Producing tubes of silicone oil with polyethylene and polystyrene surface particles in a silicone oil-in-castor oil emulsion

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Project report

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Trondheim February 2014

Preface

This project report is a summary of results obtained in experiments done at the Department of Physics at the Norwegian University of Science and Technology (NTNU), Trondheim.

The main focus of the project was to take a closer look at emulsions and how oil droplets suspended in another oil would be influenced into being deformed, in particular whether it was possible to produce tubes out of a droplet of silicone oil suspended in castor oil. Different methods were applied, to see how the lengths and the aspect ratios changed with certain different factors. Some of the factors were not varied in the experiments done in connection with this project report, so the process of making tubes should be investigated further in the future. The results presented in this project report are part of a preliminary investigation for the Master's thesis to be written through the remaining part of this semester.

The report is written for my peers. Hence, a basic understanding of microfluidics and electrostatics is preferred.

I would like to thank my supervisor, Jon Otto Fossum, for giving me the opportunity to work at the laboratory for Soft and Complex Matter Studies, Alexander Mikkelsen for his patience and helpfulness in answering my ever-present questions and my friends, my fellow master students, for the motivation obtained from their positivity. Last, but not least - a large thanks to my family for their support, especially to my sister, Elna Marie, for the inspiration, encouragement and good advice she is always giving me.

Trondheim, 06.02.2014
Arne Halvor Thingstad Pedersen

Abstract

The goal for this project was to investigate whether it was possible to make long tubes (of length l) out of silicone oil droplets suspended in castor oil. The aspect ratio - $a = l/d$, the relationship between the length and the diameter of the tubes - was used to be able to compare the tubes.

Different methods were applied, to see how the lengths and the ratio changed with varying factors. An electric field was applied on the droplet, so that it was deformed. At high field strengths Quincke rotation would occur, making the process unpredictable. Nevertheless, good results were obtained. Through another method the droplet could be influenced manually. This was done by moving pipette tips alongside the droplet, so that the surrounding fluid would deform it. In the last method an external object of a known diameter and mass was allowed to fall through two fluids adjacent to each other with a layer of surface particles at the interface. To obtain the longest tubes, it was found that the size of the particles, the friction between the object and the fluid, and the relationship between the cross-sectional areas of the sinking object and the base area of the container mattered.

Contents

List of abbreviations

PE: Polyethylene

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

CS: Polystyrene

CS##: Polystyrene particles of diameter ## μm

Chapter 1

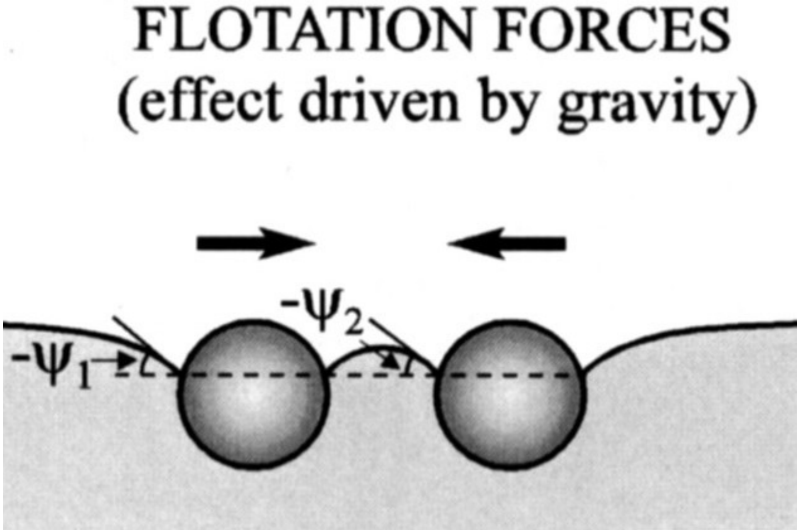
Introduction

1.1 Background and motivation

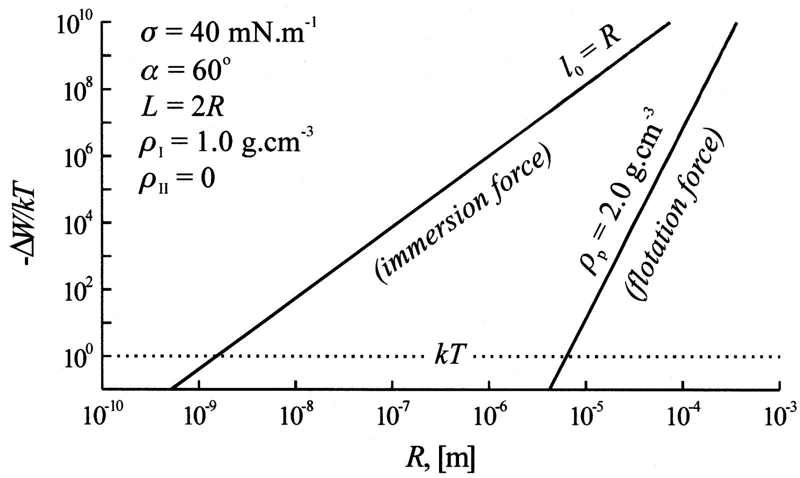
In microfluidics, fluids can be moved, controlled and manipulated on a micrometer length scale. An important way to exploit these properties is through emulsions. Emulsions are defined as a mixture of two or more immiscible liquids, a system in which small droplets exist within a surrounding fluid. They can be found in many applications used on a daily basis, such as vinaigrettes and milk as well as in some cutting fluids for metal working.

By allowing solid, microscopic particles to adsorb on the interface between the droplet and the other fluid, the droplet can be stabilized, since the particle coating would try to prevent droplets from coalescing. This is called pickering emulsions, which can be found in foods, cosmetics and oil recovery [1]. Another use for it is found in biomedicine [2].

Particles located on a fluid interface are influenced by attraction forces called lateral capillary forces, working in-between them, see Fig. 1.1a. This force is a consequence of the deformation of the liquid surface caused by the gravitational pull on the particles. Hence, the effects of gravity are stronger the more mass the particles have, causing the meniscus of the liquid to deform so that the gravitational potential energy decreases with shorter inter-particle distances. This is shown in Fig. 1.1b, in which the capillary attraction energy ΔW (in units of kT - k being the Boltzmann constant and T the temperature) is plotted against the radius R of the particles, using $L = 2R$ as the centre-to-centre distance between the two identical particles, illustrating how the attraction energy changes with distance. This means that the attraction force must increase and contribute to forming clusters of particles [3][4].



