droplets of one liquid suspended in another. By applying different methods, various ways of deforming and manipulating a droplet were observed, so that the measured lengths l and calculated aspect ratios a varied greatly. Many experiments were done, in which some factors were changed only slightly or not at all, so that there are still work to be done in the future on the topic of tubes in emulsions. Some of the background theory, methods and results presented in this thesis are based on a project report that was written during the Autumn of 2013.

This thesis is written for my peers. Hence, it is preferable to have a basic understanding of microfluidics and electrostatics.

I would like to thank my supervisor, Jon Otto Fossum, for allowing me to do experiments at the laboratory for Soft and Complex Matter Studies and Paul Dommersnes for informative lessons and conversations. I would also like to thank Alexander Mikkelsen for his support and patience in connection with everything from pondering theoretical questions to suggesting new experimental setups or fluids/particles, and my fellow master students, with whom I have had many productive discussions. Furthermore, I would like to show my appreciation for my family, who is always supporting and motivating me, and last, but not least, a large thanks to my sister, for the ever-present inspiration and encouragement she always radiates.

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Abstract

The aim of the work done in connection to this thesis was to find different methods with which long tubes of one liquid suspended in another can be made (an emulsion). Various liquids (silicone oil, castor oil, diethyl-phtalate, water, and a mixture of water and glycerol) as well as different types of surface particles were used in the hope of making tubes. When good results were obtained, the length l was measured and the aspect ratio $a = l/d$ (l=the length of the tube, d=the diameter of the tube) calculated, so that it was possible to compare the results. Eight different methods were applied, through which different factors influencing the lengths and ratios of the tubes were discovered.

After withdrawing some of the fluid from a droplet, which was then covered by buckles of particles, an electric field could be applied onto the system causing a deformation of the droplet or pipette tips could be moved manually alongside the droplet, allowing the surrounding fluid to deform it. At high field strengths, Quincke rotations occurred which made the process unpredictable. Nevertheless, satisfactory results were obtained. A third method was used, in which two droplets were coalesced into one and then deformed by an electric field or pipette tips, without any further success.

The method yielding the best results in this thesis was the one including an object, of a known diameter and volume, sinking through a particle layer situated at the interface of two liquids which are placed directly on top of each other. Factors that were found to be crucial to obtaining the longest tubes were the diameter of the surface particles, the friction between the object and the fluids and particles, and the relationship between the horizontal cross-sectional areas of the object and the container.

Four other methods were tried as well. Objects of different materials were used to pull at a particle layer situated at the interface of two liquids, yielding some interesting results. Also, a pipette was moved vertically upwards whilst releasing a liquid into another liquid, with a couple of interesting consequences. Another method included the ejection of a jet of a liquid containing particles from a pipette into another liquid, without any further success. In the last method, the idea was to pour a liquid onto another, the latter covered by a layer of particles at its surface. This gave some discouraging results. In future experiments with the last four methods, the densities of liquids in an emulsion should be matched, as long as the properties of the system do not change notably, and the surface tensions of the liquids should be paid closer attention to. Furthermore, the concentration and the type of particles are important. In the method of pulling at a particle layer, the material, and hence the friction caused, of the pulling object might matter.

Sammendrag

Målet for arbeidet med denne masteroppgaven var å finne ulike metoder for å lage rør, så lange som mulig, i en emulsjon av to væsker. Forskjellige væsker (silikonolje, castorolje, dietyl-ftalat, vann og en blanding av vann og glyserol) og ulike overflatepartikler ble brukt i prosessen med å finne en god metode. Videre var hensikten å måle rørenes lengde, samt regne ut forholdet mellom lengde og diameter, notert som lengdeforholdet $a = l/d$. Slik ble det mulig å sammenligne de resultatene som ble oppnådd. Totalt ble åtte ulike metoder brukt, og mange faktorer som er avgjørende for dannelsen av rør ble slik oppdaget.

Etter å ha fjernet noe av væsken i en dråpe, samlet overflatepartiklene seg i klumper på overflaten. Dette kunne bli utnyttet videre gjennom at et elektrisk felt ble satt på og på den måten deformerte dråpen eller gjennom at en pipettespiss ble ført fram og tilbake langs dråpen og slik lot væsken som omgir dråpen deformere den. Ved høye verdier for feltstyrken ble Quinckerotasjoner observert, noe som gjorde prosessen med å danne rør uforutsigbar. Uansett, resultatene var tilfredsstillende. En tredje metode som ble introdusert handlet om å la to dråper få koalescere før et elektrisk felt eller pipettespisser ble brukt til å deformere dråpen, uten at dette gav et nevneverdig resultat.

Den metoden som gav de beste resultatene innebar at et sfærisk objekt, med kjent diameter og volum, fikk synke gjennom to væsker (plassert over hverandre i en beholder) og partikkellaget som befant seg i overgangen mellom dem. Faktorer som spilte inn på hvor gode resultatene ble var partiklenes diameter, friksjon mellom objektet og væskene og partiklene, samt forholdet mellom de horisontale tverrsnittene av objektet og beholderen.

Fire andre metoder ble også forsøkt. Objekter av ulike materialer ble benyttet til å dra et partikkellag som befinner seg i overgangen mellom to væsker oppover. Dette var en metode som gav noen interessante resultater. I tillegg ble en pipette brukt til å frigjøre væske mens den ble trukket oppover, med brukbare resultater. Nok en metode ble prøvd. En pipette tilførte en stråle av en væske ned i en annen væske som befant seg i en beholder. En siste metode handlet om å la en væske bli helt ovenfra og ned i en beholder som inneholdt en annen væske som var dekket av partikler. Ingen av de to siste metodene førte til gode resultater. Dersom nye framtidige eksperimenter skal gjøres med de siste fire omtalte metodene, er det nok noen faktorer som må ses videre på. Tetthetene til væskene bør være nogenlunde like og må derfor tilpasses så langt det lar seg gjøre uten å endre egenskapene til væskene nevneverdig. Videre så kan det være lurt å ta mer hensyn til overflatespenning og dens innvirkning på resultatet. Det viste seg imidlertid at konsentrasjonen av partikler også kan spille en rolle. I metoden hvor et partikkellag blir dratt med av et objekt, så kan materialet i dette ha noe å si for friksjonen mellom objekt og væsker og partikler.

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List of abbreviations

PE: Polyethylene

PE##-##: Polyethylene particles of diameter ##-## μm

CS: Polystyrene

CS##: Polystyrene particles of diameter ## μm

CA##: Particles consisting mainly of poly(methyl methacrylate) (PMMA) with a diameter ## μm

PMMA: Particles consisting of poly(methyl methacrylate)

NaFH: Particles of Sodium-fluorohectorite

d-ph: The fluid diethyl-phtalate

Liquid 1/liquid 2: Describing an experimental setup with the liquid 2 in a container and liquid 1 on top of it or being added to the container from above.

Contents

Chapter 1

Introduction

1.1 Background and motivation

Microfluidics has been an important field of study in recent years due to many applications, amongst them the inkjet technology used in computer printers. Another application is emulsions, or the mixture of two immiscible liquids [1]. In a system such as this, small droplets can exist within a surrounding fluid (the continuous phase), in a stable two-phase system. The droplet, the dispersed phase, is in an equilibrium state when it is spherically shaped, as a consequence of surface tension at the interface of the liquids. Emulsions are found in many different applications which are used daily, such as milk and vinaigrettes as well as in cutting fluids for metal working.

Due to not being solid spheres, droplets can easily be destabilized. To counteract this, surface particles have been used in research projects. Particles located at the interface of two fluids are influenced by attraction forces, called lateral capillary forces [2]. Such flotation forces are caused by a deformation of the liquid interface due to the gravitational pull on the particles, causing smaller particles (radius $r<$ 5-10 μm) to barely deform the liquid at all. Furthermore, the force increases with larger particles (and hence the larger centre-to-centre inter-particle distance). Also, particles situated at a liquid interface might not be freely floating, but instead be partially immersed in a liquid film. The energy of capillary attraction will then be larger than the flotation forces for the same particle size, and might be much larger than kT, even for particles with diameters of a few nanometers [3]. The long-range attraction forces between particles at a fluid interface is indicated through an experiment in which a water droplet with a few freely floating crystallites is suspended in oil [4].

Due to the inter-particle attraction forces and that the energy of the particles is lower when they are located on the interface between two liquids rather than in one of the liquids alone, colloidal particles may be strongly bound to the interface between two liquids, thus creating functional membranes or capsules. Solid colloidal capsules, called colloidosomes, may also be made. This occurs when particles are

linked or fused to the surface of a droplet which have been through the process of pickering emulsion [5][6]. Pickering emulsions are found in foods, cosmetics and oil recovery [5], as well as in biomedicine [7]. These are caused by microscopic particles adsorbing on the interface between a droplet and a surrounding fluid. The particle coating works as a stabilizing factor for the emulsion since it prevents the droplets from coalescing.

Colloidal particles exhibit many properties that might be exploited, such as altering the surface properties or volume either by changing the temperature or the type of solvent, or by applying an electric field. An important application in the future might be to use microemulsions to increase the efficacy of drug delivery in a human body by reducing the dose and consequently minimizing the side effects. Microemulsions have several advantages - they are thermodynamically stable and easy to prepare, the formation of such emulsions are reversible and they can act as supersolvents by solving both hydrophilic and lipophilic drugs [8]. Microemulsions can also respond to changes in pH-value, so that drug release can be done by using pH-responsive colloidal capsules to obtain the opposite of pickering emulsions, which would mean that the capsule breaks up when it moves into an area with a different pH-value [6]. In connection to medical applications, it is important that no liquids or particles are causing a danger for the human body.

By applying an electric field to a system of fluids motion is caused, and in reverse, fluid flow can create an electric field [9]. Electric fields applied on fluids might have different implications on the behaviour of a droplet. It may be deformed, start to rotate or break up into smaller droplets as well as coalesce with other nearby droplets. Consequently, the system gets complicated due to many forces at work. A droplet will react on an electrical force caused by free charges moving around close to the surface of the droplet, both on the inside and on the outside, interfacial surface tension and drag forces created by the viscosity of the fluids.

Some experiments on droplets of a dielectric material have been done recently. Inducing a capillary attraction between like-charged particles (PMMA) located at a water-oil interface by applying an electric field, it was found that fields in dipolar materials induce surface charges which distort the interface [4]. This dipolar interaction contributes to cause long-range repulsion between particles in a confined area, thus an ordering of particles, even crystallization, can be created at the interface. Furthermore, a form of ordering of particles has been found to occur even without a confined area, indicating that attractive forces also has to be present. These forces are caused by interfacial deformation. Electric fields have been tried on other systems as well, for instance a silicone oil-in-castor oil emulsion with various particles [6]. With fluorohectorite clay particles or polyethylene (henceforth: PE) particles a ribbon-shaped film perpendicular to the direction of the electric field was observed on the surface of the droplet, whereas with a combination of PE beads and metallic-coated glass beads the former particles were organized in a ribbon perpendicular to the field and the metallic particles in chain-like structures parallel to the field (Fig. 1.1a). Hence, the conductivity of the particles situated at the interface of two

dielectric liquids determined the behaviour of different particles in an electric field. To produce anisotropic functional colloidosomes, solidification can be achieved by either UV light or heating (creating bridges between the surface particles) [10].

The production of advanced capsules, such as Janus capsules, might be an interesting field of study for the future [11]. This occurs when an electric field E is applied onto an emulsion with two droplets containing PE beads of different colours, thus obtaining the ribbon-like structure mentioned above, before coalescence of the droplets are caused by both the electrohydrodynamic (EHD) flow and the electrostatic forces. Thus, the resulting droplet has two "faces", see Fig. 1.1b. Also, the uses of Janus particles (with a functional asymmetry and directionality) might be many in the future, amongst them in biomedicine, in which such particles with only one hemisphere covered with ligands can interact with a cell membrane during receptor-mediated particle uptake [12].

(a)   (b)
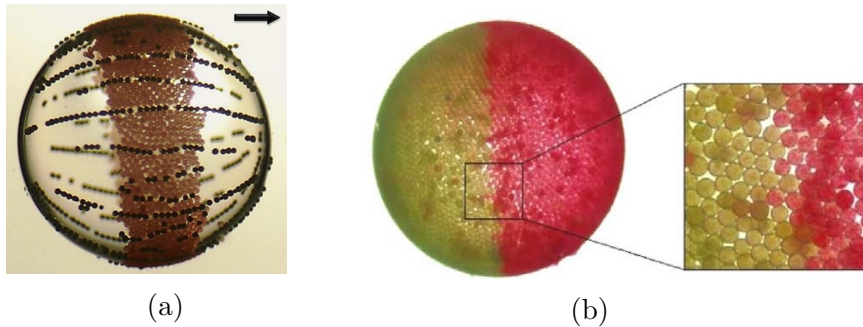
Figure 1.1: Colloidal armouring of droplets in emulsions. (a) shows how PE beads are situated in a ribbon-shaped film (perpendicular to the direction of the E-field) on the interface of a silicone oil-in-castor oil emulsion and how the metallic-coated glass beads are located in chain-like structures parallel to the E-field. The field strength was E=250 V/mm and the drop radius $\sim$ 1 mm. (b), on the other hand, illustrates the coalescence of two droplets containing particles of different colours, creating a two-faced Janus capsule. Here, PE beads of diameter 50$\pm$ 3 μm and an electric field strength of 250 V/mm were used. (a) and (b) are adapted from [6] and [11], respectively.

To manage to control an emulsion, the movement of free charges at the droplet surface, surface tension and drag forces need to be understood. Also, buoyancy forces and the densities of liquids and particles must be taken in to consideration. An application in which much of this knowledge has to be applied is during oil spills at sea. To handle this situation, a method based on gravity-induced encapsulation of oil by applying sand has been suggested [13]. Threatening already fragile ecosystems, the oil should be handled with care without including detergent-like chemicals or direct burning. Sand, consisting of relatively large particles and being a natural material, is spread over the spill, and due to flotation forces it gathers in large rafts, which after a while gets too heavy to stay afloat, thus being destabilized. An oil

drop is in this way forced to sink due to being wrapped in a layer of sand grains at the surface. The question is if this situation could be further utilized in the future, for instance with a long cylindrical stick being pushed downwards onto the raft so that the droplet sinking could be deformed into a different shape than a sphere.

Another way of achieving a non-spherical shape of a droplet of one liquid suspended in another liquid, is through double emulsions. In Fig. 1.2a, such emulsions are made with two droplets ($n=2$) of water situated in a water-in-oil-in-water emulsion, and a similar system is seen in Fig. 1.2b, in which $n=6$ and the oil has evaporated so that the 15 nm hydrophobic SiO_2 nanoparticles, originally located in the oil phase (toluene), are packed onto the interface between the water droplets and the surrounding water. Also, in the future, more complex structures might be generated, like asymmetric colloidosomes with different nanoparticles on the inner and the outer surface of the shell. The two types of nanoparticles must have different wettabilities, one of them initially situated in the water phase and the other in the oil phase [14]. Furthermore, the fabrication of non-spherical particles is possible, for instance to produce toroidal polymer particles. This can be done through phase separation in an axisymmetrical flow field inside a microcapillary device, in which a polymer is dissolved in droplets of a certain solvent [15].

(a)   (b)
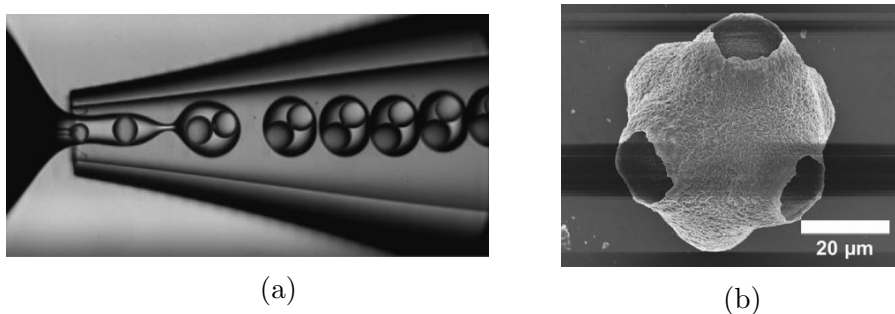
Figure 1.2: Double emulsions resulting in non-spherical colloidosomes with multiple compartments. In (a) $n = 2$ droplets of water in a water-in-oil-in-water emulsion can be seen, whereas (b) shows $n = 6$ internal droplets after the oil (which included the 15 nm hydrophobic SiO_2 nanoparticles) has evaporated. Adapted from [14].

An interesting topic to look at is jets and the instability, or break-up, of such collimated streams. Liquid jets, found both on the scale of the universe and on subatomic length scales, are widely encountered both in nature, technology and basic science, for instance nuclear fission or DNA sampling, medical diagnostics, sprays or jet engine technology [16]. From Leonardo da Vinci until this day, jets have sparked an interest in the human mind. da Vinci thought that the break-up of a jet into droplets was a consequence of the gravity overcoming the cohesive properties of a water jet, which is not entirely correct as it is the surface tension the gravity must overcome. Mariotte agreed upon this incorrect conclusion because a jet directed vertically upwards does not break up, and claimed that a break-up occurs when the a fluid jet has become as 'thin as a hair' [17]. Furthermore, in 1805

Laplace and Young discovered that surface tension was the crucial factor for the break-up of a jet [18] [19]; the tension acts like an elastic membrane for a hanging droplet, whereas for a cylindrically shaped droplet the radial curvature *drives* the break-up [16]. Thus, the surface of the liquid is minimized, and the radius of the jet is diminished until it reaches zero. This is a paradox; the greater the surface tension γ (hence the cohesion between the liquid molecules), the faster the break-up. Further experiments were done after this, amongst them by Savart who observed that break-up occurs spontaneously and independently of any external force or jet direction [20]. Also, the laws of fluid motion were developed by Navier and Stokes so that the tools for a mathematical understanding of the break-up of jets were there. More recently, some work on the instability of jets (the sinusoidal perturbations of a liquid jet) has been done [21] [22].

1.2   Problem

A system of two fluids and surface particles may together have many interesting properties and interact in a particular way. The aim of the work done in connection to this thesis was to obtain tubes in an emulsion of two liquids, with the help of a few types of surface particles at the interface of these. To obtain tubes that were as long as possible, various experimental setups and methods were used. If the combinations of fluids and particles do not yield any good results, these combinations or even entire methods can be eliminated from experiments in the future.

In this thesis, tubes were defined as stretched droplets of one liquid suspended in another, the interface of the liquids covered by surface particles. Also, the cross-sectional area of the tubes should be circular and the diameter fairly constant along the entire length of the tube. Both the lengths and the diameters were measured and, consequently, the aspect ratio $a = l/d$ (l=length and d=diameter of the tube) could be calculated, thus making it easier to compare the tubes obtained during the experiments.

1.3   Thesis structure

There are seven main chapters in this thesis, one of which is this introduction. An overview of the relevant information needed to understand emulsions can be found in the chapter of Background theory, which is succeeded by an explanation of the experimental setups and methods in the Method chapter. Observations are presented in the Results section before being discussed in detail in the Discussion section. Furthermore, the findings are summarized in the Conclusion chapter, before suggestions for more experiments or projects are introduced in the Further work chapter.

Chapter 2

Background theory

2.1 Emulsions

An emulsion is a mixture of two normally immiscible fluids, one of which (the dispersed phase, henceforth called liquid II) suspended as a droplet in the other (the continuous phase, henceforth called liquid I). It emerges in mixtures of oil and water, in the forms of oil-in-water or water-in-oil emulsions, or in mixtures of two oils of different viscosities and densities. The internal structure of emulsions is not static, due to operating with liquids, and the dispersion of droplets is normally considered to be statistically distributed. The interacting surface tensions and viscosities of the liquids are playing a part in an emulsion, as well as the polarities of the liquids (hence: the charge distribution on the interface of the liquids).