(a)



(b)

Figure 1.1: Flotation forces and how they correspond to the size of particles situated on the surface of a droplet. Fig. (a) shows two identical particles and the attraction forces between them. The strength of the flotation forces working between them is governed by the mass of the particles. In Fig. (b) the correspondence between the size of the particles (the inter-particle distance is in this plot defined as $L = 2R$) and energy of the capillary attraction ΔW (in units of kT), hence the force with which the particles attract each other, is illustrated. The larger the diameter of the particles (and hence the larger mass), the larger the force between the particles. Figure adapted from [3].

Colloidal particles may thus strongly bind themselves to the interface between two liquids and can consequently create functional membranes or capsules, since the energy is lower when a particle stays on the interface rather than in one of the liquids alone. Colloidosomes, solid colloidal capsules, can also be made. This is possible if particles are linked or fused on the surface of droplets which have gone through the process of pickering emulsion [1][5]. However, colloidal particles can also have many other properties. Their surface properties or volume can be altered by changing either the temperature or the type of solvent, or they can by influenced by an external electric field. Another application might be drug release with the help of pH-responsive colloidal capsules, so that the opposite of pickering emulsions can be achieved when the colloidal particle moves to an area with a different pH-value [5].

Electric fields cause motion in fluids, and in reverse, fluid flow can participate in creating an electric field. [6] When an electric field is applied, a droplet can behave in a few different ways. It can deform, start rotating or break up into smaller droplets, or it might coalesce with other drops. This gives rise to a complicated system, in which many forces are at work. The drop responds to an electrical force which is created due to the free charges moving around close to the surface of the drop, both on the inside and the outside, drag forces caused by the viscosity of the fluids and interfacial surface tension.

1.2 Problem

An environment of two fluids can be exploited in the lab to discover more about their properties and how they interact. The goal of this project was to investigate whether it was possible to produce tubes out of silicone oil drops suspended in castor oil. In order to make the tubes as long as possible, different methods were considered.

Tubes were defined as a stretched droplet of one liquid suspended in another, where the droplet is covered by surface particles. The idea was to obtain tubes with circular cross-sections of approximately constant diameter along the entire length. To quantify this, both the actual length and the diameter of the tubes were measured. Thus, the ratio $a = l/d$ (l=length of the tube, d=diameter of the tube) was calculated, so that it would be convenient to compare the tubes with each other.

1.3 Report structure

This project report is divided into six main chapters. The introduction is succeeded by the chapter of Background theory which gives an overview of the relevant theory needed to understand emulsions. The setups used in the experiments are explained in the Method chapter. The Results and discussion chapter presents the obtained results which are also discussed in detail. Furthermore, the discussion part is summarized in the Conclusion chapter, before suggestions for more projects that can be investigated is presented in the Further work chapter.

Chapter 2

Background theory

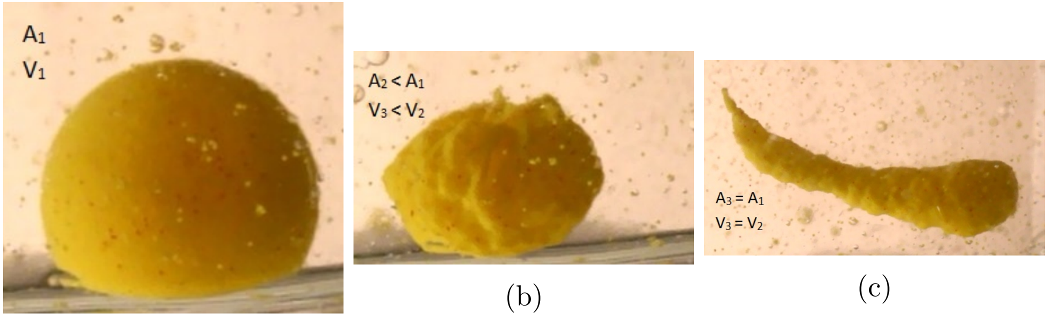
2.1 Emulsions

An emulsion is a mixture of two normally immiscible fluids, one of which (the dispersed phase) suspended as a droplet in the other (the continuous phase). 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 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 [7]. 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 [8]. To stabilize the emulsion, surface particles can be used.

2.2 Geometric properties of oil droplets being formed into tubes

When using a pipette to create a new drop of a certain oil (in the rest of this chapter called oil II), including surface particles, suspended in another oil (from this moment on called oil I), the drop would form as a sphere with most particles on the surface. This case of a two oil system with surface particles is found illustrated in Fig. 2.2. 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. 2.1 would not work fully in practice, but it shows the principle of the process.



(a) (b) (c)

Figure 2.1: 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 oil II done between (a) and (b), and caused by an applied external electric field or manual deformation with pipette tips between (b) and (c).

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

$$\begin{aligned} A_1 &= 4\pi R_1^2 \\ V_1 &= \frac{4}{3}\pi R_1^3, \end{aligned} \tag{2.1}$$

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 oil II (including the particles which are not on the surface) from the drop so that the volume ratio of surface particles to oil increases. Thus, as it is possible to see in Fig. 2.1, the volume changes due to the amount of oil II that was taken away. 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. (2.1), 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 practise, since the assumption of not losing any surfactants to the surroundings, into either the syringe or the surrounding oil I, can not hold entirely. However, in this project this was seen as an acceptable approximation.

2.3 Surface particles and the importance of their energy

Particles mixed into an oil are observed to almost exclusively be situated on the surface of an oil droplet suspended in another oil, 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 oils, in the other oil and on the interface of the two liquids. The energy E is given by the equation

$$E = \gamma A, \tag{2.2}$$

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 oil II being suspended in oil I, and given that the particle size is not comparable to the molecular scale, the interactions on a molecular level can be described as the particle-oil I, the particle-oil II and the oil I-oil II interfacial tensions expressed by γ_I, γ_{II} and γ_{I-II}, respectively [1]. Defining the variables E_I, E_{II} and E_{I-II} as the energies of the particle when it is located in oil I, oil II and at the interface between the oils, 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

$$\Delta E = -\pi r^2 \gamma_{I-II}(1 \pm cos(\theta_c))^2, \tag{2.3}$$

in which γ_{I-II} is the surface tension between oils 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 oils (see Fig. 2.2). The angle θ_c, the Young-Dupré contact angle, can further be expressed as $\cos\theta_c = (\gamma_I - \gamma_{II})/\gamma_{I-II}$ [1].

The particles are most importantly used as a way of creating a shell around the drop of oil II, but also to indicate how the drop is deforming and rotating. Upon increasing the concentration of surface particles in oil 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.

2.4 Droplet deformation

Deformation of a droplet (oil II) which is suspended in another liquid (oil I), might be done in various ways. Those investigated in this project are electric fields, manual

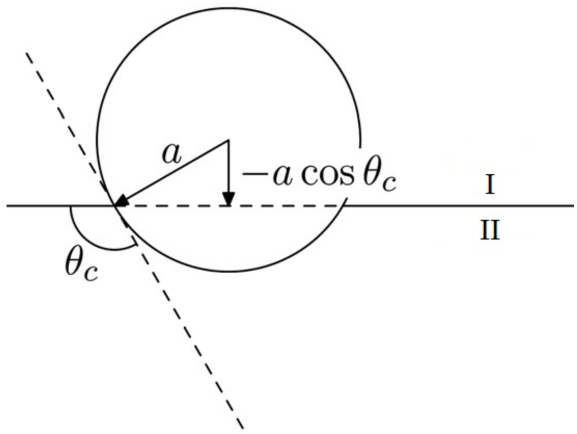


Figure 2.2: Two immiscible fluids and a surface particle. At the interface of two fluids, the particle is located with a larger proportion of its volume inside oil I. θ_c is the contact angle of the two fluids, an angle at which the particle is stable. [1].

deformation by pipette tips and the effects of gravity. Fig. 2.3 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 [6], also be quantified through using the diameters of the deformed drop parallel and normal to the direction of the incident electric field (see Fig. 2.3), as following

$$D = \frac{d_{||} - d_{\perp}}{d_{||} - d_{\perp}} = \frac{9}{16}\frac{r\epsilon\epsilon_0 E^2}{\gamma}\frac{(\hat{\epsilon} - \epsilon)^2}{(\hat{\epsilon} + 2\epsilon)^2} \cdot F, \tag{2.4}$$

where D is expressed by the dielectric properties of the drop and its surroundings; r is the drop radius, $\hat{\epsilon}$ the dielectric constant of the drop, ϵ the dielectric constant of the surrounding fluid, ϵ_0 is the vacuum permittivity, γ the interfacial tension and E the applied external electric field [9]. The factor F takes into account other effects than the dielectric properties, such as viscosity and conductivity.

An electric field directed upwards in the plane is applied on a droplet of oil II in Fig. 2.4. Hence, the field will in oil I induce a charge distribution in which the positive charges can be found on the bottom side of the drop of oil 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 oil I, resisting 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 the electric field $\vec{E}$ applied from the electrodes of the cell, the drop is deformed so that it takes the shape of an oblate spheroidal drop, as depicted in Fig. 2.3. As the strength of the external electric field is increased, both oils would have to move charges around in the respective liquids quicker and more charges will be

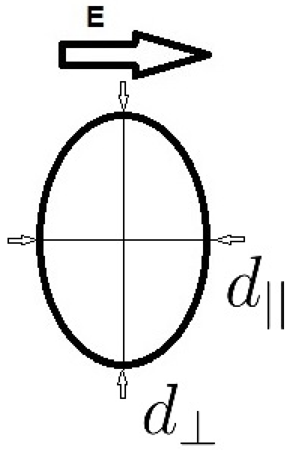


Figure 2.3: A deformed droplet in an applied external electric field. Droplet deformation is here described by the variables $d_{||}$ and $d_{\perp}$, which mean the diameters of the drop parallel and normal to the incident electric field, respectively. A silicone oil droplet suspended in castor oil has an oblate shape ($D<0$), which comes as a consequence of the electric field working horizontally from left to right in the figure.

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 oil 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.

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

$$SR = \frac{t_{c\,I}}{t_{c\,II}} = \frac{\frac{\epsilon_I}{\sigma_I}}{\frac{\epsilon_{II}}{\sigma_{II}}}, \tag{2.5}$$

where $S = \epsilon_I/\epsilon_{II}$ is the permittivity ratio and $R = \sigma_{II}/\sigma_I$ the conductivity ratio. Hence, from Eq. (2.5), one obtains that the conductivity response in the case of

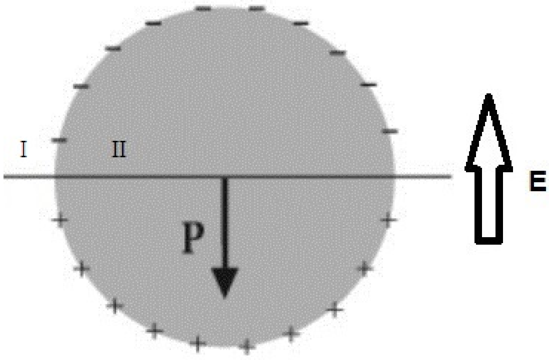


Figure 2.4: The charge distribution in oil I close to the surface of the droplet of oil II, with a resulting dipole moment inside the drop directed oppositely to the electric field. Figure adapted from [10].

$\sigma_{II} < \sigma_I$ 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 of the outer fluid. By Fig. 2.4, one can see how the drop would act in an external electric field $\vec{E}$ and how the dipole moment $\vec{p}$ (hence the polarization) works in the opposite direction of the incident field, diminishing $\vec{E}$ inside the drop.

When operating with small, almost non-conductive particles on the surface of the drop of oil II suspended in oil I, an electric field applied to the system will at relatively small values cause a deformation of the drop only. However, when the field strength increases and the drop becomes unstable, the torque will cause the drop to start tilting, see Fig. 2.5, 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.

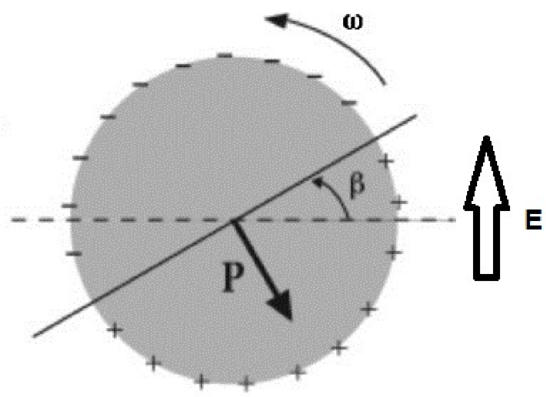


Figure 2.5: An illustration of Quincke rotation. When charges on the inside of the drop can not keep up with the movement of the charges on the outside any longer, the droplet needs to make up for the non-equilibrium state of charges. As is described in this figure, the drop starts rotating with a rotational axis normal to the incident electric field. The field $\vec{E}$ is directed upwards in the plane, as indicated by the arrow. Figure adapted from [10].

Chapter 3

Method

There might be many different possible methods to apply if the aim is to obtain tubes made out of silicone oil drops whose surface is covered by particles. In this project report, the focus will be on four methods. The length of the tube l was to be measured and the aspect ratio a =length/diameter calculated, so as to get an indication of the limitations of the respective methods.