Emulsions can be found in many applications used daily, amongst them inkjet technology in computer printers and food, as in mayonnaise, homogenized milk and butter. Also, emulsions are used in hairstyling and cosmetics, and for medicinal purposes, as in pharmaceutics. Microemulsions can be applied to deliver vaccines and kill microbes [23] [24] [25], in which nanoemulsions of soybean oil and particles of diameter 400-600 nm are typical. There is currently much funding to projects including nanoemulsion based vaccines [24]. Even in class B fires [26], emulsifying agents are found to be effective due to their ability to encapsulate a small, thin-layer spill of a flammable fluid, trapping the burning fluid in the water phase (in a fluid-in-water emulsion).

The droplets in question can be classified by their size: Macroemulsions (found for instance in milk) are systems consisting of droplets of diameters larger than a micrometer, whereas microemulsions consist of droplets with smaller diameters. The former being in a metastable state, it prefers to go through a separation of phases so that the area of contact between phases is minimized, while the latter are stable since coalescing the droplets would not let the mixture gain energy [1]. Hence, small drops must be influenced by weak interfacial tensions if they are to exist in an emulsion, because capillary effects favour large drops and will try destabilizing the droplets, forcing them to coalesce [27]. To stabilize the emulsion, surface particles

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can be used, for instance as in pickering emulsions. This can be called emulsifiers, a material increasing the kinetic stability of the emulsion by interacting with both liquids.

2.2   Surface tension

All fluids are a congregation of molecules, between which the distance is comparable to the diameter of the molecule. The intermolecular forces (van der Waals forces) are short-ranged and strong, as described in Fig. 2.1a. Being situated relatively far from the surface, densely packed molecules in the bulk would repel each other whereas a molecule at the surface will experience attractive forces, that is a net force $\Sigma F \neq 0$ pulling it into the bulk of the liquid. Hence, the molecules achieve the lowest possible potential energy (an equilibrium state) when the liquid acquires a large volume to surface ratio, i.e. as a droplet, achieving a minimization of intermolecular forces. Consequently, to increase the surface area of a liquid, work must be done. Surface tension is defined as the work needed per unit increased area (assuming a constant temperature) and can be written as [28] [29]

$$\gamma = \frac{dW}{dA},$$
(2.1)

in which W is the work exerted on interfacial molecules and $A = 4\pi R^2$ the area of a certain amount of fluid. Assuming that a droplet (liquid II) is suspended in another liquid (liquid I) (as seen in Fig. 2.1b), the hydrostatic pressures would be p_{II} and p_I, respectively. If this system is to exist, the pressure inside the droplet must exceed that of the surrounding liquid. A relationship for this pressure difference might be derived by taking a closer look at the interfacial force F:

$$F = (p_{II} - p_I)A = (p_{II} - p_I)4\pi R^2.$$
(2.2)

Since this force must be balanced by the force due to surface tension, and that the infinitesimal increase in the area of the droplet due to an infinitesimal increase in the radius is expressed as

$$dA = 8\pi R dR,$$
(2.3)

the infinitesimal amount of work done can be found:

$$dW = FdR = 4\pi R^2(p_{II} - p_I)dR.$$
(2.4)

Hence, the Equations (2.3) and (2.4) yield an expression for the surface tension, assuming that the shape of the droplet is spherical,

$$\gamma = \frac{4\pi R^2(p_{II} - p_I)dR}{8\pi R dR} = \frac{R(p_{II} - p_I)}{2}.$$
(2.5)

It can also be shown for a curved surface, as the one in Fig. 2.1c, that the capillary pressure p_c may be expressed as

$$p_c = \Delta p = \gamma \left(\frac{1}{R_x} + \frac{1}{R_y} \right),$$ (2.6)

in which $\Delta p = p_{II} - p_I$ is the pressure difference (called the Laplace pressure) between the inner and the outer fluid, γ the surface tension, and R_x and R_y the two radii of curvature of a differential patch of surface. Eq. (2.6) is known as the Laplace equation.
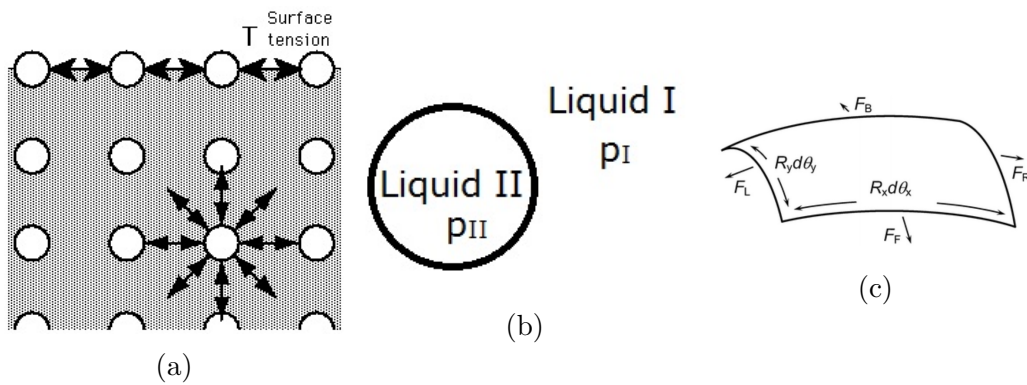
Figure 2.1: Regarding surface tension. (a) illustrates the short-ranged intermolecular forces (van der Waals forces) between the molecules in a liquid. In the bulk of the liquid, the forces between the densely packed molecules are repulsive. However, for the molecules at the surface, the net force will be $\Sigma F \neq 0$ and attractive, directed into the bulk of the liquid. In (b) a droplet of liquid II suspended in liquid I is drawn with the belonging pressures p_{II} and p_I, respectively. A curved surface patch of infinitesimal size, with the forces F_F, F_B, F_L, F_R (forwards, backwards, left and right, respectively) at work due to a pressure difference inside and outside the droplet, is shown in (c). $\delta\theta_x$ and $\delta\theta_y$ illustrate the amount of bend over the tiny patch. (a) was adapted from [30], (c) from [31].

2.3 Instability of jets

Jet instability is a factor that is relevant for emulsion, a situation in which two fluids are influencing each other. Already in 1686, decay of a stream of water flowing from a hole in a container was observed [17]. It was assumed that gravity or other external forces were to blame, however, a uniform force can not cause drop formation. Later, it was found that the surface tension (which was discovered in 1805 [18] [19]) of a liquid was the crucial factor for the occurrence of jet instability, in particular that the surface area was reduced as a consequence of perturbations of long wavelengths [33]. Furthermore, it was found that surface tension had to work against inertia, which opposes the motion of fluids over longer distances, as well as that small
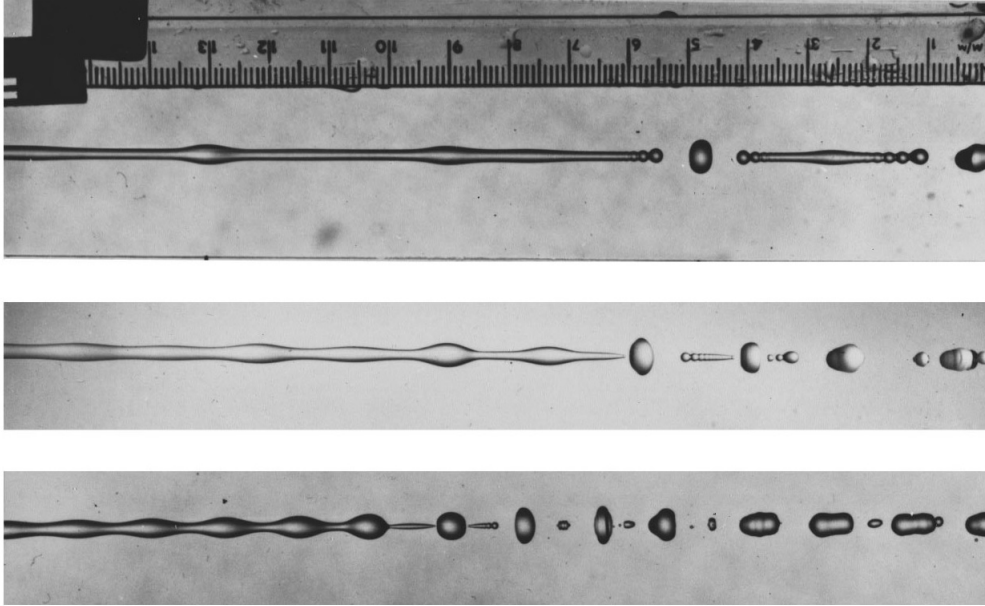
Figure 2.2: A vertically decaying jet of water in air for three different wavenumbers. Small perturbations were added to the system by vibrations from a loudspeaker. The bottom picture illustrates a situation in which $x=0{,}683$, which is a value very close to the Rayleigh mode, whereas the middle picture shows a jet at a longer wavelength ($x=0.25$) with secondary swellings. At even longer wavelengths ($x=0.075$), as described in the top picture, these secondary swellings are indistinguishable. Adapted from [21] and [32].

perturbations on a column of a liquid has got an optimal wavelength, $\lambda_R = 9r$, at which the perturbations grow at the fastest rate [34]. This also determines the typical size of drops.

The instability of a jet is described in Fig. 2.2, in which the relationship between different wavelengths (and hence the wavenumbers k in $x = ka$) and the break-up into droplets is presented. The closer one gets to the Rayleigh mode (neglecting the effect of the surrounding fluid), at which $x = 0.696$, the higher is the wavelength and also the break-up frequency of droplets.

An important factor when looking at the decay of a liquid jet, is the reduced wave number,

$$x = ka_0 = \frac{2\pi a_0}{\lambda}, \tag{2.7}$$

in which a_0 is the radius of the unperturbed jet and λ the wavelength of the perturbations. At $x<1$, the jet is unstable due to the perturbations and consequently, at small viscosities, the value $x_R = 0.696$ (the Rayleigh mode) is when the perturbations grow fastest. If $x>1$, on the other hand, irregular break-up can be observed due to small random perturbations with components of $x<1$ influencing the jet.

Also, the equation

$$\xi = \epsilon cos(kz), \tag{2.8}$$

with ξ as the displacement in the r-direction of a particle located at the surface of the column and ϵ as the amplitude of varicosity, describes a system with jet instability. Furthermore, the variable part in the pressure (assumed to be constant [35]),

$$p = \frac{T\xi(k^2a^2 - 1)}{a^2}, \tag{2.9}$$

includes the surface tension T and earlier explained variables. With the help of these formulas and the Stokes current function ψ [36], it was found that the perturbations grow fastest at x=0.568 when the surrounding fluid is taken into account. Doing so, the relationship between the viscosities of the fluids, $\mu^{'}/\mu$=0.91 ($\mu^{'}$ is the viscosity of the fluid inside the column whilst μ is the viscosity of the surrounding fluid) mattered. In the Rayleigh mode, $\mu^{'}/\mu \to \infty$ (a jet of water in air) which yields x=0.696.

2.4 Surface particles and the importance of their energy

Particles mixed into a liquid are observed to almost exclusively be situated on the surface of a droplet if suspended in another liquid, given that the droplet has had some time to obtain a state of equilibrium. This can be explained by looking at the amount of energy the particles have at three locations; in one of the liquids, in the other liquid and on the interface between them. The energy E is given by the equation

$$E = \gamma A, \tag{2.10}$$

with A as the surface area which is in contact with a liquid with a property γ, defined as the surface tension of the liquid. In the case of a droplet of liquid II being suspended in liquid I, given that the particle size is not comparable to the molecular scale, the interactions on a molecular level can be described as the particle-fluid I, the particle-fluid II and the fluid I-fluid II interfacial tensions expressed by γ_I, γ_{II} and γ_{I-II}, respectively [5]. Defining the variables E_I, E_{II} and E_{I-II} as the energies of the particle when it is located in fluid I, fluid II and at the interface between them, respectively, it is possible to find expressions for how the energies of the particles in the various situations relate to each other.

By evaluating these variables in the formulae $E_{I-II} - E_I$ and $E_{I-II} - E_{II}$, it can be found that E_{I-II} is smaller than either of the energies E_I or E_{II}. Hence, the total energy gain for the particle in placing itself on the surface of a liquid, can be expressed as

$$\Delta E = -\pi r^2 \gamma_{I-II}(1 \pm cos(\theta_c))^2, \tag{2.11}$$

in which γ_{I-II} is the surface tension between liquids I and II, and θ_c the contact angle at the point at which the surface of a particle intersects with the interface of the liquids (see Fig. 2.3). The angle θ_c, the Young-Dupré contact angle, can further be expressed as $\cos\theta_c = (\gamma_I - \gamma_{II})/\gamma_{I-II}$ [5].
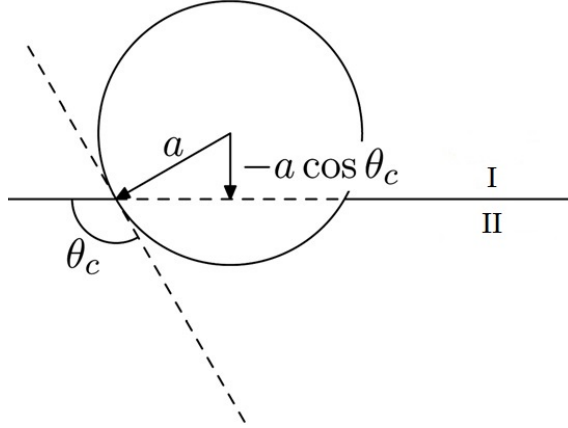
Figure 2.3: Two immiscible fluids and a surface particle. At the interface of two fluids, the particle is located with a larger proportion of its volume inside fluid I (the surrounding fluid). θ_c is the contact angle of the two fluids, an angle at which the particle is stable. [5].

The particles are most importantly used as a way of creating a shell around the drop of liquid II, but also to indicate how the drop is deforming and rotating. Upon increasing the concentration of surface particles in liquid II, tubes can, with the help of an external electric field or by manually stretching the drop with pipette tips, be made. This deformation occurs since the force applied on the drop by the electric field or the pipette tips changes its form and thus increases the surface area, so that more particles are able to move towards the surface from inside the drop, jamming the surface so that the droplet stays in a non-spherical shape.

2.5   Particles bound to fluid interfaces

Particles situated on a fluid interface are influenced by attraction forces, also called lateral capillary forces, see Fig. 2.4a. They are created due to the liquid interface being deformed by the gravitational pull on the surface particles. Hence, the more mass of the particles, the stronger is the effects of gravity. As a consequence of this, the meniscus of the liquid is deformed, causing the gravitational potential energy to decrease with shorter inter-particle distances. If the radius of the particles gets too small, $r < $ 5-10 μm, the energy of the capillary interaction between the floating particles becomes negligible, due to the lack of interfacial deformation. Moreover, as an analogy between capillary and electrostatic forces, the interfacial particles could

be said to act as if they have a 'capillary charge', which contains information about the magnitude of the deformation of the interface and can be both positive and negative. This 'charge' occurs as a consequence of a point-like perturbation due to an external force f situated perpendicular to the interface [37] [38]. In addition to this, it is possible to express the potential between two arbitrary charges Q_1 and Q_2, which is separated by a lateral distance s, as an analogy to Coulomb's law in electrostatics [39],

$$V_{cap}(s) = \frac{Q_1 Q_2}{2\pi\gamma} \ln\left(\frac{s}{L}\right), \tag{2.12}$$

in which γ is the surface tension at the interface and L the large distance cut-off, for instance the system size or capillary length. However, the analogy ends here, since two particles of the same 'capillary charge' attract each other, as opposed to what is the case for electric charges [2][39].

(a)

(b)
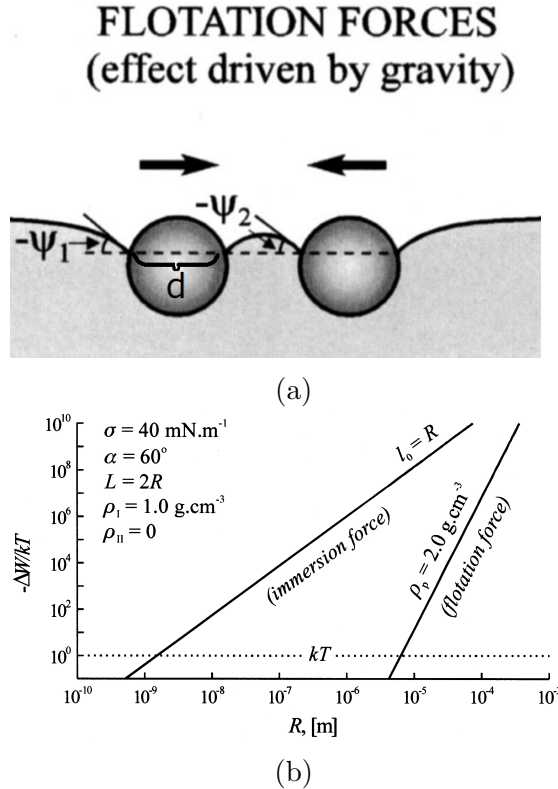
Figure 2.4: Flotation forces and the correspondence between flotation forces and the particles located at the surface of a droplet. In (a) two identical particles and the attraction forces working between them is illustrated (with a contact line d), whereas (b) shows how the capillary attraction forces ΔW (in units of kT) between two particles depend on the centre-to-centre distance (the inter-particle distance $L = 2R$) between them. Hence, the larger the particle diameter (and thus the particle mass), the larger the inter-particle capillary attraction forces. Adapted from [2].
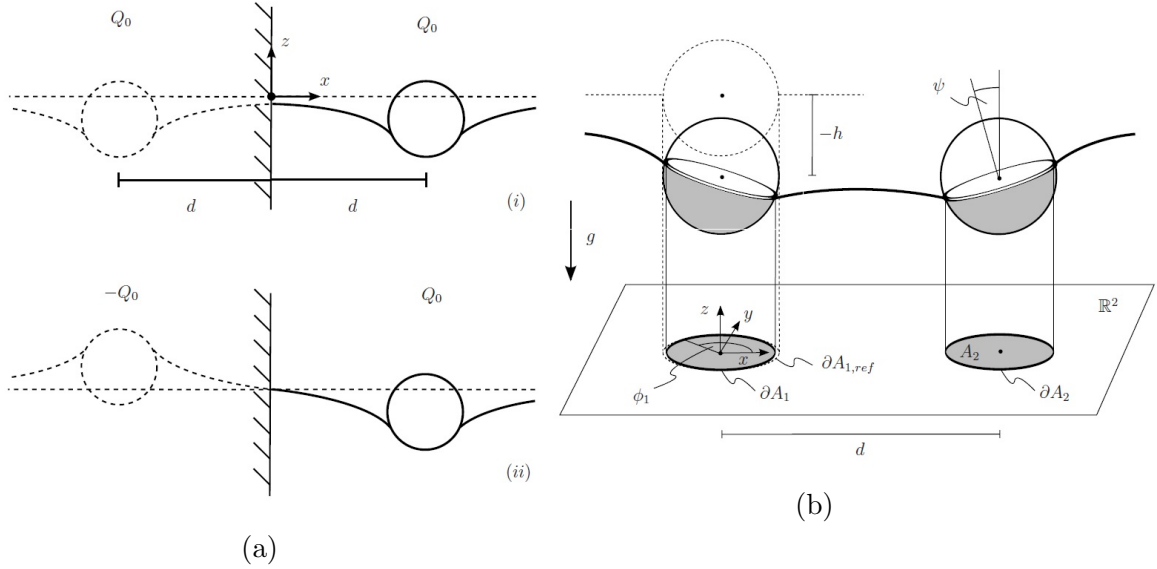
Figure 2.5: A capillary monopole of charge Q_0 located close to a wall with an image charge on the other side is shown in (a). This figure shows the two types of boundary conditions at $x = 0$. In (i) there is a free contact line whereas in (ii) the contact line is pinned. (b) shows two heavy particles at the surface of a liquid and the angle with which they are tilted relative to a horizontal surface. The particles are represented as flat disks due to that the contact lines are pinned, and the dashed lines show the situation if the particle was causing no deformation of the liquid surface. The height h shows the movement of the centre of mass of the particle. Adapted from [39].

Imagine a liquid surface touching the wall of a particular container. Assume that the surface is flat in the absence of a particle, so that the contact angle between the liquid and the wall is $\theta_0 = \pi/2$, whereas in the presence of a particle, located at a distance $x = d$ away from the wall ($x = 0$), the boundary conditions at the wall will determine the interfacial shape of the liquid. After the discovery of that the meniscus between a particle and a wall behaves like the meniscus between two identical particles [40], again an analogy to electrostatics can be introduced: An image force Q' can be placed on the other side of the wall, at $x = -d$ [39][41]. The boundary conditions will then typically consist of either a free contact line causing attractive capillary image forces (an image charge of $Q' = Q_0$, see Fig. 2.5a(i)) or a pinned contact line causing repulsive capillary image forces ($Q' = -Q_0$, see Fig. 2.5a(ii)). In the first case, the slopes of the interface (at the wall) caused by the two charges cancel out, resulting in $\theta(x) = \theta_0$, whereas in the latter the total deformation at the wall will cancel out and the angle $\theta(x)$ will differ from θ_0. In Fig. 2.5b floating particles at a liquid surface is illustrated through a tilt angle ψ of the contact line relative to the line perpendicular to a horizontal surface. The particles are shown as flat disks as well, due to that the contact lines are pinned. The dashed lines illustrate the case of an non-deformed surface. The tilt angle ψ

and the elevation h of the particles determine the boundary conditions of the shape of the fluid interface at the particles.

In Fig. 2.4b, the capillary attraction energy, denoted ΔW in units of kT, where k is the Boltzmann constant and T the temperature of the system, is plotted against the radius R of the surface particles, defining $L = 2R$ as the centre-to-centre distance between two identical particles. Thus, Fig. 2.4b describes the change in attraction energy with the distance between particles, so that an increase in the distance L (an increase in the size of the particles) would mean a stronger attraction between the particles, contributing to forming clusters of particles [2][42].

2.6 Dielectric sphere in electric field

Electric fields will be important for some of the experiments that will be done in connection to this thesis. Therefore, the electric field for a solid dielectric sphere located in another dielectric material, as seen in Fig. 2.6, will be derived [43] [44], despite that a solid sphere is a simplified model for fluids. In the calculations, 'II' will signify the fluid of the droplet and 'I' the surrounding dielectric fluid.
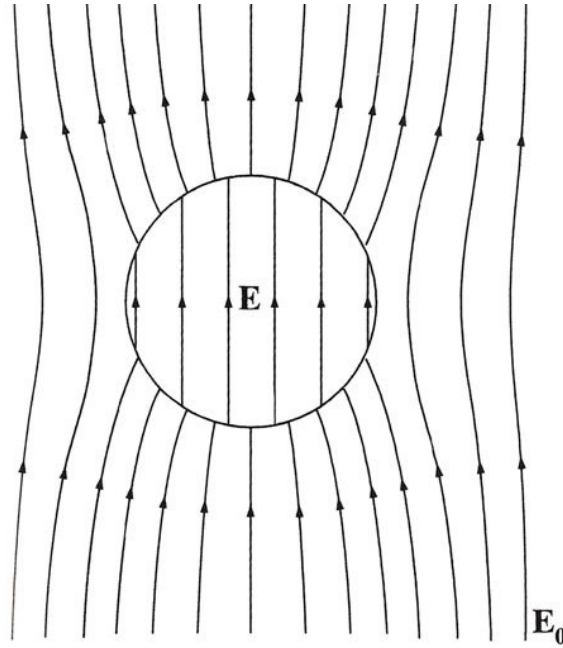
Figure 2.6: A uniform electric field applied onto a dielectric sphere. This figure shows the field both inside and outside the sphere. Adapted from [43].

By applying Gauss' law, electric charge distribution in an electric field can be expressed as

$$\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0}, \tag{2.13}$$

in which ρ is the charge density and ϵ_0 the vacuum permittivity. Furthermore, $\vec{E} = -\nabla V$ relates the potential to an incoming electric field, and the combination of this expression and Eq. (2.13) results in $\nabla^2 V = 0$.

For a sphere of a homogeneous linear dielectric material of radius R located in a uniform electric field, the boundary conditions are

$$V_{II} = V_I, \qquad \text{at } r = R \qquad (2.14\text{a})$$

$$\epsilon_{II} \frac{\partial V_{II}}{\partial r} = \epsilon_I \frac{\partial V_I}{\partial r}, \qquad \text{at } r = R \qquad (2.14\text{b})$$

$$V_I \rightarrow -E_0 r \cos(\theta), \qquad \text{for } r \gg R \qquad (2.14\text{c})$$

where V_{II} and V_I are the potential inside and outside a droplet in an emulsion, respectively, and are given by

$$V_{II}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta), \qquad (2.15\text{a})$$

$$V_I(r, \theta) = -E_0 r \cos(\theta) + \sum_{l=0}^{\infty} \frac{B_l}{r^{l+1}} P_l(\cos\theta). \qquad (2.15\text{b})$$

By applying the boundary conditions, the equations

$$A_l = B_l = 0, \qquad \text{when } l \neq 1 \qquad (2.16\text{a})$$

$$A_1 = -\frac{3}{\epsilon_r + 2} E_0, \qquad \text{for } l = 1 \qquad (2.16\text{b})$$

$$B_1 = \frac{\epsilon_r - 1}{\epsilon_r + 2} R^3 E_0. \qquad \text{for } l = 1 \qquad (2.16\text{c})$$

can be derived. This leads to the potential inside a sphere

$$V_{II}(r, \theta) = -\frac{3}{\epsilon_r + 2} E_0 r \cos\theta, \qquad (2.17)$$

and hence the field inside the droplet is

$$\vec{E} = \frac{3}{\epsilon_r + 2} \vec{E_0}, \qquad (2.18)$$

with $\epsilon_r = \epsilon_{II}/\epsilon_I$ (ϵ_{II} is the permittivity of the droplet and ϵ_I that of the surrounding fluid). Thus, it has been shown that an electric field is uniform inside a droplet of a dielectric material.

Furthermore, there will be a potential outside the droplet given as

$$V = \frac{B_1 \cos\theta}{r^2}, \qquad (2.19)$$

and the potential of a general dipole field is defined as

$$V = \frac{p \cos\theta}{4\pi\epsilon_0 r^2}. \qquad (2.20)$$

By combining Equations (2.16c), (2.19) and (2.20), the total dipole moment can be obtained:

$$\vec{p} = 4\pi\epsilon_0 \frac{\epsilon_{II} - \epsilon_I}{\epsilon_{II} + 2\epsilon_I} R^3 \vec{E}_0, \tag{2.21}$$

and thus the polarization $\vec{P}$, the dipole moment per unit volume, can be found:

$$\vec{P} = \frac{\vec{p}}{\frac{4}{3}\pi R^3} = 3\epsilon_0 \frac{\epsilon_{II} - \epsilon_I}{\epsilon_{II} + 2\epsilon_I} \vec{E}_0. \tag{2.22}$$

The polarization $\vec{P}$ is, like the electric field, constant inside the droplet. Lastly, the polarization charge on the surface of the dielectric material may be written as

$$q_p = \vec{P} \cdot \hat{n} \tag{2.23}$$

where $\hat{n}$ is defined as the unit vector perpendicular to the surface of the sphere. As a consequence of this, it is possible to conclude that there will be two poles - with negative charges at one pole and positive at the other.

2.7 Droplet deformation

Deformation of a droplet (fluid II) which is suspended in another liquid (fluid I), might be done in various ways. Those investigated in this project are electric fields, manual deformation by pipette tips and the effects of gravity. Fig. 2.7 displays how the droplets are deformed.

Electrorheological droplet deformation occurs if an electric field is applied onto a system consisting of a droplet suspended in another fluid. This deformation can, through the leaky dielectric model [9], also be quantified through using the diameters of the deformed drop parallel and normal to the direction of the incident electric field (see Fig. 2.7), as following

$$D = \frac{d_{||} - d_{\perp}}{d_{||} + d_{\perp}} = \frac{9}{16} \frac{r\epsilon_I E_0^2}{\gamma S(2 + R)^2} \cdot \left[S(R^2 + 1) - 2 + 3(RS - 1)\frac{2\lambda + 3}{5(\lambda + 1)} \right], \tag{2.24}$$

where D is expressed by the dielectric properties of the drop and its surroundings; r is the drop radius, $S = \epsilon_I/\epsilon_{II}$ the permittivity ratio of the outer to the inner fluid, $R = \sigma_{II}/\sigma_I$ the conductivity ratio of the inner to the outer fluid, $\lambda = \mu_{II}/\mu_I$ the viscosity ratio of the droplet fluid and the surrounding fluid, γ the interfacial tension and E_0 the applied external electric field [45] [46].

An electric field directed upwards in the plane is applied on a droplet of fluid II in Fig. 2.8. Hence, the field will, in fluid I, induce a charge distribution in which the positive charges can be found on the bottom side of the drop of fluid II, whereas the negative will occur on the opposite side. As a consequence of this, there will be a polarization inside the drop, caused by the charge distribution in fluid I, resisting
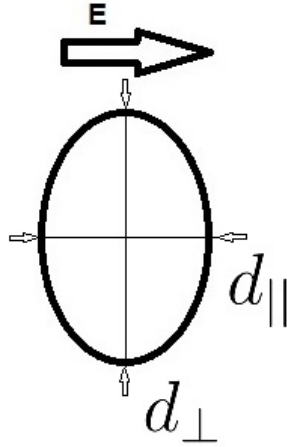
Figure 2.7: A deformed droplet in an applied external electric field. Droplet deformation is here described by the variables $d_{||}$ and $d_{\perp}$, which indicate the diameters of the drop parallel and normal to the incident electric field, respectively. In the case of a silicone oil droplet suspended in castor oil the droplet obtains an oblate shape ($D{<}0$), which comes as a consequence of the electric field working horizontally from left to right in the figure.

the already existing applied field. This means that the strength of the field inside the drop will be reduced compared to the actual applied field itself.

Due to an electric field $\vec{E}$, a drop of silicone oil suspended in castor oil is deformed so that it takes the shape of an oblate spheroidal drop, as depicted in Fig. 2.7. As the strength of the external electric field is increased, both liquids would have to move charges around in the respective liquids quicker and more charges will be induced close to the surface of the drop. When charges can not be moved fast enough inside the drop (due to having a lower conductivity than the liquid on the outside), it becomes unstable since the charge distribution now is no longer in agreement with the direction of the constant electric field. Consequently, at relatively high field strengths, Quincke rotations might occur, an effect which complicates the process of making tubes.

2.8 Quincke rotation

Quincke rotations might occur as a consequence of applying an electric field above a certain field strength in a system in which two liquids have different conductivities. That is, if a system consists of a drop of a liquid suspended in another liquid, the latter must have the highest conductivity if Quincke rotations are to be observed. Furthermore, the charge relaxation time t_c, a way of measuring how quickly charges are moved inside or outside the drop to achieve equilibrium after an external electric
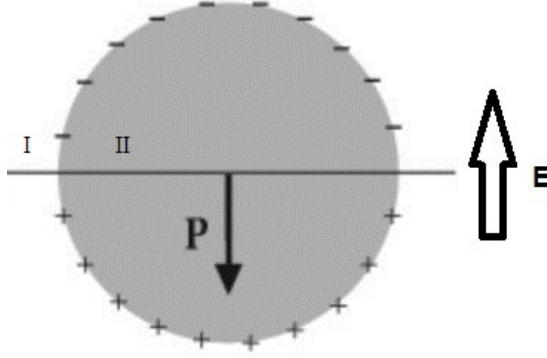
Figure 2.8: The charge distribution in liquid I close to the surface of the droplet of liquid II, with a resulting dipole moment inside the drop directed oppositely to the electric field. Figure adapted from [46].

field is applied, can be used in defining the conductivity response SR of the system:

$$SR = \frac{t_{c\,I}}{t_{c\,II}} = \frac{\frac{\epsilon_I}{\sigma_I}}{\frac{\epsilon_{II}}{\sigma_{II}}}, \tag{2.25}$$

where $S = \epsilon_I/\epsilon_{II}$ is the permittivity ratio and $R = \sigma_{II}/\sigma_I$ the conductivity ratio (I and II defined from Fig. 2.3). Hence, from Eq. (2.25), one obtains that the conductivity response in the case of $\sigma_{II} < \sigma_I$ is $SR < 1$, which means that charges in the surrounding fluid will reach the interface of the two fluids before the charges of the inner fluid do. Thus, the charge distribution of the interface is dominated by the charges in the outer fluid. By Fig. 2.8, one can see how the drop would act in an external electric field $\vec{E}$ and how the dipole moment $\vec{p}$ (and hence the polarization) works in the opposite direction of the incident field, diminishing $\vec{E}$ inside the drop. Furthermore, for a rigid sphere, the rotational rate ω,

$$\omega = \pm\frac{1}{t_{m\omega}}\sqrt{\left(\frac{E_0}{E_Q}\right)^2 - 1}, \tag{2.26}$$

is a consequence of the balance between the electric and hydrodynamic torques. Here, $t_{m\omega}$ can be expressed as

$$t_{m\omega} = \frac{\epsilon_{II} + 2\epsilon_I}{\sigma_{II} + 2\sigma_I}, \tag{2.27}$$

whilst the critical value E_Q, above which an electric field E_0 yields rotation, can be given as

$$E_Q^2 = \frac{2\sigma_I\mu_I(R+2)^2}{3\epsilon_I\epsilon_{II}(1 - RS)}. \tag{2.28}$$

Also, the distribution of induced free surface charge is

$$Q = \hat{n} \cdot (\epsilon_I \vec{E_I} - \epsilon_{II} \vec{E_{II}}) = \epsilon_I E_0 \frac{SR - 1}{S(R+2)\sqrt{1 + t_{m\omega}^2 \omega^2}} \cos(\varphi + \beta), \qquad (2.29)$$

with $\vec{E} = -\nabla V$, the electric potential V satisfying the Laplace equation $\nabla^2 V = 0$ [46].

It can easily be seen from Equations (2.26), (2.28) and (2.29) that Quincke rotations may only occur when $SR<1$, that is when the applied field exceeds a critical value E_Q.

When operating with small, almost non-conductive particles on the surface of the drop of liquid II suspended in liquid I, an electric field applied onto the system will at relatively small values only cause a deformation of the drop. However, when the field strength increases and the drop becomes unstable, the torque will cause the drop to start tilting at the angle of β,

$$\beta = \arctan\left(\frac{1}{t_{m\omega}\omega}\right), \qquad (2.30)$$

which can be seen in Fig. 2.9, and after boosting the field strength even more the drop starts rotating. The axis, around which the drop rotates, will at all times be normal to the incident electric field.
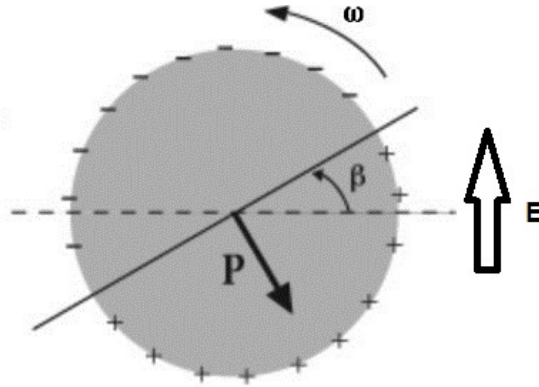
Figure 2.9: An illustration of Quincke rotation. When charges on the inside of the drop can not keep up with the movement of the charges on the outside any longer, the droplet needs to make up for the non-equilibrium state of charges. As is described in this figure, the drop starts rotating with a rotational axis normal to the incident electric field and is tilted with an angle β. The field $\vec{E}$ is directed upwards in the plane, as indicated by the arrow. Figure adapted from [46].

However, droplets are not rigid spheres, which complicates the situation greatly. A droplet located in a uniform electric field will be deformed symmetrically, assuming that the field applied is less than the critical field E_c for electrorotation of drops, but

if the field E_0 exceeds E_c the droplet will start to rotate and the liquids will have a rotational component. The straining flow affects the charge convection, causing the critical field E_c for droplet electrorotation to diverge from the critical field E_Q for Quincke rotation.

2.9 Geometric properties of oil droplets being formed into tubes

When using a pipette to create a new drop of a certain liquid II, including surface particles, suspended in a liquid I, the drop would form as a sphere with most particles on the surface. This case of a two liquid system with surface particles is found illustrated in Fig. 2.3. However, some particles would still be located inside the sphere's surface. To accelerate the process of pushing the particles to the surface, one can apply an electric field, but even then there might be particles inside the sphere due to the lack of free space on the surface. Therefore, the ideal situation depicted in Fig. 2.10 would not work fully in practice, but it shows the principle of the process.
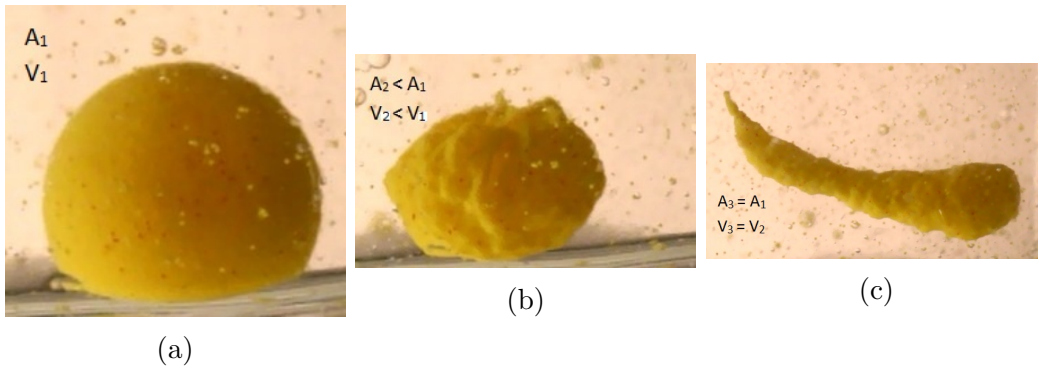
Figure 2.10: Geometric properties of the process in which tubes are made. How a tube is made is in principle illustrated through the differences in surface areas and volumes caused by the withdrawal of liquid II done between (a) and (b), and through an applied external electric field or manual deformation with pipette tips between (b) and (c).

After placing the drop of fluid II (with n particles *on its surface*) into the cell containing fluid I, and applying an electric field so that the surface is filled completely with surface particles, the surface area and the volume of the drop would then be

$$A_1 = 4\pi R_1^2$$
$$V_1 = \frac{4}{3}\pi R_1^3$$

$$(2.31)$$

with A and V as the surface area and the volume of the drop, respectively, and R as the radius of the sphere. Then, the next step would be to withdraw some of fluid

II (including the particles which are not on the surface) from the drop so that the volume ratio of surface particles to fluid increases. Thus, as it is possible to see in Fig. 2.10, the volume changes due to the amount of fluid II that was taken out. Ideally, there is still the same number n of surface particles left on the surface, shown as the leftover particles which are gathered as buckles upon the surface of the drop. Using the formulae in Eq. (2.31), the surface area and volume have now changed to A_2 and V_2, respectively, with a new radius R_2. Now, by applying an external electric field or deforming the droplet manually with pipette tips, the drop can be deformed and stretched so that the surface area increases, hence giving more space on the surface of the drop for the particles situated in the buckles. Ideally, the situation would now be that $A_3 = A_1$ and $V_3 = V_2$ (with a radius r of the tube). This is not the case in practice, since the assumption of not losing any surface particles to the surroundings, into either the pipette/syringe or the surrounding fluid I, can not hold entirely. However, in the experiments done in connection to this thesis this was seen as an acceptable approximation.