3.1 Apparatus and procedures

In Fig. 3.1, the instrumental setup for the methods in which an electric field or pipette tips were used to make tubes can be seen. A digital video camera is connected to the microscope (Carl Zeiss Stemi 2000-C), so that it is possible to document the result obtained during experiments. There are various light sources attached to the setup, which are radiating relatively homogeneously onto the the area in which the sample is placed. The sample, in this case a drop of silicone oil with polyethylene beads (PE63-75) as surface particles, is located in a glass cell, at which two of the sides are covered in a thin, transparent layer of indium tin oxide (the arrows in Fig. 3.1v indicate that the covered side of the plates are on the inside of the cell). These two sides are placed at a distance of L=15.1 mm away from each other. To be able to apply an external electric field over the contents of the cell, a voltage source (Glassman high voltage, 0-10000V, PS/MJ10P1500-22) is connected to the indium tin oxide-covered electrode plates. A pipette (ThermoLabsystems U18171 4500, 5-50 μl) is used to get the sample's initial volume quite accurately.

The applied methods of this project will be further explained in the rest of the chapter.

3.1.1 Electric field

In this method, the principle of emulsion of two oils is used - one oil exists as a droplet suspended in the other. Hence, the two immiscible fluids are put into the same glass cell, one of them existing as a droplet suspended in the other. These

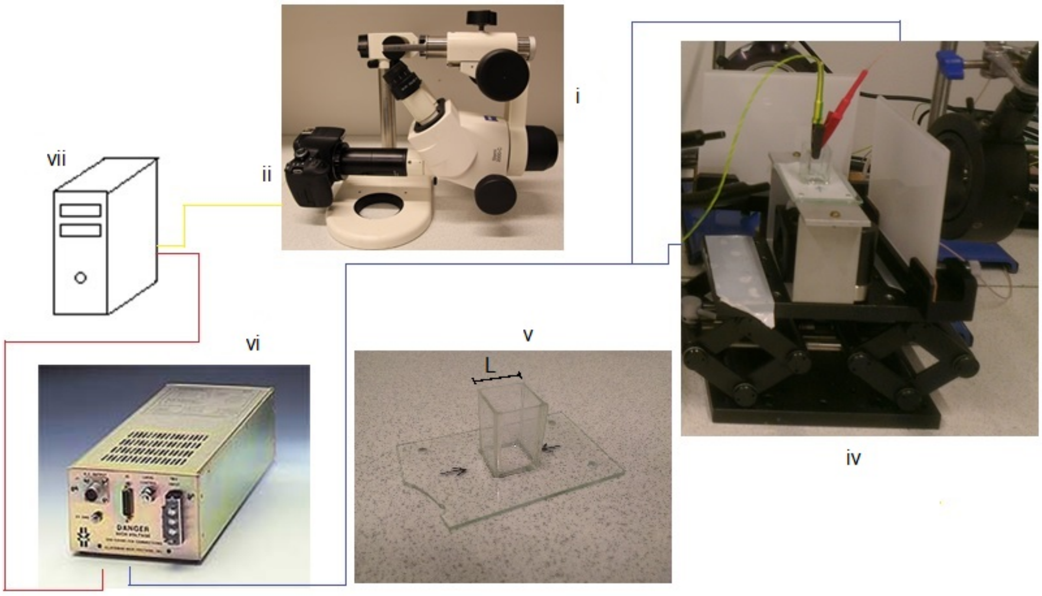


Figure 3.1: Illustration of the process of droplet deformation by electric field or manual treatment with pipette tips. The microscope (i) and the added photo camera (ii) are used to observe the occurrences of tubes in a sample cell (v) (of length L=15.1 mm), which can be moved vertically with the adjustable platform (iv). A light source (iii) is a part of the setup as well as a voltage source (vi), which is connected to a computer (vii) through a Data Acquisition (DAQ) card.

liquids are put into a quadrangular glass cell, in which two of the walls opposite each other are covered by a thin film of indium tin oxide, which, due to being a conductive material, works as electrodes. In the submerged oil drop is put small non-conductive particles, which will after some time seek to locate themselves on the interface of the drop and the surrounding oil, as explained by Eq. (2.3). The point of this method is to withdraw oil from the drop. This is most easily done by placing the drop on the bottom of the glass cell, locking it to the glass from below. When a sufficient amount of oil is taken out of the drop, the drop will be covered by buckles, due to the surplus of particles on the surface. Furthermore, the drop must be moved upwards in the cell so that it is not touching the glass cell. Then an electric field is applied, deforming (as seen in Fig. 2.3 with a silicone oil suspended in surrounding castor oil) the drop so that the surface expands, allowing particles to fill the open spaces. Consequently, the surface is stretched and tubes can be obtained.

3.1.2 Pipette tips

After having submerged an oil drop into the liquid that is located in the glass cell, and used a pipette to draw out some of the silicone oil 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

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.

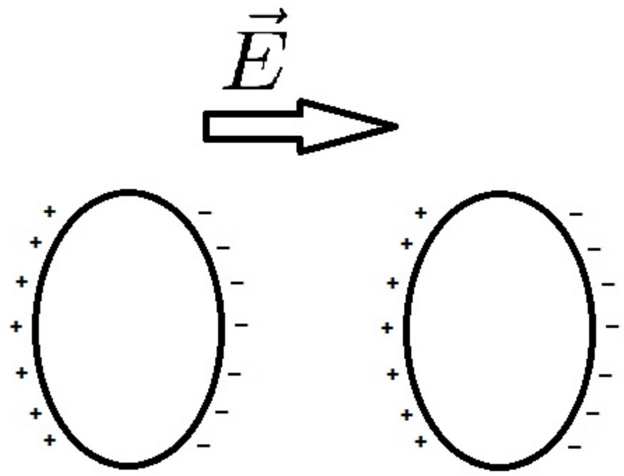


Figure 3.2: Two droplets coalescing. With an electric field directed from left to right, the charge distribution is illustrated in this figure. The dipoles of the two drops interact so that they coalesce.

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

Table 3.1: An overview of the particles used in the experiments with a sinking object.

Particle material	Particle type	Colour	Diameter μm
Polyethylene (PE)	REDPMS	Red	45-53
	UVPMS-BY2	Fluorescent yellow	90-106
Polystyrene (CS)	CS5	White	5
	CS20	White	20
	CS85	White	85

tube is filled with two liquids, one above the other, the upper containing an oil with surface particles of a certain diameter, the lower a second type of oil. Then, the particles are allowed to sink to the interface of the two oils, so that most particles would be gathered there. 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 oil so that the particles at the interface would be pulled downwards, following the sinking object. Thus, some of the upper oil (in Fig. 3.3: silicone oil of viscosity 10 cS) is pulled into the castor oil below, forming tubes. This occurs due to what is illustrated in Fig. 2.2, in which oil I is the castor oil and II the silicone oil.

The sinking objects used were a metal sphere of diameter 2 mm, glass spheres of diameters 3 and 4 mm, and plasticine of different sizes. The surface particles used are presented in table 3.1.

3.2 Sample preparations

In the electrode cell, castor oil with density 0.961 g/cm^3 was used as the surrounding fluid for the sample drop consisting of silicone oil. These drops, to which surface particles (spherical PE particles) were added, vary in size between 20 and 50 μl. This drop was a mixture of silicone oils of different concentrations; one part of a solution of viscosity 10 cS and two parts of 100 cS. The reason for this choice, was that it was easier to work with the drop when it does not move too much in the castor oil in the cell due to the effects of gravity. Being much heavier than the surrounding castor oil the drop would sink; being lighter it would float to the surface.

For the method of the sinking object, the same castor oil was used while silicone oil of 10 cS containing particles was used. The silicone oil had a particle mass concentration of 5%. In the test tube of diameter 0.85 cm, 1.5 ml of this mixture was poured on top of castor oil, while in the larger container of sides 1.40 cm the amount of silicone oil was around 3 ml.

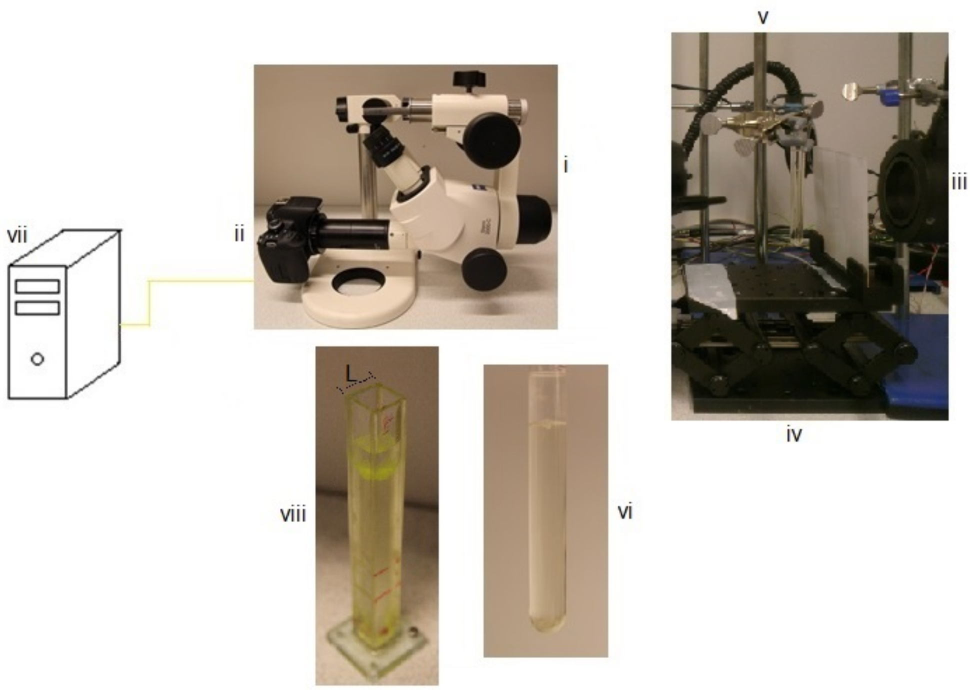
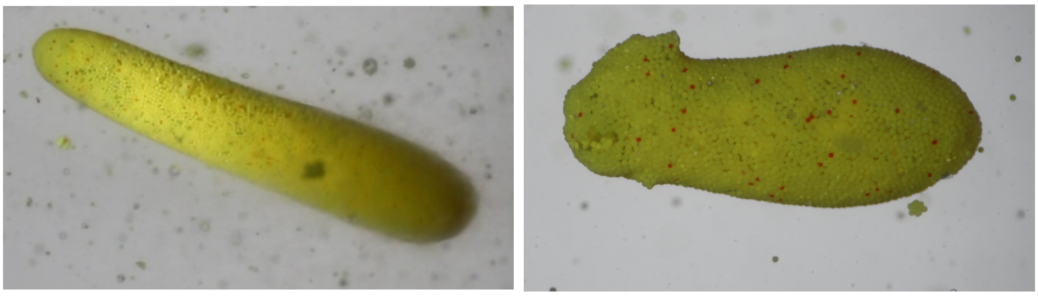


Figure 3.3: Equipment needed if an object is to fall through two immiscible fluids (of different viscosities and densities) with surface particles at the interface. A photo camera (ii) has been connected to a computer (vii) and a microscope (i), through which the test tube (vi) can be observed. A taller 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.

Chapter 4

Results and discussion

4.1 Producing tubes by applying an external electric field



(a) (b)

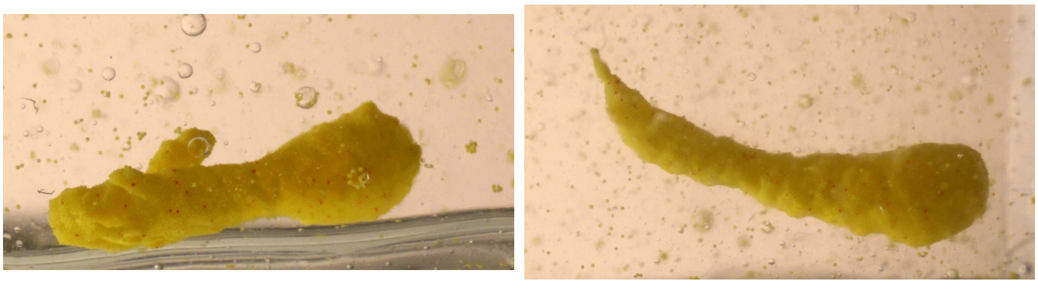
Figure 4.1: Tubes produced by applying an external electric field. The electric field operates horizontally normal to the line of sight from the microscope.

Due to the need of applying a strong external electric field to be able to stretch the drop enough so that particles can find their place on the surface of the droplet, often large deformations and Quincke rotations occur. Fig. 4.1 displays two different tubes obtained from the use of an electric field deforming a drop of silicone oil, its surface covered by PE63-75. Both are taken into account since they represent the uncertainty of using an electric field to deform the droplet.

The initial volumes of the droplets were 30 ml in both cases in Fig. 4.1. Then silicone oil was taken out of the drop and an electric field was applied onto the system. At first, the electric field strength was low and later increased to avoid that the drop should divide itself into smaller droplets or lose its surface particles, many of which now situated in buckles on the surface. When the field was turned off, the deformed and, in some situations, rotating droplet would stop moving, contract (since there was no force stretching the surface anymore) and in the end stay shaped non-spherically. The measured length and the calculated aspect ratio a was in Fig.