Chapter 3

Method

There might be different available methods to apply if the goal of the experiment is to obtain tubes from a droplet of one fluid suspended in a surrounding fluid with surface particles at the interface. This master thesis will focus on eight methods, for which the aim was to measure the length l of the tube and calculate the aspect ratio a=length/diameter to indicate the limitations of the different methods.

3.1 Apparatus and procedures

The experimental setup needed for making tubes in an emulsion with an electric field, pipette tips and droplet coalescence is illustrated in Fig. 3.1. To document the results that are obtained during the experiments a digital video camera is attached to the microscope (Carl Zeiss Stemi 2000-C). To be able to get good conditions for the camera, there are several light sources that are radiating relatively homogeneously onto the sample, in this case a droplet of a liquid (with surface particles attached to it) suspended in another liquid. The container has got two of its walls covered by thin, transparent layers of indium tin oxide, which allow the walls to work as electrodes. The arrows shown in Fig. 3.1v indicate that the conducting sides of the glass walls are on the inside of the sample cell. The distance between the electrodes is $L = 15.1$ mm. Furthermore, a voltage source (Glassman high voltage, 0-10000V, PS/MJ10P1500-22) is needed so that an external electric field can be applied on the sample. To be able to determine the size of the sample droplet as accurately as possible, a pipette (ThermoLabsystems U18171 4500, 5-50 μl) was used. In these three methods mentioned, only the combination of a silicone oil droplet suspended in castor oil was investigated.

Fig. 3.3 illustrates how tubes can be made by allowing spherical objects of different materials to sink through two liquids and a particle layer located at the interface. The materials and sizes of the objects used will be further discussed under the chapters "Results" and "Discussion". Moreover, Fig. 3.4 shows the containers used for the remaining experiments. In Fig. 3.4a the aim was to use a pipette or a syringe to release a liquid with particles and at the same time move the syringe
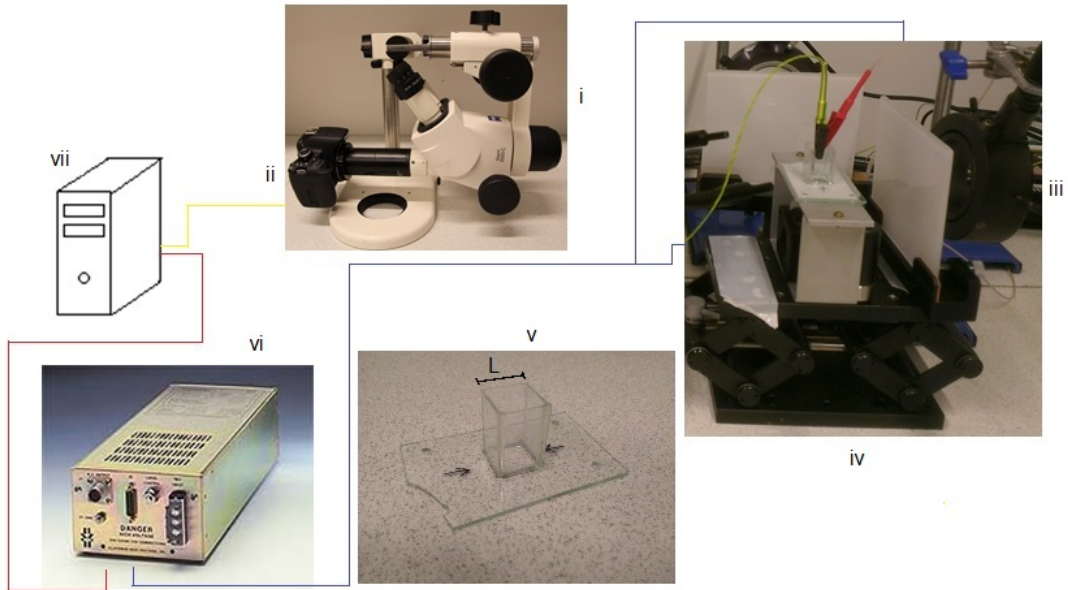
Figure 3.1: Droplet deformation by applying an electric field, by manual influence with the help of pipette tips or coalescence. To be able to observe tubes in a sample cell (v) (of length L=15.1 mm between the electrode walls) which can be moved vertically with the adjustable platform (iv), a microscope (i) with a photo camera (ii) attached is needed. Furthermore, a light source (iii) is used onto the sample cell and a voltage source (vi) is connected to a computer via a Data Acquisition (DAQ) card.

upwards in the container, whereas Fig. 3.4b illustrates a jet containing particles allowed to enter another liquid and Fig. 3.4c a jet without particles allowed to enter another liquid now covered by particles at its surface.

The methods applied in connection to this master's thesis will be explained further in the rest of this chapter.

3.1.1 Electric field

In the quadrangular sample cell mentioned previously, the principle of emulsion was used by suspending a droplet of one liquid in another liquid. By attaching the voltage source to the conducting walls of the cell, an external electric field could be applied over the content of the cell. Non-conductive particles located in a submerged droplet will after a while be found on the interface between the droplet and the surrounding liquid, due to energy considerations (as explained by Eq. (2.11)). The first step of this method is to withdraw some of the liquid from the droplet, most easily done by putting the droplet at the bottom of the sample cell, so that it sticks to the glass surface. After having withdrawn a little liquid, the surface particles start to create

buckles as a consequence of the surplus of particles located on the surface of the droplet. Then, the drop has to be transferred to a higher altitude in the sample cell, so that it will not be influenced by the glass walls. Furthermore, an electric field can be applied onto the system, deforming the droplet (as illustrated in Fig. 2.7) and thus increasing the surface area. This gives more space on the interface of the two liquids for more particles, which can participate in stretching the surface so that a tube can be made.

3.1.2 Pipette tips

After having submerged droplet into the liquid that is located in the glass cell, and used a pipette to draw out some of the liquid from the droplet, two thin pipette tips can be utilized so that the drop, partly covered by buckles, might be stretched by moving the tips back and forth along the droplet, letting the now moving surrounding fluid deform the droplet. As in the method when an external electric field was used, the resulting open spaces on the surface of the drop caused by the stretching will be filled with some of the particles that were located in the buckles.

3.1.3 Coalescing droplets
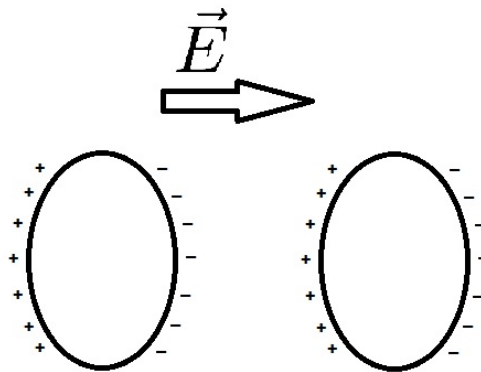
Figure 3.2: Two droplets coalescing. With an electric field directed from left to right, the charge distribution is illustrated in this figure. The dipoles of the two drops interact so that they coalesce.

Two droplets can be coalesced with the help of an external electric field to obtain non-spherical droplets jammed with surface particles. However, for this to occur the surface areas of the two initial droplets must not be jammed, since that would hinder coalescence. The coalescence process occurs as depicted in Fig. 3.2, in which an electric field is applied upon a system of two droplets suspended in another fluid. The induced charges in the surrounding fluid give rise to a polarization vector,

directed oppositely of the electric field, inside the droplets. Due to the dipoles of the drops interacting, it will be ideal for the droplets to approach each other. After the coalescence, both an electric field and pipette tips could be applied to deform the droplet into a tube.

3.1.4   Sinking objects

A fourth method for making tubes was developed through the idea of taking the different densities and viscosities of two liquids into account. In Fig. 3.3vi a test tube is filled with two liquids, one above the other. Depending on the respective densities of the liquids and surface particles (of a particular diameter), the particles are put either in the upper fluid (density $d_{\mathrm{particles}} > d_{\mathrm{fluid}}$) or in the lower fluid (density $d_{\mathrm{fluid}} > d_{\mathrm{particles}}$). Then, the system of two fluids and surface particles are allowed to reach a form of equilibrium, in which the particles are mainly located at the interface of the two liquids. Consequently, buoyancy and gravitational forces are here taken into account. The idea of this experiment was to let a small object, its cross-sectional area comparable to that of the test tube, fall through the upper fluid so that the particles at the interface would be pulled downwards, following the sinking object. Thus, some of the upper fluid (in Fig. 3.3: silicone oil of viscosity 10 cSt above castor oil) is pulled into the fluid below, forming tubes. This occurs due to what is illustrated in Fig. 2.3, with the surrounding fluid pulling more on the particles than the fluid in the droplet. In addition to this, different combinations of the two formerly mentioned oils, diethyl-phtalate, water, and water and glycerol are combined with surface particles of various types and diameters in the hope of obtaining tubes.

The sinking objects used are metal spheres of diameter 2 mm, glass spheres of diameters 3 and 4 mm, and plasticine of different sizes.

3.1.5   Pulling at particles at the interface

In this method, the same setup as in the latter method was used (see Fig. 3.3), except for the containers vi and viii for the liquids and particles. Fig. 3.3ix shows a transparent plastic cuvette, in which a particle layer is located at the interface of two liquids, which is placed on top of each other. The idea was to be able to make tubes in the upper liquid by using a thin external object, such as pipette tips, matches, plastic strips and toothpicks. It was necessary to keep various factors in mind whilst doing the experiment, amongst them the velocity with which the particles at the interface of the liquids were pulled at, as well as the type of material and the friction it caused when interacting with the liquids.

3.1.6   Releasing a liquid with particles

In Fig. 3.3 the setup is presented, whereas Fig. 3.4a illustrates in a more detailed way the principle of this method. A pipette is used to release a liquid containing
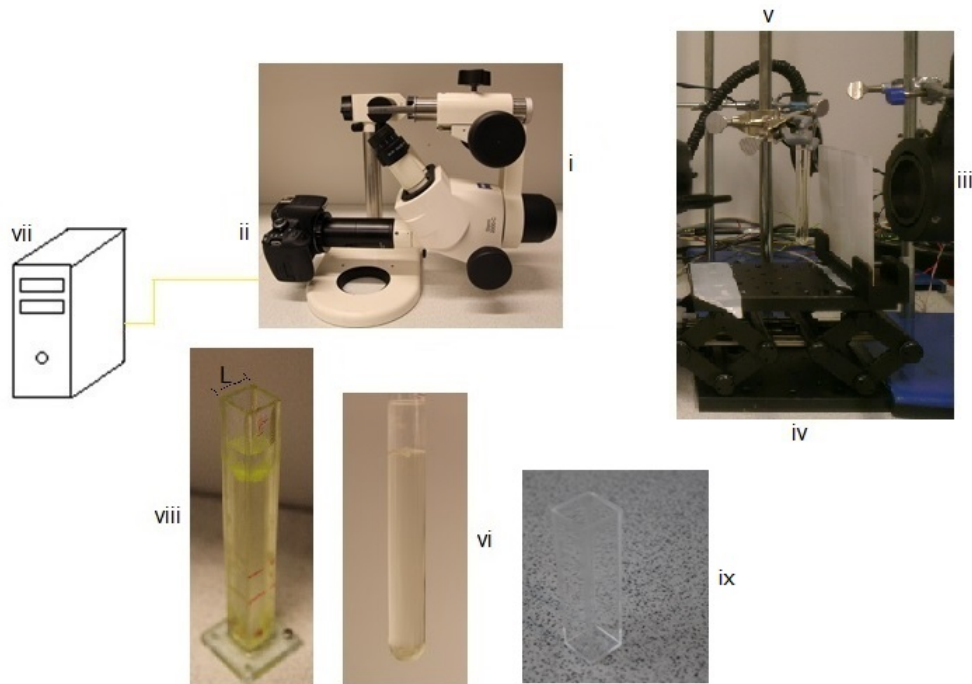
Figure 3.3: Equipment needed if the last five methods are applied. A photo camera (ii) has been connected to a computer (vii) and a microscope (i), through which the test tube (vi) can be observed. A taller container (viii) of sides L=1.40 cm was in some experiments used instead of the test tube. A light source is shown at (iii), (iv) represents an adjustable platform and (v) is the rack used to hold the test tube in place.

particles whilst the pipette itself is moved vertically upwards, thus stretching the droplet and giving the surface particles space on the interface of the two liquids to gather. Once again, the velocity of the external influencer is important to take into consideration when doing the experiments, as well as various liquids and particles of different types and diameters.

3.1.7 Releasing a jet of a liquid containing particles

Again, the setup is described in Fig. 3.3, whilst the cuvette and a more detailed depiction of this method is shown in Fig. 3.4b. Here, a fluid is put into the cuvette and a pipette or a syringe is used to eject a second liquid, containing particles, into the other liquid. The release of this jet of fluid can be done both from above and below the surface of the liquid in the container. The velocity of the ejected fluid can be varied, so that the behaviour of the two fluids can be further investigated.
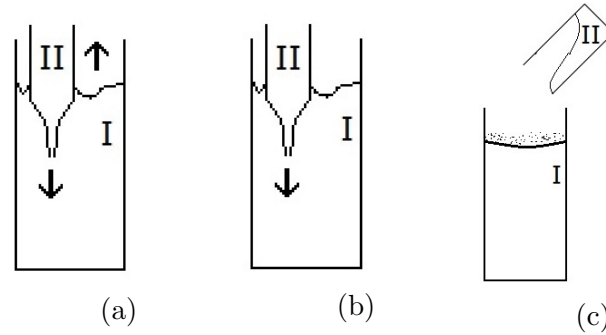
Figure 3.4: Obtaining tubes in cuvettes by using a pipette and various combinations of liquids and particles.

3.1.8 Releasing a jet of a liquid through a particle layer

This method is described in Fig. 3.4c and is built on the setup used in the former method, though differs on two crucial points - the fluid in the pipette or the syringe now does not contain particles whilst the fluid in the cuvette is covered with a layer of particles (a layer which occurred as a consequence of a relatively homogeneous solution of liquid and particles having been put into the cuvette and, with the help of time, the particles were allowed to float to the top of the liquid). This can only be done with densities corresponding to $d_{\text{liquid}} > d_{\text{particles}}$.

3.2 Sample preparations

For the first three methods, with the electrode cell, castor oil (Alfa Aesar, L04224, density 0.961 g/cm^3, viscosity 1000 cSt, electric conductivity 45 pS/m, relative permittivity 4.7) was used as the surrounding fluid for the sample drop consisting of silicone oil. These drops, to which surface particles (spherical PE63-75 particles) were added, varied in size between 20 and 50 μl. This drop was a mixture of silicone oils of different viscosities; one part of a solution of viscosity 10 cSt (Sigma Aldrich, Prod. 378321, density 0.93 g/cm^3, viscosity 10 cSt, electric conductivity $\sim$ 3-5 pS/m, relative permittivity 2.1) and two parts of 100 cSt (VWR Dow corning 200, Prod. 630074A, density 0.97 g/cm^3, viscosity 100 cSt, electric conductivity $\sim$ 3-5 pS/m, relative permittivity 2.1). This was done so that the densities of the silicone and castor oils were matched.

For the remaining five methods, different liquids were used. These were silicone oil (viscosity 10 cSt only), castor oil, diethyl-phtalate (Sigma Aldrich, Prod. 524972, density 1.12 g/cm^3), distilled water, and a mixture of water and glycerol (VWR, Prod. 24397.296, density 1.26 g/cm^3). If particles were added, the mass concentration was 5%. In the method of a sinking object with silicone oil as the upper oil (containing either CS or PE particles) and castor oil as the lower, a test tube of diameter 0.85 cm or a larger container of sides s=1.40 cm was used. In the smaller

Table 3.1: An overview of the particles used throughout the experiments.

Particle material	Provider	Particle type	Colour	Diameter μm	Density g/cc
Polyethylene (PE)	Cospheric	REDPMS	Red	45-53	0.98
		YPMS	Yellow	63-75	1.00
		UVPMS-BY2	Fluorescent yellow	90-106	1.006
Polystyrene (CS)	Microbeads Calibre	CS5	White	5	~ 1.05
		CS20	White	20	~ 1.05
		CS85	White	85	~ 1.05
Polymetylmetakrylat	Microbeads	CA40	White	40	1.2
Sodium-fluorohectorite	Corning Inc., NY [47]	NaFH	White	-	1.0

container, 1.5 ml of silicone oil containing particles was poured on top of castor oil, whilst 3 ml was used in the larger. When doing the other experiments with this method or the remaining four, also other liquids and particles were tried, but now in a cuvette of sides $s=1.0$ cm and height 4.5 cm.

The mixture of water and glycerol was mixed so that its density was matched with that of the diethyl-phtalate (hence: d-ph) with density 1.12 g/cm^3 at 20ºC. From Fig. 3.5 the right mixing ratio was found to be $\sim 50\%$ water and $\sim 50\%$ glycerol, though what was observed during experiments was that the ratio was closer to 58% and 42%, respectively.

The surface particles used in the eight methods introduced in this chapter are presented in table 3.1.

Table 4. Density of Glycerol-Water Solutions

%w Glycerine Temp. °C:	90	80	70	60	50	40	30	20	10	0
0	1.24683	1.21962	1.19200	1.16349	1.13486	1.10667	1.07892	1.05161	1.02517	0.99987
10	1.24124	1.21440	1.18701	1.15909	1.13101	1.10336	1.07623	1.04951	1.02414	0.99973
20	1.23510	1.20850	1.18125	1.15380	1.12630	1.09930	1.07270	1.04690	1.02210	0.99823
30	1.22865	1.20231	1.17519	1.14822	1.12096	1.09452	1.06856	1.04347	1.01916	0.99567
40	1.22214	1.19606	1.16920	1.14247	1.11534	1.08924	1.06371	1.03945	1.01552	0.99224
50	1.2158	1.18999	1.16338	1.13655	1.10945	1.00380	1.05849	1.03505	1.01131	0.98807
60	1.20922	1.18352	1.15683	1.13015	1.1034	1.07800	1.05291	1.02958	1.00625	0.98324
70	1.20269	1.17679	1.15036	1.12382	1.09723	1.07184	1.04729	1.02386	1.00065	0.97781
80	1.19611	1.16990	1.14384	11.1745	1.09079	1.06564	1.04093	1.01752	0.99463	0.97183
90	1.18961	1.16332	1.13730	1.11094	1.08423	1.05901	1.0343	1.01097	0.98840	0.96534
100	1.18273	1.15604	1.3018	1.10388	1.07733	1.05217	1.02735	1.00392	0.98187	0.95838
dens. at bp	1.15479	1.14004	1.12030	1.09763	1.07295	1.04947	1.02539	1.00277	0.98121	0.95838
bp	138	121	113.3	109	106	104	102.8	101.8	100.9	100

Density, grams/ml (in vacuo)

Figure 3.5: A table showing the relationship between the temperature, density of water and glycerol and the mixing ratio of the two fluids. Adapted from [48].

Chapter 4

Results

4.1 Producing tubes with an external electric field

Figure 4.1: Tubes produced by applying an external electric field on droplets of volumes 30 and $50\mu l$ in Figures (a) and (b), respectively. The electric field operates horizontally normal to the line of sight from the microscope.

Applying a strong external electric field on an emulsion so that a droplet can give space to particles on its surface might cause large deformations and Quincke rotations. Two tubes produced by the use of an electric field to deform a droplet of one part 10 cSt and two parts 100 cSt silicone oil suspended in castor oil are shown in Fig. 4.1. The surface particles covering the droplets are PE63-75. The different experiments showed that there is a large uncertainty as to whether it is possible to produce tubes, which was understood due to that the tubes differed greatly in diameter and length.

The initial volume of the droplet of silicone oil in Fig. 4.1a was 30 μl, before some of the fluid was withdrawn and an electric field applied onto the system. The electric field strength was low at first, then gradually increased due to that the droplet tended to divide itself into smaller droplets or losing its surface particles (many of which now located in buckles on the surface of the droplet after the withdrawal of oil). A deformed and sometimes rotating droplet stopped moving if the field was turned off,

contracted (due to the lack of the force from the electric field stretching the surface) and stayed in a non-spherical shape. The length l measured and the aspect ratio a calculated were 9.0 mm and 5.2, respectively. Furthermore, in Fig. 4.1b, a result involving an initial volume of the droplet of 50 μl is shown. The same procedure as before was used, and the length and the aspect ratio were found to be l=8.9 mm and a=6.7, respectively.

These results are presented in table 4.1.

4.2   Producing tubes with pipette tips

As a consequence of energy considerations, explained through Eq. (2.11), particles will try to move towards the interface between a droplet of silicone oil and the surrounding castor oil. This process can be accelerated by applying a weak electric field. With no such field influencing the emulsion, silicone oil can be withdrawn so that the volume, and hence the surface area, decreases, causing the particles to be located in buckles at the surface. Furthermore, the next step would be to move two pipette tips back and forth alongside the droplet, allowing the surrounding fluid to deform it, so that a larger surface area, onto which particles can locate themselves, is created.

Figure 4.2: The use of pipette tips to obtain tubes of silicone oil suspended in castor oil. The particles used were PE63-75.

The tube shown in Fig. 4.2 had the length l and the aspect ratio a 8.6 mm and 4.8, respectively. Other experiments were done with this method as well, but none brought about a better observation than the tube shown in Fig. 4.2. The result is presented in table 4.1.

Table 4.1: The lengths l measured and aspect ratios a calculated when applying an electric field or manually deforming droplets to obtain tubes.

Fig. no.	Length l	Aspect ratio a
	mm	
4.1a	9.0	5.2
4.1b	8.9	6.7
4.2	8.6	4.8

4.3   Coalescing droplets to obtain tubes

In the two methods mentioned above, only one droplet was used in the emulsion, whereas in this method the idea was to start off with two smaller droplets that were forced to coalesce, and thus hopefully creating a deformed surface jammed with particles. However, this method was not very successful. To coalesce, droplets will have to avoid having their surface jammed with particles, and, consequently, no surplus of particles is there to help the stretching of the surface of the coalesced droplet so that a tube can be made. A picture of the situation moments after the coalescence can be seen in Fig. 4.3a. After applying an electric field or manually deforming the droplet with pipette tips, the droplet would return to an approximate spherical shape, see Fig. 4.3b. Consequently, if tubes were to be obtained, the potential surface area of the droplet would have to be reduced which would mean to decrease the volume by withdrawing some of the liquid from the droplet and then try one of the two former methods.

(a)

(b)
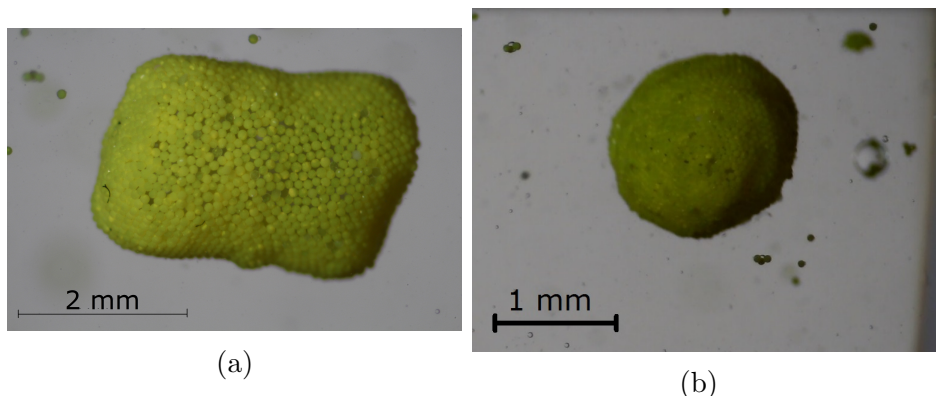
Figure 4.3: Obtaining tubes by coalescence. In (a) two drops have coalesced into one, before an electric field have been applied onto the droplet which takes an approximate spherical shape, see (b).

4.4 A sinking object in a cell containing two different fluids

This method was based on the idea of allowing an object of known diameter and mass to sink through two immiscible fluids of different viscosities and a particle layer at the interface. The fluid combination of castor oil/silicone oil (henceforth: upper oil/lower oil), no matter the viscosity of the silicone oil, put into glass containers of different horizontal cross-sectional areas, yielded no tubes. Fig. 4.4 illustrates this. An object has sunk through an interfacial particle layer, pulling some particles and castor oil along with it so that it seemed that a tube was made, but before long it broke up into droplets.

(a)

(b)
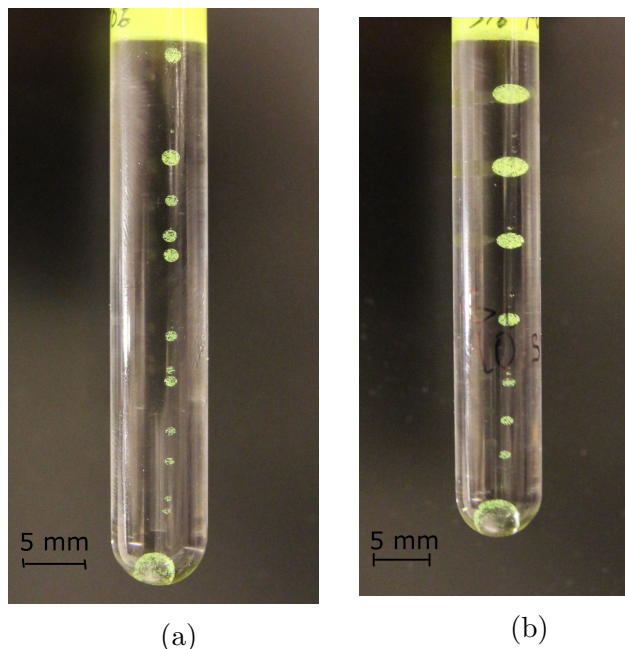
Figure 4.4: Castor oil with particles put on top of silicone oil (viscosity of 10 cSt). No tubes were obtained. As sinking objects, glass spheres of diameters 3 and 4 mm were used in (a) and (b), respectively, in a test tube of diameter 0.85cm. The surface particles mixed into the castor oil was spherical PE90-106.

By reversing the system, with silicone oil of 10 cSt on top of castor oil (silicone oil/castor oil), some interesting results were obtained. Different factors were changed, though one at a time: the particle diameter and type, the horizontal cross-sectional area of the containers as well as the diameter of the sinking objects. In Fig. 4.5, test tubes of diameter d=0.85 cm were used, with spherical CS85 or CS20 mixed into the silicone oil. The diameter of spherically shaped glass objects was changed, yielding the results in Fig. 4.5a (d=3 mm) and 4.5b (d=4 mm). The tendency was that the object with the larger diameter gave thicker and less transparent tubes.

(a)

(b)

(c)

(d)
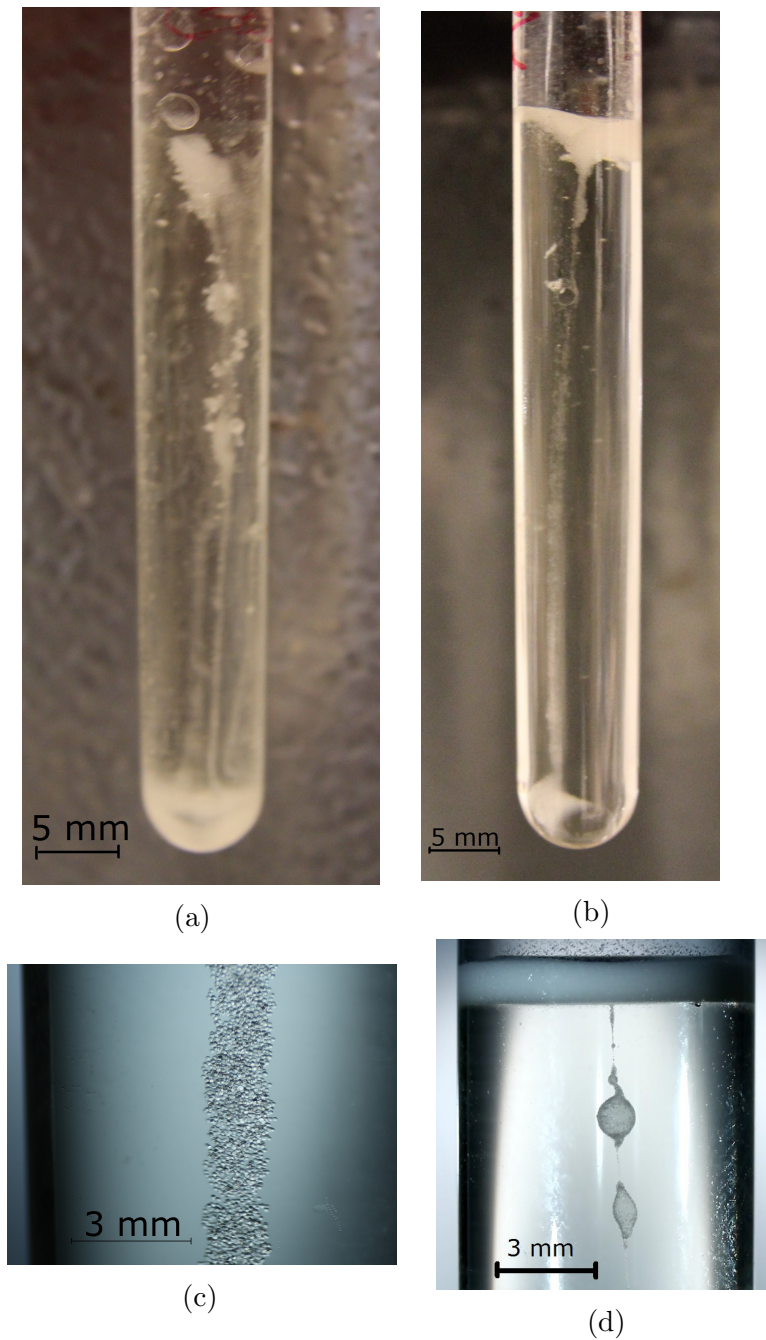
Figure 4.5: Glass spheres of different diameters sinking through an interfacial layer of CS particles. The sinking object used in (a) and (d) was a sphere of diameter $d=3$ mm, whereas a glass sphere of $d=4$ mm was used in both (b) and (c), the latter of which showing close up how CS particles are organized on the surface of a tube. The first three figures include CS85, whereas in the last, (d), CS20 was used. The lengths measured in both (a) and (b) were $l=6.3$ cm and the aspect ratios a were left uncalculated since the tube did not exist on their own in the castor oil.

In Figures 4.5a and 4.5b, the tubes (measured lengths $l \sim 6.3$ cm) are still connected both to the interface of the silicone and castor oils and to the object at the bottom of the container. This indicates that it is possible to obtain even longer tubes with this combination of fluids and particles, and thus no conclusion could be drawn as to whether there is a relationship between the lengths of the tubes and the two object diameters. The aspect ratio a was not calculated since the tube did not exist in a stable state in the castor oil on its own (away from the interface or the object). How the particles are organized on the surface of the tube in Fig. 4.5b can be seen up close in Fig. 4.5c. In Figures 4.5a and 4.5d two different particle diameters are compared (CS85 and CS20, respectively), with an object size of d=3 mm.

The same system with silicone oil/castor oil was used with spherically shaped PE45-53 put into the silicone oil. In Fig. 4.6a a glass sphere of diameter d=3 mm was used to obtain a tube of length l=1.0 cm and aspect ratio a=24, whereas a glass sphere of d=4 mm yielded l=1.1 cm and a=22 (see Fig. 4.6b). Furthermore, an approximate sphere (plasticine) of diameter d=5.5 mm was allowed to sink in a test tube in Fig. 4.6c, resulting in a length of 2.4 cm and a ratio of 37.

(a)
(b)
(c)
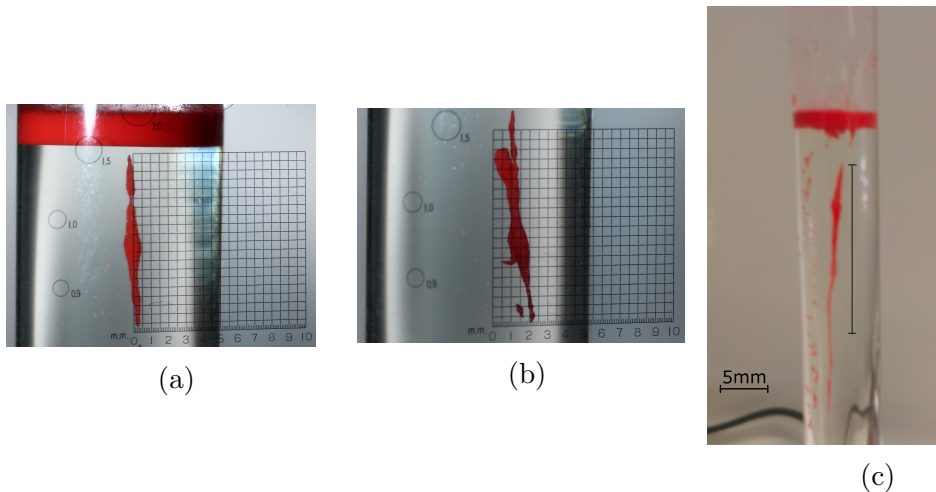
Figure 4.6: Glass or plasticine spheres as sinking objects with red PE45-53 as surface particles mixed in silicone oil in a test tube of diameter d=0.85 cm. In (a) a glass sphere of d=3 mm was used, in (b) a glass sphere of d=4 mm, whereas spherically shaped plasticine of diameter d=5.5 mm was used as a sinking object in (c). In (a), (b) and (c) the tube lengths measured were found to be 1.0, 1.1 and 2.4, respectively, and the corresponding aspect ratios calculated were 24, 22 and 37.

Even larger particles (PE90-106) were mixed into silicone oil in the hope of obtaining tubes in a test tube of diameter 0.85 cm, and different sizes on the sinking objects were tried. The tubes obtained in Figures 4.7a and 4.7c, with object diameters of 3 and 4 mm, respectively, and Fig. 4.7e, with a plasticine sphere of diameter 6.0 mm, yielded tube lengths of 1.0, 1.9 and 2.9 cm, respectively, with correspond-

Table 4.2: The measured lengths l and the calculated aspect ratios a found in experiments with the method of sinking objects and silicone oil/castor oil. If 'd' is stated, only droplets and no tubes were obtained, and 'x' means that a tube is still stuck at the interface (of the silicone and castor oils) and the object on the bottom of the test tube, thus not existing on its own in the castor oil.

Fig. no.	Particle type	Object type	Object diameter d mm	Length l of tube mm	Aspect ratio a
4.5a	CS85	Glass	3	63	x
4.5b	CS85	Glass	4	63	x
4.5d	CS20	Glass	3	d	d
4.6a	PE45-53	Glass	3	10	24
4.6b	PE45-53	Glass	4	11	24
4.6c	PE45-53	Plasticine	5.5	24	37
4.7a	PE90-106	Glass	3	10	13
4.7b	PE90-106	Glass	3	d	d
4.7c	PE90-106	Glass	4	19	21
4.7d	PE90-106	Glass	4	d	d
4.7e	PE90-106	Plasticine	6.0	29	25
4.7f	PE90-106	Plasticine	6.5	40	74
4.8a	PE90-106	Metal sphere	2	d	d
4.8b	CS85	Metal sphere	2	65	x

ing values of the aspect ratios 13, 21 and 25. Figures 4.7b (object: d=3 mm), 4.7d (object: d=4 mm) and 4.7f show results obtained in a taller container with a square horizontal cross-sectional area of sides s=1.4 cm, but only in the latter picture a tube was obtained. The length measured and aspect ratio calculated were l=4.0 cm and a=74 with a sinking plasticine object of diameter d=6.5 mm. All results are presented tidily in table 4.2. Note that the results shown in table 4.2 can not be reproduced if the viscosity of the silicone oil is changed to 100, 1000 or 10000 cSt.

Small spherically shaped metal objects of diameter d=2 mm with less friction against the silicone and castor oils were used as well. These spheres weighed less than the glass spheres of diameters 3 or 4 mm. In Fig. 4.8a, only droplets were produced by these metal spheres with PE90-106 located at the interface of the oils, but Fig. 4.8b shows a tube, which stuck to the interface and the object at the bottom of the container, covered by CS85 particles.
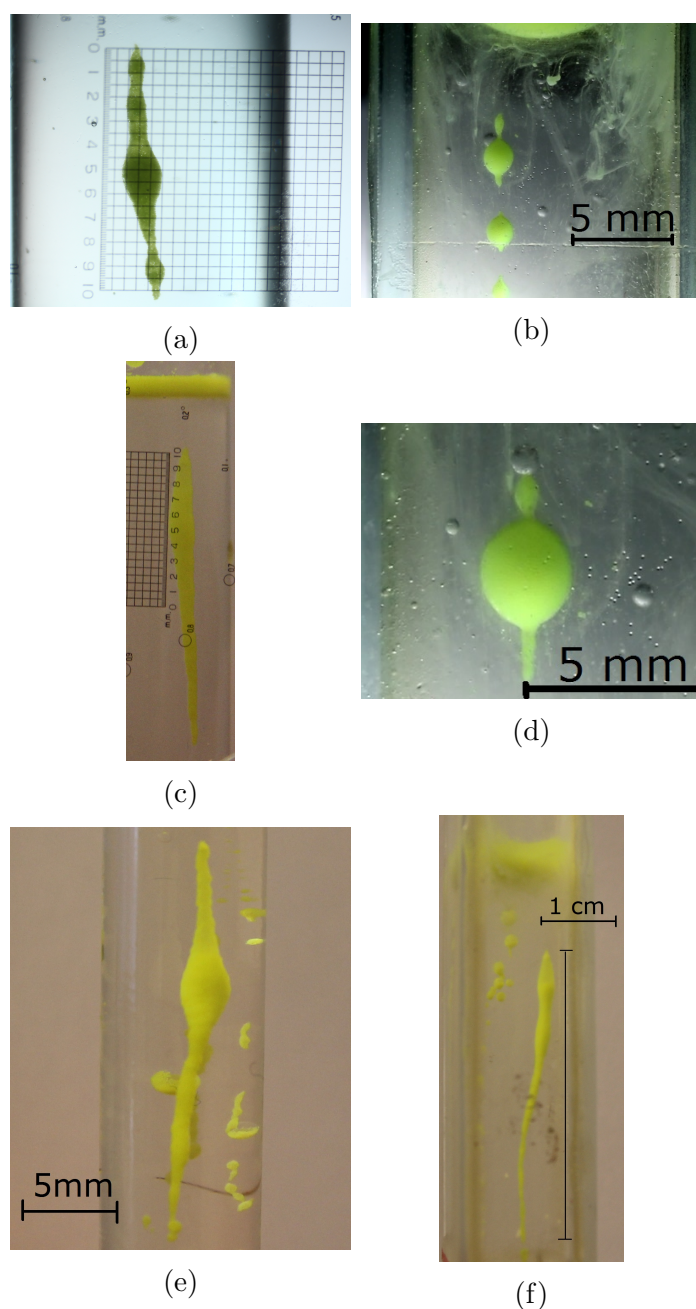
Figure 4.7: Glass or plasticine objects with a layer of fluorescent yellow particles, PE90-106. Here, two different containers were considered - a test tube of diameter 0.85 cm (seen in the left hand side column) and a higher container with a square base area with sides s=1.40 cm (the right hand side column). A glass sphere of diameter d=3 mm was used in (a) and (b) as the sinking object, whereas in (c) and (d) a sphere of d=4 mm was utilized. (e) and (f) illustrate even larger sinking objects of plasticine, diameters d=6.0 mm and d=6.5 mm, respectively. The lengths l obtained in (a), (c), (e) and (f) were 1.0, 1.9, 2.9 and 4.0 cm, respectively, and the corresponding aspect ratios 13, 21, 25 and 74.