4.1a measured to be 9.0 mm and 5.2, respectively, while the similar variables were 4.1 mm and 2.7 for the tube in Fig. 4.1b.

The results of two other experiments are shown in Fig. 4.2. The start volume was here 50 μl. After the electric field was applied and then turned off, the lengths and the ratio a found were 5.9 mm and 4.5 for Fig. 4.2a and 8.9 mm and 6.7 for Fig. 4.2b. These results can be found systematized in table 4.1.



(a) (b)

Figure 4.2: Making tubes with the help of an electric field.

4.2 Producing tubes with pipette tips

Placing a silicone oil drop in the castor oil in the glass cell, over time the particles will, due to energy considerations (see Eq. (2.3)), locate themselves on the interface of the two oils, a process which can be accelerated if a weaker electric field is applied. After it is turned off, silicone oil can be withdrawn from the droplet, so that some of the particles are located in buckles on the surface. Obtaining tubes with the help of pipette tips can be done by trying to move the them alongside the drop, back and forth, so that the particles in the buckles get a chance of finding a place on the surface.

(a) (b) (c)

Figure 4.3: The use of pipette tips to obtain tubes.

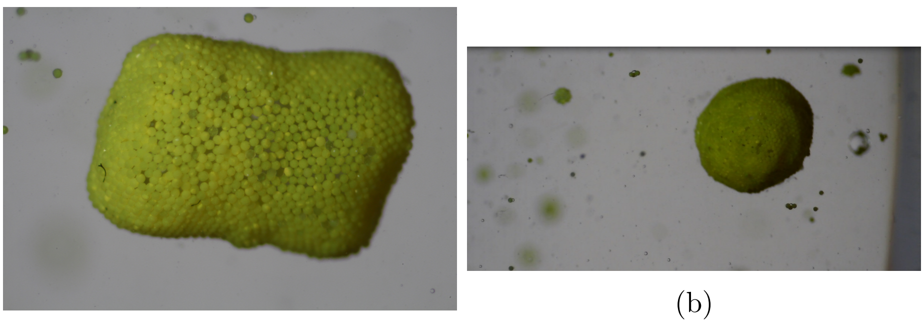
In Fig. 4.3a pipette tips were used to make the tube with length and aspect ratio a 7.8 mm and 4.4, respectively. For the tube in Fig. 4.3b, the two values were 8.6 mm and 4.8, whereas for the tube in Fig. 4.3c the values were 8.1 mm and 4.8. These results are shown in table 4.1.

Table 4.1: The lengths and values of the aspect ratio a in the cases of applying an electric field or manually deforming droplets to obtain tubes.

Fig. no.	Length l mm	Aspect ratio a
4.1a	9.0	5.2
4.1b	4.1	2.7
4.2a	5.9	4.5
4.2b	8.9	6.7
4.3a	7.8	4.4
4.3b	8.6	4.8
4.3c	8.1	4.8

4.3 Coalescing drops to obtain tubes

Instead of starting off with a large droplet as was done in the two methods discussed above, one can start off with two smaller drops and make them coalesce in the hope of getting a deformed surface packed with particles. However, this method was not very successful, due to that each of the droplets can not be entirely covered with particles if they are to coalesce. This makes it difficult to avoid that the coalesced drop would end up in a spherical shape, because there are not enough particles to cover a stretched surface. As can be seen in Fig. 4.4a, two drops have been coalesced and deformed into a non-spherical shape, only to go back to an approximate sphere after an electric field is applied (see Fig. 4.4b). In this case, using pipette tips to try to deform the drop did not work either. From here on, to have a chance of obtaining longer tubes one must diminish the potential surface area of the drop, that is to take out some of the oil inside the drop, and try one of the two methods above.

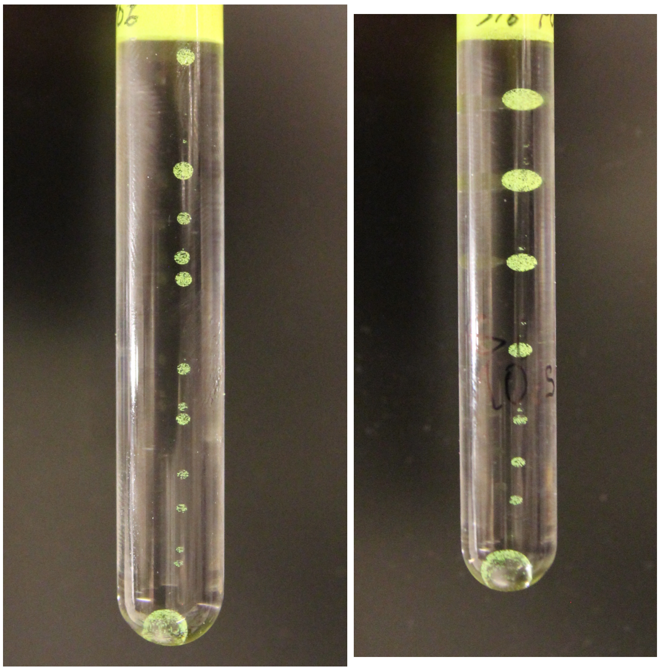


(a) (b)

Figure 4.4: This figure illustrates the process in which two drops have been coalesced to obtain the deformed drop seen in a, before an electric field is applied and the drop gets an approximate spherical shape in (b).

4.4 A sinking object in a cell containing two different fluids

Yet another method was investigated, a method based on an object of known diameter and mass sinking through two immiscible fluids of different viscosities. Trying to mix surface particles into castor oil and placing it on top of silicone oil (no matter the viscosity) in a glass cell, no tubes were obtained. The sinking object fell through the interface, pulling some particles with it into the fluid below so that it looked like a tube was made, but before long it broke up into droplets, as seen in Fig. 4.5.