(a)

(b)
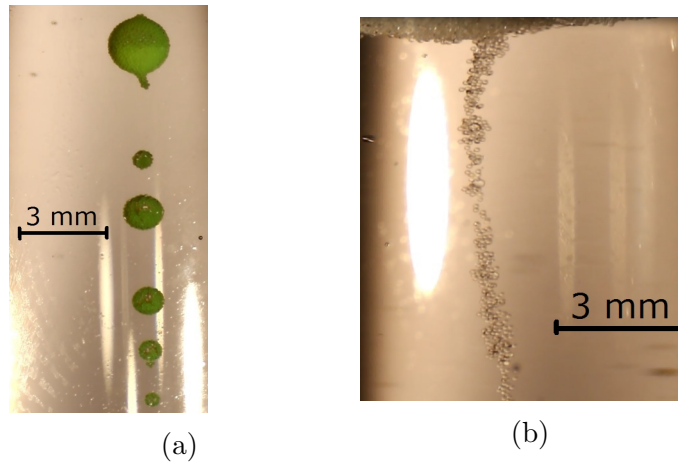
Figure 4.8: Metal spheres of diameter d=2 mm as a sinking object in an environment of silicone oil/castor oil with different particles at the interface. In (a) only drops were produced with PE90-106 as surface particles, whereas a thin tube of length l=6.3 cm was obtained in (b) with CS85 as particles.

(a)

(b)

(c)

(d)
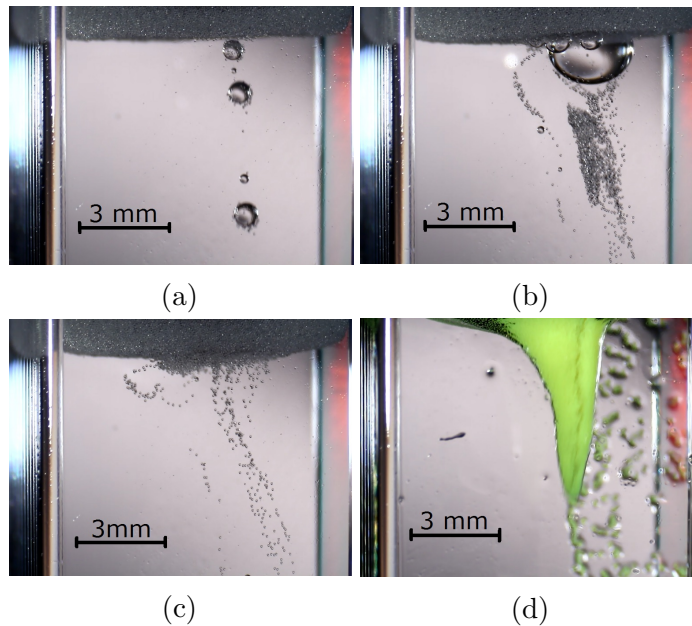
Figure 4.9: The system of silicone oil/d-ph with a sinking object involved. (a), (b) and (c) show the consequences of the same glass sphere of diameter d=3 mm sinking through the two liquids. The first depicts how the first droplets made by the objects look like before they are elevated to the interface and the second shows a larger droplet, which has let go of the object at the bottom of the container, now located at the interface, whereas the latter shows how all the droplets are absorbed back through the interface and into the upper oil. (d) describes the same combination of liquids, but now with PE90-106 particles at the interface.

There are many possible combinations for two liquids in a container. Henceforth, such a system will be presented as upper liquid and lower liquid with a / in-between.
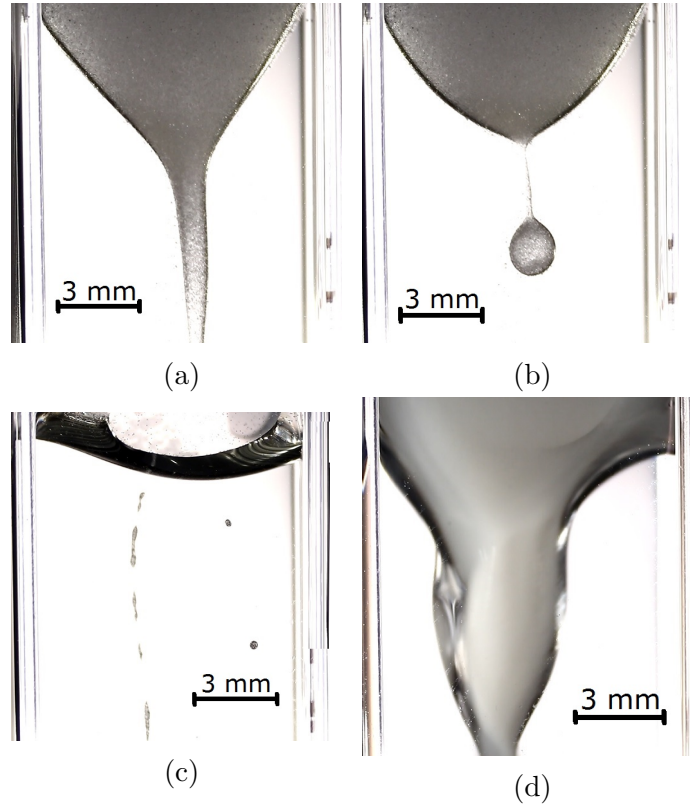
Figure 4.10: Particle layers of CA40 and NaFH at the interface of two liquids. (a) and (b) describe a situation of silicone oil/castor oil with CA40 particles, in which the former picture shows how the particle layer was stretched as a consequence of the object penetrating it before the tube broke up into a droplet, depicted in the latter picture. A system of water/castor oil with CA40 as the particles on the interface is illustrated in (c), in which small tubes can be seen. They were stable, but short and thin. (d) shows a system of water/d-ph with NaFH as surface particles, where the particle layer is shown in a deformed state before it rose back up to the interface. A glass sphere of diameter $d=3$ mm was used as a sinking object.

In Fig. 4.9, the combination of silicone oil as the upper oil and diethyl-phtalate as the lower is used, shortened as silicone oil/d-ph. Figures 4.9a, 4.9b and 4.9c describe the process of a glass sphere of diameter $d=3$ mm falling through a layer of CS85 particles. The first picture illustrates how the sphere falls through the particle layer and the d-ph, leaving a few droplets of silicone oil in its wake, whereas the second picture, taken only moments later, shows how a larger droplet had let go of the object at the bottom and now arrived at the interface of the two liquids. The last picture shows that the droplets now have been absorbed back through the particle layer into the silicone oil. However, the shape created in Fig. 4.9d was made of

the same liquids, but now with PE90-106 as surface particles. The shot was taken moments after the object let go of the silicone oil and the particle layer. However, the oil and the particles never let go of the interface, causing the shape in Fig. 4.9d to be pulled back up into the silicone oil.

Figures 4.10a and 4.10b show the same experiment with silicone oil/castor oil in two steps, the former showing the stretching of the particle layer (CA40) due to the upper liquid being pulled downwards by the sinking object, the latter showing how the stretched fluid breaks up into a droplet. Furthermore, Fig. 4.10c shows the short, thin tubes obtained in a system of water/castor oil with CA40 as surface particles, whereas Fig. 4.10d presents NaFH (Sodium-fluorohectorite) particles in a situation with water/d-ph.

(a)   (b)   (c)
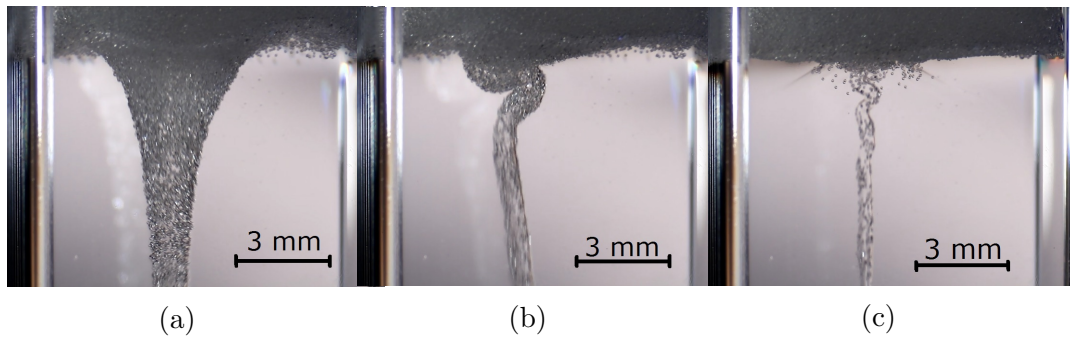
Figure 4.11: The phenomenon of a curling tube in a system of castor oil/d-ph with CS85 particles. A glass sphere of diameter $d=3$ mm was used as a sinking object. Almost immediately after letting go of the object, the situation in (a) occurs, whereas (b) and (c) describe the same experiment after a short while. The experiment yields a tube length $l \sim 2.9$ cm.

An interesting phenomenon which was observed, was some sort of a curling tube, due to buoyancy working between fluids of different densities. In Fig. 4.11 the system used has a combination of castor oil/diethyl-phtalate (d-ph) and CS85 and the process of making tubes is illustrated in three steps, in which Fig. 4.11a shows the system directly after a glass sphere of diameter $d=3$ mm is allowed to sink through the particle layer located at the interface of the two liquids. The main observation is described in Fig. 4.11b where the long tube, still stuck at the object situated at the bottom of the container and at the particle layer, curls and pushes up through the particle layer. As can be seen in Fig. 4.11c, the tube now has a much smaller diameter and the rest of the tube has been pushed upwards through the particle layer and into the upper liquid. The length of this curling tube was $\sim$ 2.9 cm.

This tube producing behaviour was observed with PE90-106, CA40 and NaFH particles as well, and even by adding no particles to the system of co/d-ph the curling again occurred. However, the curling was not seen with other combinations of fluids, such as water/d-ph and silicone oil/d-ph (even with silicone of higher viscosities, 500

and 1000 cSt, the curling phenomenon was not observed). It is relevant to mention that this phenomenon will not occur if the upper oil has a higher density than the lower, due to the buoyancy forces working on the liquid in the tube and the particles.

Furthermore, water was tried as a liquid in the process of obtaining tubes, which is seen in Fig. 4.12. Fig. 4.12a presents a system of water/d-ph with CS85 particles in which no tubes or even droplets were obtained, whereas Fig. 4.12b shows a system of castor oil/water with PE90-106 as surface particles and a hint of a tube on the right hand side of the figure, along the wall (though the liquid did never let go of the interface of the liquids).

(a)   (b)
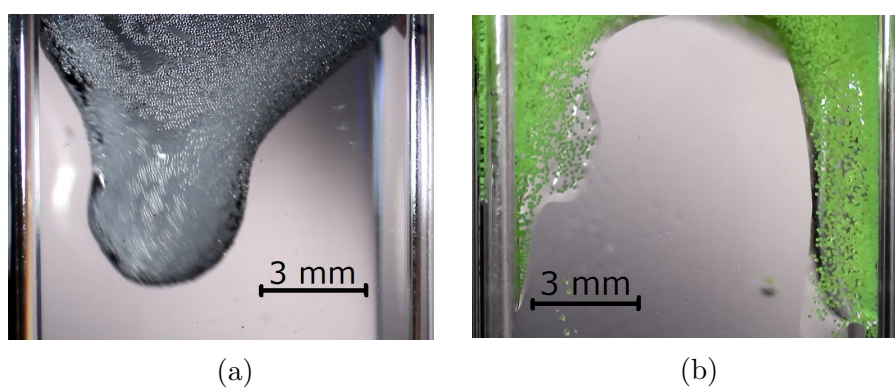
Figure 4.12: Examples of the possible systems including water as one of the liquids. (a) describes a system of water/d-ph with CS85 as particles. No tubes or droplets were created here. A situation of castor oil/water with PE90-106 can be seen in (b), in which a kind of a tube can be observed along the right hand side of the picture. The castor oil was sticking to the walls of the container rather than creating a tube, which could float freely in the water.

A quite unique observation was done with water+glycerol/d-ph (likewise, with d-ph/water+glycerol), where it did not matter whether the mixture of water and glycerol was added to the d-ph or the other way around - the same phenomenon occurred either way. Instead of placing themselves on top of each other, the two liquids in question found the system more stable when the water+glycerol mixture existed as a droplet inside the d-ph, as seen in Fig. 4.13a. Regardless of the new observations, experiments were done in the hope of obtaining tubes, as shown in Fig. 4.13. In Fig. 4.13b, CS85 was used as the type of particles mixed into d-ph in a container with water+glycerol/d-ph, whereas the use of PE90-106 as surface particles resulted in an open hole in the particle layer at the interface (due to that the close to non-polar particles are immiscible with the water (polarity issues)). Fig. 4.13c shows a system of d-ph/water+glycerol with PE90-106 in both liquids. The same result was obtained with the use of CS85.

(a) (b) (c)
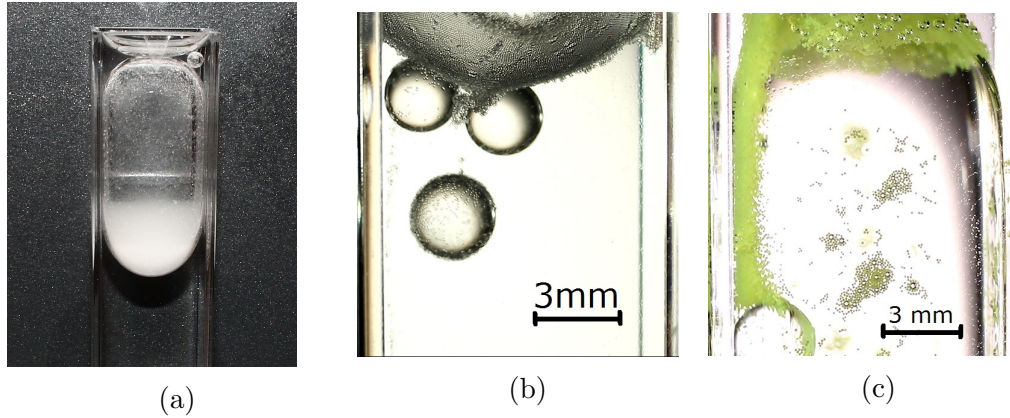
Figure 4.13: System of liquids including a mixture of water and glycerol as one of the liquids. In (a) the behaviour of water+glycerol in another liquid is described (CA40 particles situated there for contrast reasons). (b) shows a system with water+glycerol/d-ph and CS85 with only droplets uncovered by particles as the result, whereas (c) illustrates a situation with d-ph/water+glycerol and PE90-106. In the latter picture, the glass sphere of diameter d=3 mm can be seen at the bottom left corner to illustrate the problem about this system. The special behaviour of the water/glycerol mixture makes the glass spheres search for the corners of the container rather than to go through the lower liquid.

All the results obtained with these combinations of fluids and the particles in question can be seen summarized in table 4.3.

Table 4.3: A summary of the registered results when using the method of a sinking object. 'co' and 'so' represent castor oil and silicone oil, respectively, whereas 'w' means water, 'w+g' water and glycerol, and 'd-ph' diethyl-phtalate. The particles used are listed in the left hand column. Furthermore, 'nd' means that no droplets were obtained and 'd' means that droplets were the result of an experiment, whilst 't' stands for tubes, 'c' for the curling phenomenon shown in Fig. 4.11, 'sw' for that the liquids switched places due to gravity, 'imm' for the particles being immiscible with the liquid in question (caused by polarity) and '-' for a combination of liquids and particles not tried.

	co/so	so/co	co/w	so/w	co/d-ph	so/d-ph	w/d-ph	w/co	w/so	w+g/d-ph	d-ph/w+g
CS85	nd	t	nd	nd	c	d	nd	sw	sw	d	nd
PE90-106	nd	t	nd	nd	c	d	nd	imm	imm	d	nd
CA40	d	d	nd	nd	c	d	nd	d	nd	-	-
NaFH	sw	d	nd	nd	c	d	nd	sw	sw	-	-

4.5 Pulling at particles at the interface
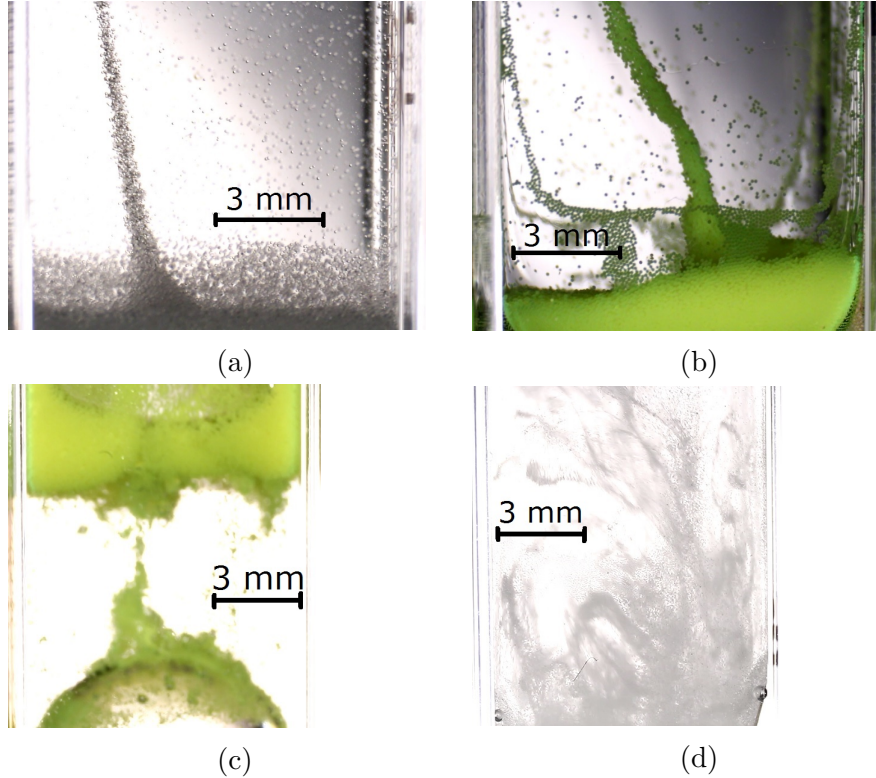
Figure 4.14: Pulling at a particle layer located at the interface of two liquids. (a), with castor oil/d-ph and CS85, describes a situation in which a tube is made, though it still sticks to the particle layer at the interface. The length was measured to be $l \sim 1.0$ cm and the aspect ratio $a \sim 20$. A similar situation can be seen in (b), only with silicone oil/d-ph and PE90-106, yielding $l \sim 0.8$ cm and $a \sim 12$. (c) shows a system of d-ph/water+glycerol. Particles have here let go of the water mixture, due to polarity issues, so that a lot of them are located at the top of the d-ph as well. Mostly, only particles were drawn away from the interface. Another system, water/silicone oil with CA40, is illustrated in (d). The pipette did not succeed in pulling the silicone oil vertically upwards, so that only particles were observed moving around in the water.