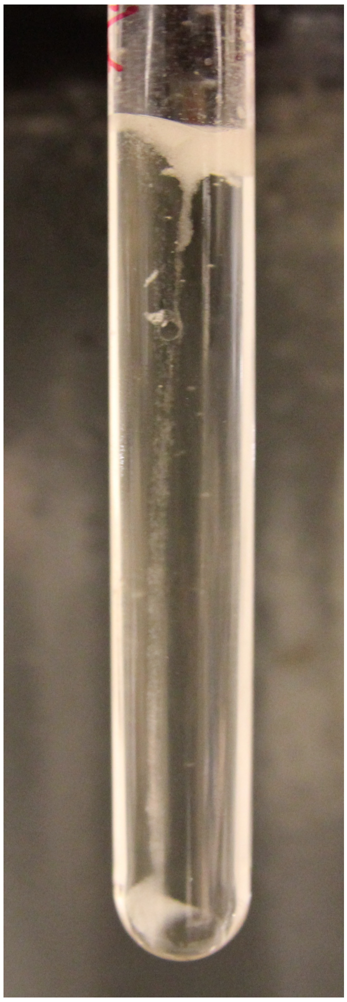


(a) (b)

Figure 4.5: Particles mixed into castor oil and put on top of silicone oil (here: viscosity of 10cS). No tubes were obtained. In (a) and (b) glass spheres of diameter 3 mm and 4 mm, respectively, were sinking in the test tube of diameter 0.85cm. Spherical PE90-106 were used as surface particles.

However, particles put into silicone oil of viscosity 10cS placed on top of castor oil, gave some very interesting results. A few factors were changed, though one at a time: the size and type of the surface particles, the volume of the sinking objects and containers (hence the horizontal cross-sectional area). In Fig. 4.6, test tubes of diameter d=8.5 mm were used, having spherical CS85 or CS20 mixed into the silicone oil. By switching between different sizes of the sinking objects, spherically shaped glass particles of diameters 3 mm (fig. 4.6a) and 4 mm (fig, 4.6b) being used, one can see a tendency to obtaining thicker and less transparent tubes with larger spherical objects.

(a)



(b)

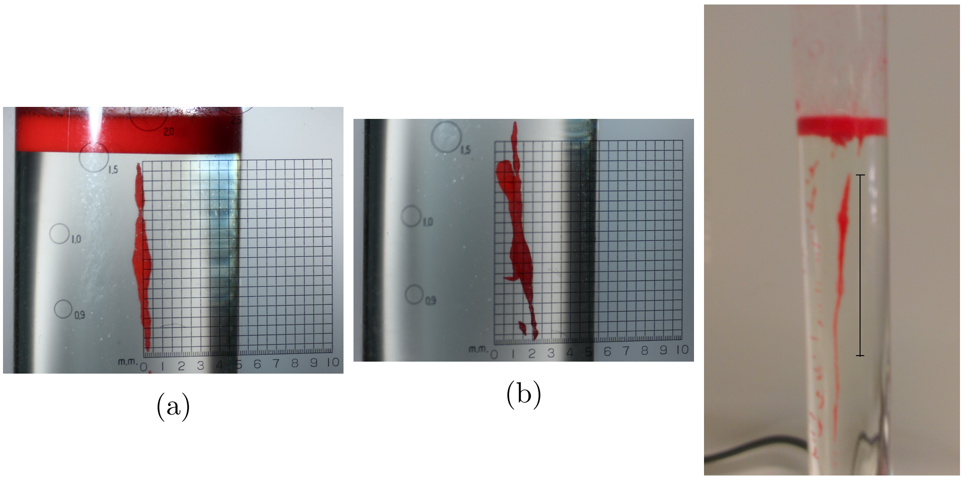
(c)

(d)

Figure 4.6: Objects of different sizes falling through a layer of CS particles. In (a) and (d) a glass sphere of diameter d=3 mm was used as the sinking object, whereas the object was of d=4 mm in both Figures (b) and (c), the latter of which showing a close-up illustration of how CS particles act when located on the surface of a tube. The three first figures include CS85, whereas the last, Fig. (d), has got CS20.

Since this method results in tubes which are still connected to the interface of the two fluids and to the object at the bottom of the test tube, it seems it should be possible to obtain even longer tubes. Therefore, it was not possible to find any difference between the lengths of the two tubes due to the two sizes of the sinking objects. Fig. 4.6c shows the tube from Fig. 4.6b up close, illustrating how the particles are organized. Comparing two different particles sizes was also done, as can be seen in Figures 4.6a and 4.6d, with a glass sphere of d=3 mm as the sinking object. The length of the tubes shown in Figures 4.6a and 4.6b were both measured to be 6.3 cm. The aspect ratio a was not calculated in these cases, due to that the tube still stuck to the interface of the two oils and the sinking object at the bottom of the test tube. Thus, the tube can not be said to be stable on its own in the castor oil.

Instead of putting CS particles into the silicone oil, spherically shaped PE45-53 were mixed with the fluid. Now, a glass sphere of diameter d=3 mm was used in Fig. 4.7a, in which a tube of length 1.0 cm and ratio a=24 was obtained. Allowing a sphere of d=4 mm to fall through the test tube, as seen in Fig. 4.7b, a tube with a length of 1.1 cm and a= 22 was made. In Fig. 4.7c an approximate sphere of d=5.5 mm made out of plasticine was put into the test tube, giving the results 2.4 cm in length and a=37.



(a) (b) (c)

Figure 4.7: Different objects of known diameters were sinking in a test tube of diameter d=8.5 mm with silicone oil containing PE45-53. In (a) a glass sphere of d=3 mm was used, in (b) a glass sphere of d=4 mm. The sinking object in (c) was made out of plasticine and had a diameter d=5.5 mm.

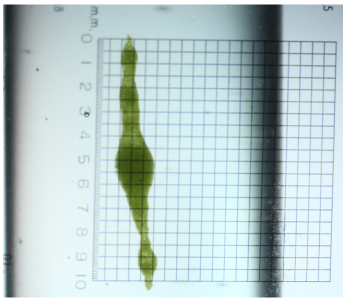
Trying with even larger particles, PE90-106, the same experiment was done with different sizes of objects sinking in a test tube of diameter 8.5 mm; glass spheres of diameter d=3 mm and 4 mm, figures 4.8a and 4.8c, respectively, and plasticine of diameter 6.0 mm in Fig. 4.8e. In the other three figures, 4.8b (glass sphere of diameter d=3 mm), 4.8d (sphere size d=4 mm) and 4.8f (plasticine object of diameter d=6.5 mm), a taller glass container with a square horizontal cross-sectional area of sides 1.4 cm was used.

The tubes obtained in the Figures 4.8a, 4.8c, 4.8e and 4.8f yielded lengths of 1.0 cm, 1.9 cm, 2.9 cm and 4.0 cm, respectively, while the corresponding values of the aspect ratio were found to be 13, 21, 25 and 74. These values are presented more systematically in table 4.2.