After attempting the method of the sinking object, the opposite process was used to try to obtain tubes. Instead of allowing an object to fall through the two liquids and the particle layer at the interface, an external object (toothpicks, matches, pipette tips and plastic cable ties) was now used to pull at the particle layer. The goal was to achieve tubes by pulling some of the lower fluid along with some of the particles up into the upper fluid. Fig. 4.14a contains a combination of castor oil/d-ph with CS85 as surface particles. The tube that can be seen (still stuck to the particle layer at the interface of the two fluids) has a length $l \sim 1.0$ cm and

Table 4.4: Results obtained by using the method of pulling at a particle layer which is located at the interface of two liquids. 'co' and 'so' represent castor oil and silicone oil, respectively, whereas 'w' means water, 'w+g' water and glycerol, and 'd-ph' diethyl-phtalate. The particles used are listed in the left hand column. Furthermore, 'nd' means that no droplets were obtained and 'd' means that droplets were the result of an experiment, whilst 's' stands for tubes that have not let go of the particles at the interface and 'o' for a situation in which there is an open space in the middle of the particle layer at the interface. 'sw' tells us that the liquids switched places due to gravity and 'p' that there are only particles and no liquid pulled along by the pipette. '-' stands for a combination of liquids and particles not tried.

	co/so	so/co	co/w	so/w	co/d-ph	so/d-ph	w/d-ph	w/co	w/so	w+g/d-ph	d-ph/w+g
CS85	s	d	o	o	s	nd	o	sw	sw	nd	p
PE90-106	s	p	o	o	s	s	o	sw	sw	nd	p
CA40	d	d	d	p	nd	nd	p	p	p	-	-
NaFH	sw	d	d	nd	nd	d	nd	sw	sw	-	-

an aspect ratio $a \sim 20$. Another combination of fluids and particles looked at, was silicone oil/d-ph and PE90-106, seen in Fig. 4.14b. The total length of the tube (without it having let go of the interface) was measured to be $l \sim 0.8$ cm, whereas the aspect ratio was calculated to be $a \sim 12$. The pulling on the particles and the lower liquid had more or less the same effect as in the former picture, since the liquid and particles, initially being pulled upwards, let go of the external object before the interface.

Due to the hydrophobic properties of the PE90-106 particles, a choice was made to include particles in both liquids, d-ph/water+glycerol, shown in Fig. 4.14c. This was done because it seemed like a smart move to have as many particles as possible available in the container so that a layer of particles could be created at the interface of the fluids. Alas, no good results were obtained. As shown in Fig. 4.14c, some particles could be loosened from the interface with only a very small amount of water+glycerol solution with it, mostly with the consequence of allowing some particles to float to the top of the container (the density of the d-ph being much higher than that of the particles). Furthermore, Fig. 4.14d shows a fourth result obtained by applying this method. A combination of water/silicone oil and CA40 particles was not very successful, since the particles seemed uninterested in both pulling the silicone oil upwards with them and sticking to the pulling object. These particles ended up sinking back to the interface after a few seconds.

All results obtained through the use of this method are presented in table 4.4.

4.6   Releasing a liquid with particles

To use a pipette to release a liquid in another would normally cause the injected fluid to create a spherical droplet. However, through this method the aim was to see if it was possible to obtain tubes by using a pipette to inject a fluid into another whilst moving the pipette upwards. In Figures 4.15a and 4.15b, a combination of silicone oil/castor oil was used with CS85 and PE90-106 particles, respectively. The former picture shows a tube which is about to break up into separate droplets, whereas the latter shows a similar situation, only after the break-up. Furthermore, Fig. 4.15c illustrates the importance of taking the corresponding densities of the two fluids into consideration when doing this kind of experiments. The castor oil was attempted released into the d-ph, only to discover that no matter how fast the pipette was pulled upwards, the released fluid (including particles) rose to the top of the container. The particles used in the castor oil was PE90-106.

The findings after applying this method is stated in table 4.5.

(a)   (b)   (c)
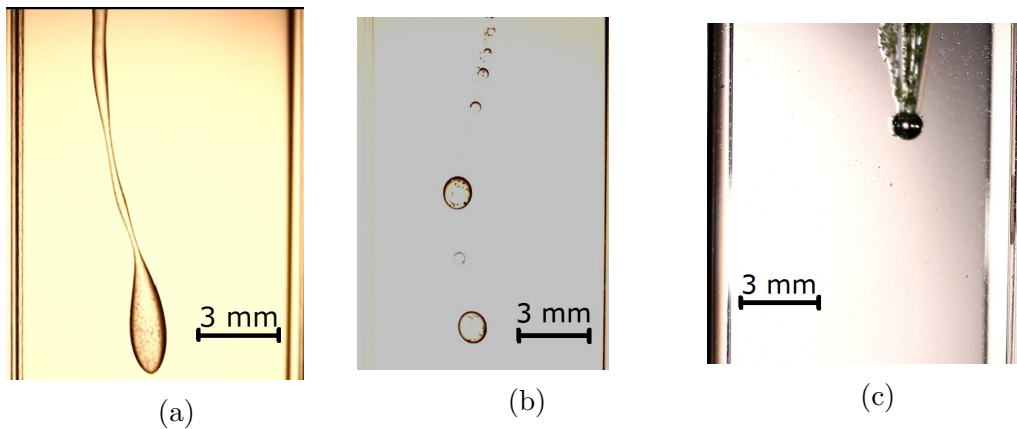
Figure 4.15: Releasing a liquid, including particles, with a pipette which is moved vertically upwards at the same time. (a) and (b) describe a system in which silicone oil, containing particles, is injected into castor oil. The former shows the system, with CS85 particles, in a non-stable state a short while before the tube breaks up into droplets, whereas the latter shows stable droplets containing PE90-106. (c) shows a situation with castor oil being injected into d-ph, and what the difference in densities of the two liquids result in - buoyancy forces cause the castor oil to rise to the surface of the d-ph.

Table 4.5: Releasing a liquid containing particles with a pipette whilst pulling the pipette upwards. 'co' and 'so' represent castor oil and silicone oil, respectively, whereas 'w' means water, 'w+g' water and glycerol, and 'd-ph' diethyl-phtalate. The particles used are listed in the left hand column. Furthermore, 'd' means that droplets were the result of an experiment, whilst 'b' stands for the buoyancy which causes the droplet to float to the top of the liquid situated in the container, as shown in Fig. 4.15c. 'imm' stands for that the particles are immiscible with a liquid (due to polarity issues).

	co/so	so/co	co/w	so/w	co/d-ph	so/d-ph	w/d-ph	w/co	w/so	w+g/d-ph	d-ph/w+g
CS85	d	d	b	b	b	b	b	d	d	d	d
PE90-106	d	d	b	b	b	b	b	imm	imm	imm	d

4.7 Releasing a jet of a liquid containing particles

(a)   (b)
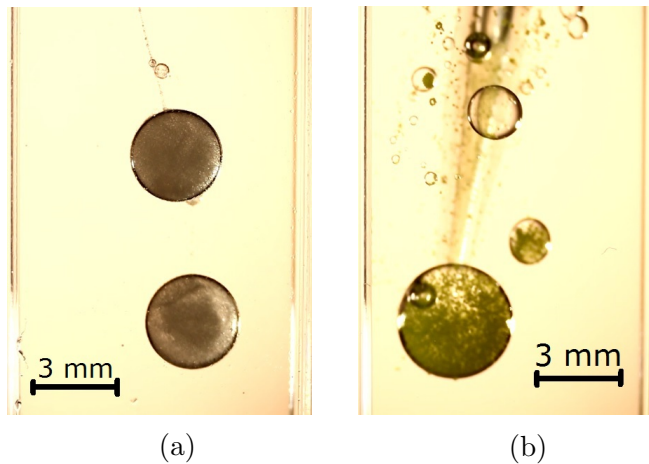
Figure 4.16: Releasing a jet of a liquid, which contains particles, into another liquid with a pipette. Both (a) and (b) illustrate a system in which silicone oil, with particles, is injected into castor oil. Whilst the system in the former picture includes CS85 particles, the latter contains PE90-106.

Yet another method for making tubes was examined. It consisted of silicone oil/castor oil and particles CS85 and PE90-106 in Figures 4.16a and 4.16b, respectively. No matter the velocity at which the oil in the pipette was ejected, only drops were created in the other liquid. Also, combinations like castor oil/d-ph and silicone oil/d-ph were tried, getting more or less the same result as in Fig. 4.16, but now with fewer particles on the surface of the droplet since many particles were stuck in the pipette whilst the castor oil was ejected.

No tubes were made by allowing liquid to be ejected from above the surface of

Table 4.6: Releasing a jet of a liquid containing particles into a liquid situated in a container. 'co' and 'so' represent castor oil and silicone oil, respectively, whereas 'w' means water, 'w+g' water and glycerol, and 'd-ph' diethyl-phtalate. The particles used are listed in the left hand column. Furthermore, 'd' means that droplets were the result of an experiment, whilst 'b' stands for the buoyancy which causes the droplet to float to the top of the liquid situated in the container, as shown in Fig. 4.15c. 'imm' stands for that the particles are immiscible with a liquid (due to polarity issues).

	co/so	so/co	co/w	so/w	co/d-ph	so/d-ph	w/d-ph	w/co	w/so	w+g/d-ph	d-ph/w+g
CS85	d	d	b	b	b	b	b	d	d	d	b
PE90-106	d	d	b	b	b	b	b	imm	imm	imm	b

the liquid situated in the container. The liquids located themselves orderly on top of each other when doing experiments with combinations of liquids, except for in the case of d-ph/water+glycerol, which created the same situation as was observed in Fig. 4.13a.

The results of all experiments done in connection to this method is presented in table 4.6.

4.8 Releasing a jet of a liquid through a particle layer

(a)

(b)
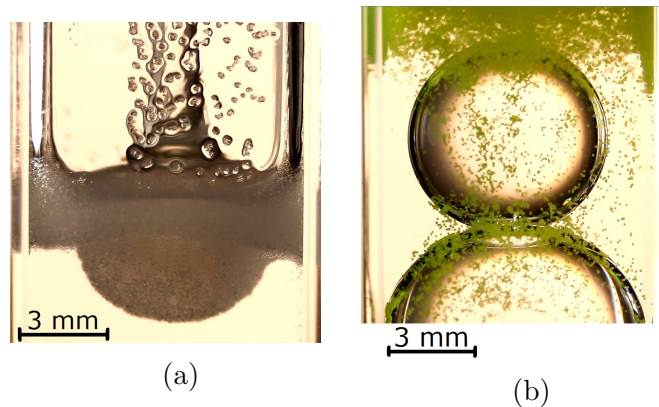
Figure 4.17: A jet of liquid poured through a layer of particles on top of another liquid. (a) shows a situation in which the liquid (here: d-ph) already situated in the container at the beginning of the experiment has a higher density than the one (here: castor oil) being poured from another container. The particles used were CS85. The combination of liquids in (b) was water+glycerol/d-ph and the particles used were PE90-106. Here, droplets were created, which later coalesced into one.

The goal of this method was to let a jet of one liquid penetrate the surface, covered with particles, of another which is situated in a container. Several combinations of liquids were tried, however, only a liquid of a higher density than the particles CS85 and PE90-106 could be used as the liquid in the container, since the particles had to be located at the surface. The systems involving silicone oil or water being poured into a cuvette containing d-ph gave the same result as with castor oil being poured into d-ph, shown in the Fig. 4.17a, in which the surface is deformed downwards due to the force of the liquid being poured into the cuvette. No tubes or droplets were created, however, since the difference in densities of the two liquids was too large.

Droplets were obtained through allowing water+glycerol to be poured into a container of d-ph, as seen in Fig. 4.17b, droplets which later coalesced into one. This occurred with both particle types CS85 and PE90-106. To turn the system around, allowing the cuvette to contain water+glycerol instead, gave a result much similar to the one in Fig. 4.17a.

The obtained results due to the use of this method can be found in table 4.7.

Table 4.7: Pouring a jet of a liquid through a particle layer situated on top of another liquid. 'co' and 'so' represent castor oil and silicone oil, respectively, whereas 'w' means water, 'w+g' water and glycerol, and 'd-ph' diethyl-phtalate. The particles used are listed in the left hand column. Furthermore, 'd' means that droplets were the result of an experiment, whilst 'top' means that the liquid being poured from above ends up on top of the particle layer (see Fig. 4.17a) and 'temp' stands for a droplet being created only temporarily before it rises up to and through the particle layer into what now has become the upper liquid in the container. 'imm' stands for that the particles are immiscible with a liquid (due to polarity issues).

	co/d-ph	so/d-ph	w/d-ph	w+g/d-ph	d-ph/w+g
CS85	top	top	temp	d	d
PE90-106	top	top	temp	d	imm

Chapter 5

Discussion

By applying an electric field, it might be difficult to predict the influence it would have on a droplet, whether it would be deformed and/or rotated (Quincke rotations). Therefore, it was easier to obtain good results through using pipette tips. Nevertheless, some of the results obtained with an electric field influencing the system of two liquids and surface particles were satisfying regarding the length l and aspect ratio $a = l/d$ (d=tube diameter) of the tubes. However, the aim of the experiments was to obtain tubes of a constant diameter along the entire length, which was not necessarily the case for the tubes made through the experiments. Other disadvantages of applying an electric field (especially a strong field) to obtain tubes, were that the droplets tend to divide themselves into two or more smaller droplets and that the particles situated in buckles at the surface of the droplets tend to let go of the surface, reducing the number of particles available for the making of a tube. By using pipette tips, the deformation could, to a higher degree, be controlled manually by pulling and pushing the droplet in a wanted direction, thus easier making the diameter closer to constant along the entire length of the tube. The limitation to how long the tube could be made depended upon the relationship between the surface area of the droplet (and hence, the volume) and the number of particles available at the surface. In general, it seemed that the more silicone oil that was withdrawn from the droplet, the longer the tubes could be made and the higher values of the aspect ratio a were achieved. However, there is a catch to this generalization. To take out too much fluid from the droplet would mean to reduce the possible surface area onto which the particles can be located, so that the droplet would exist with buckles all over it no matter how much it is pulled at.

In Fig. 4.1 different initial volumes were used for the droplets, but no particular conclusion was found as to whether the initial volume had something to say for the final result. The lengths measured for the tubes in the Figures 4.1a and 4.1b (and other experiments done) were comparable, even though the initial volumes were 30 and 50 μl, respectively. The lack of difference in the results might be due to some uncertainty factors, such as the withdrawal of fluid from the droplets as well as the particles being torn away from the buckles at the surface of the droplet by an external electric field.

A less successful method applied on the system of silicone oil/castor oil (henceforth, this will indicate upper liquid/lower liquid in a container) was to make tubes out of a droplet (its surface jammed with particles) which is a result of the coalescence of two droplets, seen in Fig. 4.3. Due to that the initial droplets can not be entirely covered with particles if coalescence of droplets shall occur, there were too few particles compared to the surface area of the coalesced drop to be able to make a tube. From here, the methods of applying an electric field or deforming droplets manually by pipettes have to be used, so it seems the best solution is to start off with one drop containing particles both at the surface and within. Thus, there are a lot of particles in reserve so that the newly exposed surface, caused by the stretching, can be filled and the drop can exist in a stable state as a tube rather than a sphere.

Applying the method of a sinking object, various combinations of fluids and particles were used. A system that was investigated, was that of castor oil/silicone oil in a glass test tube. No tubes were created, despite that the viscosity of the silicone oil was varied between 10, 100, 1000 and 10000 cSt and different particle types and sizes were used. This result occurred due to the described situation in Fig. 2.3, where the surface particles favour the castor oil rather than the silicone oil (fluid I and fluid II, respectively). The observation of no tubes with this combination of fluids, might be the consequence of the superior polarity of the castor oil molecule, pulling at the particles to a larger degree than the silicone oil does. Thus, the droplet made by the sinking object collapses in on itself and breaks up into smaller droplets. Another reason for the malfunction of the castor oil/silicone oil system might be the surface tensions of the fluids.

Also, the opposite combination of fluids was tried, with much greater success. When having a system of silicone oil/castor oil, the former oil is pulled downwards through the interface of the two fluids, pulling particles along with it. Now, the castor oil will help expand the tube by pulling at the particles, a greater part of which will now be located in the castor oil (depicted as oil I in Fig. 2.3), so that a tube can exist.

The particles at the interface of two liquids in a system used in the method of a sinking object, were deposited at the interface through being allowed to sink to the bottom of the silicone oil during a short time period. Due to that the particles are not entirely tidily located, there is a lot of open space, to which the particles can move, if necessary. An important observation done throughout the experiments, was that the tubes depended strongly on the particles diameter - the larger the particles, the longer the tubes. This can be a consequence of that larger particles are heavier and have a larger volume, since a larger force then is needed to move the particles to the side when an object is sinking through the interfacial particle layer. Bearing in mind that larger identical particles attract each other more than smaller (according to Fig. 2.4a) and that the energy of the particles is higher when it is moved away from the interface (see Eq. (2.11)), the object is decelerated, hence it has more time to pull particles downwards with it. This is underlined through the Figures 4.6b

and 4.7c with the lengths 1.1 cm and 1.9 cm, respectively, using a glass sphere of diameter d=4 mm. In addition to this, there is a correspondence between the size of the sinking object and the aspect ratio a. Values for both the length and the ratio increase with larger object sizes, a conclusion which can be drawn from Fig. 4.7. Even though the values of the aspect ratio for the tubes in Figures 4.6a and 4.6b are quite similar, the principle of the correlation between object sizes and aspect ratios is underlined by the results obtained from the Figures 4.6b and 4.6c.

The observation of the tube length dependency upon the object size seems to be correct, however, another opposing idea came up. The aim of experiments done with the methods of a sinking object or a pulling object would be to increase the volume ratio of particles to fluid, and thus the objects should be of smaller diameters so that the diameter ratio $q = d_{particles}/d_{tube}$ grows larger. However, by decreasing the object diameter, and hence the tube diameter, the objects were not necessarily able to pierce through the particle layer (diameter $d \leq 1$ mm) or pull enough particles/liquid with them. This could be further investigated in the future.

In addition to depending on the mass (and consequently, the volume) of the particles, the length of the tubes also seemed to correlate to the relationship between horizontal cross-sectional areas of the object and the container. It was observed that objects of large cross-sectional areas compared to that of the container produced the longest tubes. This is illustrated by the Figures 4.7c and 4.7d, and also by 4.7e and 4.7f which show that, above a certain diameter of the object, the longest tube can now be found in the container with the largest cross-sectional area.

The largest easily observed difference between the CS and the PE particles, was the tendency to stick to each other. In the case of CS particles, this meant that longer tubes could be observed, if any were achieved. This property could be both an advantage and a disadvantage - the former due to that the particles would more easily stick to the object when it sinks through the interface of two liquids, the latter since the particles could, to a larger degree, stick to the particle layer rather than the object. What would occur depends on the respective properties of the liquids and particles. Again, the size of the particles at the interface of the liquids matters. The larger the particles, the longer the tubes. This is shown in the Figures 4.5a and 4.5d with CS85 and CS20, respectively, and a sinking object of diameter d=3 mm. Despite the fact that the use of CS particles gave better results for the lengths and aspect ratios than PE particles, the tidiness of particles at the surface is lower. Instead of being located in one layer, as with the PE particles in Fig. 4.6a, the CS particles tended to place themselves in two or more layers, as shown in Fig. 4.5c. This lack of order gives rise to another problem - it is not easy to see whether the tube is hollow or if it is a long tail of particles left behind by the sinking object, see Figures 4.5a, 4.5c and 4.8b. This problem has to be investigated further in the future.

The friction between the object and the fluids and particles is also a factor that has to be taken into consideration. As can be seen from using PE90-106 particles, shown in the Figures 4.7a and 4.8a with a glass sphere of diameter d=3 mm and

a metal sphere of diameter d=2 mm, respectively, it is advantageous to have a certain amount of friction in the liquids. The velocity with which the object passes through the particle layer at the interface of the two liquids also matters. With larger velocities (less friction), less particles would be pulled along with the object. This was observed with a metal sphere (rather than the glass sphere) - due to the lower amount of friction, the object sinks faster through the upper liquid, obtaining shorter tubes or none at all.

The stability of the tubes varied depending on the particle type. Tubes covered by PE particles stayed stable for days, as opposed to those made with CS particles. After a short time period, the CS started to grow into lumps, thus increasing the density of particles. Finally, the lumps got too dense and, consequently, sunk to the bottom of the container.

The method of a sinking object was used for another combination of fluids as well. This time, silicone oil/d-ph was used along with a glass object of diameter d=3 mm as the sinking object. The three Figures 4.9a, 4.9b and 4.9c show the same experiment with CS85 particles in three steps. Due to a a relatively large difference in densities of the two fluids, the silicone oil, in the form of droplets, quickly started rising towards the interface. Secondly, a larger droplet with a tail of surface particles finally let go of the object now located at the bottom of the container and lastly, as shown in Fig. 4.9c, the droplets were absorbed upwards through the particle layer and back into the silicone oil above. On the other hand, in Fig. 4.9d PE90-106 was used as surface particles, resulting in a tube, still stuck at the interface, before it rose back up to the particle layer. This experiment yielded no stable droplets or tubes. Fig. 4.9 shows typical results obtained by investigating combinations of other liquids with this method.

Water is an interesting liquid for several reasons, one of which is that it is harmless for the body and thus possible to use for medicinal purposes [6] [7]. Because of this, it was desirable to see if water could be used as one of the liquids in the process of obtaining tubes. A promising result was obtained through the use of water/castor oil with CS85 as particles, yielding short, thin tubes, seen in Fig. 4.10c, caused by the corresponding polarities and surface tensions of the liquids and particles. All in all, water was difficult to apply due to the need of adapting to the viscosity and polarity, but most importantly the density of another liquid. The latter factor plays a crucial role due to the resulting buoyancy forces working on the least dense liquid whilst present in the other. This was the idea behind why the silicone oil was matched to the density of the castor oil for the first three methods (by mixing silicone oils of different viscosities, 10 cSt and 100 cSt), and this is the reason that most of the obtained results with water ended with producing droplets only or nothing at all. As seen from Figures 4.10d and 4.12a from the method of a sinking a object, Fig. 4.14d for the method of pulling a liquid through a particle layer into another liquid, as well as from castor oil/water or silicone oil/water in tables 4.5 and 4.6, the difference in densities of the two liquids matter.

As a consequence of this, a combination of two liquids with more or less the

same density had to be found. And thus, glycerol was chosen to be added to water so that the density of diethyl-phtalate (1.12 g/cm^3) could be matched with that of water and glycerol. This gave rise to an interesting occurrence, which allowed the water and glycerol to, instead of placing itself on top of the liquid already situated in the container, locate itself below the surface of that liquid and try to be stable as a droplet, minimizing the contact surface of the two liquids (see Fig. 4.13a). This occurred both in castor oil, silicone oil and d-ph and complicated things even further, as seen in Fig. 4.13c, in which a glass sphere of diameter d=3 mm was sinking through d-ph situated above the water+glycerol mixture, and thus being led to one of the corners of the container instead of going through the middle of the particle layer. By never entering the region of water+glycerol, no tube of d-ph can be made by the object, and only particles are pulled downwards along with the glass sphere. Problems also came during experiments in which pipette tips were used to pull at the particle layer at the interface of two liquids. Particles had the tendency of moving away from the middle of the curved interface of d-ph/water+glycerol, as observed in Fig. 4.14c. Hence, it was not possible to pull enough particles upwards along with the pipette tip to be able to make tubes in this case. Only a few particles could be loosened from the interface, but no water+glycerol could be found inside the region of d-ph.

This leads to the next factor of interest. Viscosities might matter in some cases, especially with the method of a sinking object, in which some resistance in the liquid could be wished for, so that the object is decelerated to a larger degree than what is the case in water. However, the viscosity should not be too high either, since the object would then never be able to pass through the upper liquid, let alone the particle layer. Doing experiments with silicone oil/castor oil and CS85 or PE90-106 particles, tubes were obtained if the silicone oil had a viscosity of 10 cSt, but no tubes were created if the oil was of 100 cSt. The fact that water has a low viscosity might also be the problem in the case described in Fig. 4.14c, where the water+glycerol mixture is not possible to pull upwards into the d-ph. With a higher viscosity, the mixture could possibly bind itself to the pulling object to a larger degree. Various objects, by which the particle layer was pulled at, of different materials were tried, so that the friction between the liquid and a certain material could be exploited. Even glasspaper was used on plastic pipette tips (yielding the best results without glasspaper), toothpicks and cable ties to see if that could increase the friction between the object and the liquids, without any further success. Hence, the deformation of the interface caused by gravitational pull on the particles gave rise to lateral capillary forces (described in Fig. 2.4a) which were stronger than the forces between the pulling objects and the particles or liquids. Thus, the particles favoured to stick to the interface rather than the pulling object. The main problem that occurred with these pulling objects, was that they did not pull enough of the particles with them, so that in the experiments (of the last four methods) yielding droplets the particles were too few to be able to jam the droplet surface. Perhaps an increased concentration of particles partly could solve this problem.

An intriguing observation, caused by the surface tensions of the fluids, is described in Fig. 4.11, in which CS85 particles and a system of castor oil/d-ph were used during experiments done in connection to the method of sinking objects. The large difference in density of the two liquids made the tube rise from the object at the bottom of the container to the interface with a velocity that depended upon the size of the glass sphere - the larger the diameter, the larger the velocity of the rising tube. After a while the tube was much thinner and a form of jet instability occurred. The jet started to stretch and contract along the length of the tube, giving an impression of displaying a wavelength dependent jet which was about to break up into droplets, see Fig. 2.2. But still, the tube curled directly underneath the particle layer, as described in Fig. 4.11c. An important question to ask is whether this curling phenomenon would be observed if the liquids were not moving relative to each other. To find out about this, further experiments will have to be done with liquids of matching densities, that is if there was a way to increase the density of castor oil without changing its properties. Furthermore, it is relevant to ask whether enough particles are present on the surface of the curling fluid to be able to create tubes if the fluid were to be cut at the particle layer and at the object at the bottom of the container. Note that this curling behaviour occurred even when no particles were present, however, no other combinations of fluids gave this result.

There were some tendencies that some of the particles combined with certain liquids did give none or a few good results only. CA40 and NaFH were in general quite difficult to handle in both the methods of a sinking object and the one of an object used to pull at the particle layer at the interface of two liquids. Due to the density of CA40 being much higher than that of the liquids and the tendency for the NaFH particles to congregate, they tended to sink quite easily, and they bound themselves to a larger degree to the interface of liquids, as described in Fig. 2.4b on how the flotation forces between particles behave relative to the size of the particles. This lack of good results are illustrated through the Figures 4.10d and 4.14d, with NaFH and CA40, respectively, as well as in table 4.3, in which no tubes were created with CA40 or NaFH when allowing an object to sink through silicone oil/castor oil, which yielded good results for CS85 and PE90-106. Another example of the problem with these two particles types can be read from the table 4.4, where no tubes or droplets were obtained with castor oil/d-ph. Even PE90-106 caused some troubles due to its hydrophobia. Not showing any inclination to mix with water or water+glycerol, the particles tended to locate themselves in lumps at the surface of the water+glycerol mixture, as shown in Fig. 4.14c.

Some of the tubes obtained throughout the experiments were still stuck to either the particle layer on an interface of two fluids or to an external object. For the method of sinking objects some relevant results are presented in Figures 4.5b (silicone oil/castor oil) and 4.11 (castor oil/d-ph), with CS85 in both figures and a difference in densities of the two fluids in the latter causing the tubes to rise quickly to the interface. In both cases the tubes were stuck at the object on the bottom of the container. Figures 4.14a (with castor oil/d-ph and CS85) and 4.14b (with

silicone oil/d-ph and PE90-106) show tubes that were obtained as a consequence of applying the method of pulling at particles at the interface of two fluids. Here, the difference in densities led to that the tubes sunk back onto the interface after a short while. Despite this, the tubes seemed to be relatively stable, so it would probably be possible to cut the tubes at the interface and at the object to see whether the tube could exist on its own in the other fluid. Methods for this could be further developed in the future.

The last three of the applied methods did not yield any satisfying results. However, when applying the method of releasing a liquid with particles, Fig. 4.15a shows an interesting part of the process of making tubes this way. Before breaking up into smaller droplets, the vertical movement upwards of the pipette caused the fluid to stretch into a thin tube, though there were not enough particles available to jam the surface. Furthermore, when applying the method of releasing a jet of a liquid containing particles, the velocity of the jet from the pipette was too low to be able to observe a tube, so only droplets were created through this method. The last method yielded quite different results dependent upon the combination of fluids. In Fig. 4.17a castor oil was poured onto a layer of CS85 particles resting on top of d-ph, but due to the issue of different densities the castor oil never managed to penetrate particle layer at the interface. The same result was achieved with silicone oil being poured on top of d-ph. In Fig. 4.17b a mixture of water and glycerol was poured onto d-ph and a layer of PE90-106. Relatively large droplets were created, but due to a shortage of particles it was impossible to cover the droplets entirely and possibly, obtain tubes. In all of these three methods, matching of densities was a factor of significance, as displayed in Figures 4.15c and 4.17a.

Chapter 6

Conclusion

There are possibly many different methods for making tubes with the help of surface particles in an emulsion of two liquids. Applying an electric field over a droplet of one liquid suspended in another in a glass cell was unpredictable, since it is not possible to have a complete control of the deformation and Quincke rotations occurring in every direction. However, the results obtained were acceptable. The most optimal tube produced throughout the experiments, fulfilling relatively well the requirement of a tube to have a fairly constant radius along its entire length, had a length l=9.0 mm and an aspect ratio a=5.2.

Acceptable results were also obtained through the method of manually stretching droplets with pipette tips after some of the fluid has been withdrawn from the droplet. Good values of lengths and ratios were observed, an example of which can be seen in Fig. 4.2 showing the most preferable result since the radius is more or less constant along the length of the tube.

Coalescence of droplets to make tubes was not successful as a method. This was due to that the surface area of the two initial droplets can not be covered entirely by particles if they are to coalesce and, hence, the final droplet can not be stretched enough to make tubes due to the low number of particles compared to the surface area. This is shown in Fig. 4.3.

The longest tubes were obtained through the method of sinking objects, in which an external object (glass, metal or plasticine spheres) was allowed to fall through a layer of particles situated at the interface of two immiscible liquids (put on top of each other in a container). Fig. 4.7f shows a container of a square base area of sides 1.40 cm, in which a manually formed plasticine sphere of diameter d=6.5 mm was allowed to fall through a system of silicone oil/castor oil and PE90-106 particles at the interface. Thus, a tube of length l=4.0 cm was produced. Also, smaller objects were tried out in this large container, without any success. However, by using a test tube of diameter 0.85 cm good results were obtained also with smaller objects. The longest tube had a length l=2.9 cm and an aspect ratio a=25, as shown in Fig. 4.7e. Though the lengths of the tubes are quite satisfying, their diameters are not, since they are not constant along the entire length of the tube. Thus, it can be fair to discuss whether these stretched droplets are to be called tubes when comparing

to the results obtained with an external electric field or by pipette tips. Satisfying results were obtained with CS85 particles as well, however, it was not possible to determine whether the tubes were hollow, and thus if they can be called tubes.

A correlation between the horizontal cross-sectional areas of the objects and containers was observed. Larger objects tended to participate in producing the longest tubes. Furthermore, the amount of friction between the object and the fluid plays a role in the experiments. More friction causes a smaller velocity with which the object penetrates the particle layer at the interface of two liquids, allowing the object to pull more particles with it, and thus longer tubes are made.

All in all, water yielded no good results, except one. By allowing an object to sink through water/castor oil with CS85 particles at the interface (Fig. 4.10c), short and thin tubes were obtained. The combination of fluids and particles was found to be ideal due to the viscosities of the fluids and the polarity of the fluids and particles, but most importantly the densities of the fluids. The latter factor was a main contributor to that mainly droplets or nothing at all were observed when doing experiments based on the last five methods described under the Chapter about methods.

To avoid this problem, the important thing was to find a fluid that could be mixed into one of the fluids in the experiments, so that the densities could be matched. This was achieved by applying glycerol to water, so that density of the mixture could be matched against d-ph. However, this combination of fluids did not prove to be the best of alternatives, due to an observation, displayed in Fig. 4.13a, done with water+glycerol minimizing its contact surface in each of the fluids silicone oil, castor oil and d-ph. The method of a sinking object did not lead to any good results for the fluid combination of d-ph/water+glycerol, since the object thus was allowed to fall through the upper fluid before being forced to one of the corners of the container, causing it to sink in d-ph rather than to pierce through the interface and into the water+glycerol region. The reversed combination, water+glycerol/d-ph, resulted in the creation of droplets with too few particles at the surface to get jammed enough to produce tubes. Also, the system shown in Fig. 4.14c, gave no good results, due to that only a few particles was situated in the middle of the curved interface of the liquids and most of them along the walls and corners of the container.

Viscosities, or the resistance in a liquid, might be an important factor during experiments. This applies in particular to the method of a sinking object, in which the viscosity of the liquid determines the velocity with which the object penetrates the layer of particles. Note that the system of silicone oil/castor oil yielded tubes only when the silicone oil had a viscosity of 10 cSt, but none were obtained if the silicone oil consisted of 100 cSt. The low viscosity of water might be one of the reasons for the low number of possible applications, but too high a viscosity would not serve the system of liquids either. In the method using a pulling object, a higher viscosity of water+glycerol or d-ph might result in that the fluid would bind itself more easily to the object. Hence, there will be a larger chance of producing tubes. In connection to this, another factor must be taken into account. Friction between the

pulling object and the fluids and particles might matter. No such relationship was found from the experiments done in this thesis, even though glasspaper was used to make the surface of the objects more uneven (method of a pulling object). Pipette tips yielded the best results, as seen in Figures 4.14a and 4.14b, though it seemed that the particles favoured the liquids rather than the pulling object. Objects of different materials can be tried in the future.

CA40 and NaFH particles were difficult to apply together with certain fluids. Due to density of CA40 and the tendency of the NaFH to congregate, the particles started to sink in the fluids quite quickly in accordance with the principle described in Fig. 2.4b. This is mirrored through the observations done when using the method of sinking objects with silicone oil/castor oil as the combination of fluids, with which some of the best tubes were obtained, as seen in Figures 4.6c and 4.7f with PE45-53 and PE90-106, respectively. PE90-106 particles caused some problems in the experiments, as well, due to their hydrophobia. The creation of lumps at the surface of water or water+glycerol, made these particles difficult to work with. The particle concentration in a liquid is a factor to take into consideration. In many experiments yielding droplets in the last four methods described in the Chapter called Method, too few particles were situated at the surface to be able to jam the droplet.

The combination of castor oil/d-ph gave an interesting result. The large difference in densities caused the castor oil, that was pulled along with a sinking object, to rise quickly to the interface of the liquids. This curling phenomenon might be a result of the surface tensions, or the relative movement of the fluids, but the latter statement has to be investigated further through experiments in which the density of castor oil can be matched against that of d-ph. A certain amount of particles was observed on the surface of the curling fluid, however, if the fluid were to be cut at both the interface and at the object at the bottom of the container, it might not be enough of them to jam the surface of the tube. This phenomenon was observed with all of the particle types (CS85, PE90-106, CA40, NaFH), as well as without. Castor oil/d-ph was the only combination of fluids yielding this observation.

The method of releasing a liquid with particles gave a result that looks promising, see Fig. 4.15a. The consequence of the upwards movement of the pipette was that a long tube was created, but there were too few particles available if the goal was to jam the surface of the droplet, shaping it as a tube.By releasing a jet of a liquid containing particles, only droplets were made. This was due to that the velocity of the jet was neither high enough nor constant. The droplets seen in Fig. 4.17b, created when using the method of releasing a jet of a liquid through a layer of particles, looked promising, however, too few particles were situated on the surface of the droplets if the surface was to be jammed. In all of these three methods, the difference in densities was a factor that mattered.

Chapter 7

Further work

Trying to make tubes in emulsions, it became clear that there are many factors playing a role in the experiments that were carried out. More work needs to be done so that the findings of this thesis can be developed further.

In the methods in which an external electric field was applied or a droplet manually deformed by pipette tips, the initial volume of the droplets supplied might matter. Also, the concentration c of particles is an interesting factor that could be investigated further. The first three methods in the Chapter concerning the applied methods did not reveal a correspondence between the concentrations and the lengths of the tubes, since this factor was not changed.

To find out whether tubes could be obtained by increasing the diameter ratio $q = d_{\mathrm{particles}}/d_{\mathrm{tube}}$ the size of the particles could be increased. Also, the diameter of the sinking object could be reduced so that the diameter of the tube will be smaller, seen that the object is able to penetrate a particle layer. Furthermore, different materials could be tried as objects, so that the effect of friction could be further investigated. This is relevant in particular to the method of a sinking object, in which the mass and volume of the spherical objects need to be held the same throughout all experiments, and to the method of pulling at a layer of particles. Further work with water should be encouraged, due to its properties relative to humans. For instance, a system worthy to take a closer look at is the one illustrated in Fig. 4.10c with water/castor oil and CA40 particles. The consequences of applying either CA particles of a larger diameter or objects of smaller diameters could be interesting to investigate further.

Some of the experiments yielded tubes that were still stuck at the interface of two liquids or at the object at the bottom of the container. Using the methods of a sinking object and of pulling at a particle layer at the interface of two liquids, an experimental setup could be made so that the tubes were cut where they were stuck at a particle layer and/or an object. Then, it would be possible to conclude if the tubes in Figures 4.5a, 4.5b, 4.11, 4.14a and 4.14b could be stable on their own or not. The first two figures have to be investigated even further in longer test tubes of the same diameter (0.85 cm), to see whether the tube lets go of the interface or the object at the bottom. Whether the tubes are hollow, and thus can be called tubes,

should also be looked at. Furthermore, when applying the method of a sinking object, there is a factor that is important if tubes are to be made. To obtain longer tubes, it was found that the horizontal cross-sectional area of the sinking objects should be relatively large compared to that of the container. This was the case for both particle types CS85 and PE90-106.

The curling phenomenon in Fig. 4.11 should be looked at through increasing either the density of the castor oil or the concentration of particles. In the case of the former change of the system, it would be interesting if the curling would occur if the densities of the fluids were matched. The concentration of particles should also be increased in the last three methods that are described in the Chapter Methods. Furthermore, the velocity at which the fluid is supplied to the container when applying the method in which a jet of a fluid including particles is injected, was not constant nor high enough, so a new non-manual setup should be made for this. In the method of a jet of a liquid being released through a particle layer, something else than a cuvette should be used to supply a fluid to the container at a higher and constant velocity.

A problem experienced again and again, was that the difference between the densities of the liquids mattered. To avoid this, the castor and silicone oils could be mixed with a different fluid so that the densities of these fluids and d-ph could be matched. This could be tried on all of the last five methods described in the Chapter about the methods. Also, the viscosities of the fluids might play an important role for the outcome of the experiments. This was seen by allowing an object to sink through a system of silicone oil/castor oil when the viscosity of the silicone oil was changed. Tubes were obtained when the silicone oil had a viscosity of 10 cSt, but no tubes were created with 100 cSt.

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