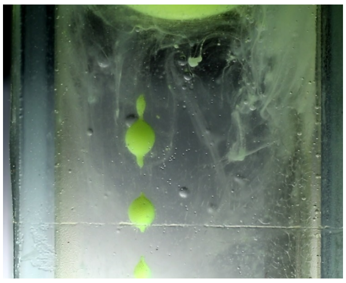
Instead of using glass spheres or plasticine as the sinking object, small metal spheres (weighing less than the glass spheres of diameters 3 and 4 mm) with less friction against the oils were also tried. Only drops were visible after allowing a metal sphere to fall through PE90-106 located at the interface of the silicone and castor oils (Fig. 4.9a). The top of a tube with CS85 at the interface is seen in Fig. 4.9b, a tube that still sticks to the interface of the two oils as well as the object at the bottom of the test tube.

Table 4.2: Lengths of tubes an their calculated values of the aspect ratio a when using the method of sinking objects. If '-' is stated, no tubes were obtained in that specific case, only droplets. 'x' means that a tube still stuck to the interface of the two oils and the object on the bottom of the test tube, thus not existing on its own in the castor oil.

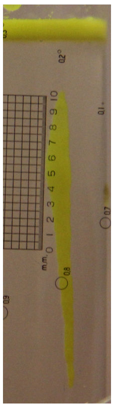
Fig. no.	Particle type	Object type	Object diameter d mm	Length l of tube mm	Aspect ratio a
4.6a	CS85	Glass	3	63	x
4.6b	CS85	Glass	4	63	x
4.6d	CS20	Glass	3	-	-
4.7a	PE45-53	Glass	3	10	24
4.7b	PE45-53	Glass	4	11	24
4.7c	PE45-53	Plasticine	5.5	24	37
4.8a	PE90-106	Glass	3	10	13
4.8b	PE90-106	Glass	3	-	-
4.8c	PE90-106	Glass	4	19	21
4.8d	PE90-106	Glass	4	-	-
4.8e	PE90-106	Plasticine	6.0	29	25
4.8f	PE90-106	Plasticine	6.5	40	74
4.9a	PE90-106	Metal sphere	2	-	-
4.9b	CS85	Metal sphere	2	65	x



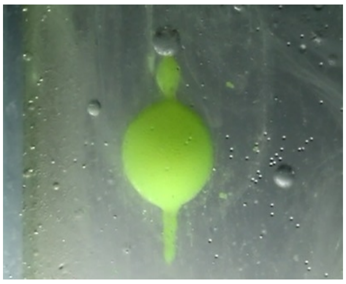
(a)



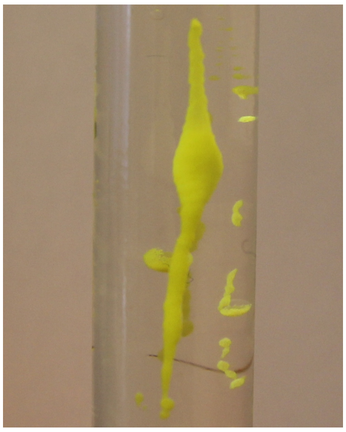
(b)



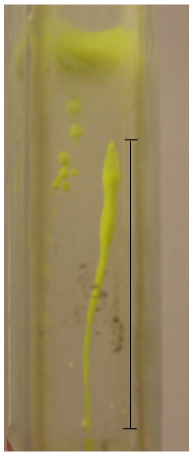
(c)



(d)

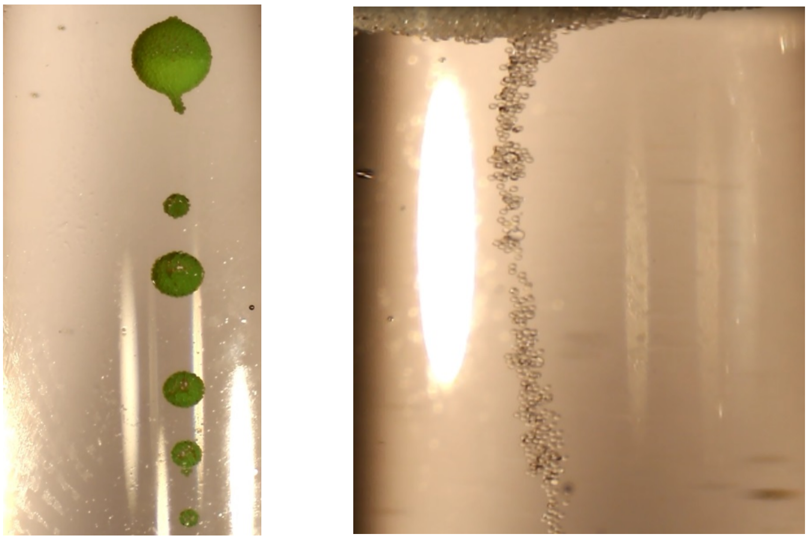


(e)



(f)

Figure 4.8: Allowing objects of known diameters and mass sink through a layer of fluorescent yellow particles, PE90-106. Here, two different containers were considered - a test tube of diameter 8.5 mm (seen in the left hand side column) and a higher container with a square base area with sides of 1.40 cm (the right hand side column). In Figures (a) and (b) the sinking object used to create the tubes and droplets was a glass sphere of diameter d=3 mm, whereas a sphere of d=4 mm was utilized in (c) and (d). (e) and (f) illustrate even larger sinking objects of plasticine, diameters d=6.0 mm and d=6.5 mm, respectively.



(a) (b)

Figure 4.9: Results obtained by allowing metal spheres to sink through a particle layer on the interface of the silicone and castor oils. In (a) only drops were produced (with PE90-106 as surface particles), whereas a thin tube was obtained in (b) with CS85 at the interface of the two oils.

4.5 Comparing the methods

Since it is difficult to predict how a droplet influenced by an electric field will deform and/or rotate, it was easier to obtain good results by using pipette tips. However, some of the varying results obtained when the external field was applied were good when it comes to length and the aspect ratio a, though the tubes did not necessarily have a constant diameter. Another problem with applying the electric field was that the drop started dividing itself into two or more smaller droplets or letting go of the particles located in buckles at the surface when the electric field was too high. With the use of the pipette tips, it was at all times possible to push and pull the tube in the wanted direction so that one could control the deformation. The limitation to how long the tube could be made depends upon the relationship between the number of particles and the surface area of the drop. The more silicone oil that is taken away from the suspended droplet, the larger the chance to get long and thin tubes with a good value of the ratio a. However, if too much fluid is withdrawn, there is too little surface area onto which the particles can locate themselves. Hence, no matter how much the droplet is pulled at, it stays small with buckles covering it.

The results given based on the tubes in Figures 4.1 and 4.2 are not entirely conclusive as to whether the size of the initial drop has got something to say for the end result. In the former figure an initial silicone oil drop of 30 ml was suspended in the castor oil, whereas in the latter the volume was chosen to be 50 ml. The reason for the lack of difference between them might be due to some uncertainty factors -

the fact that it is relatively easy to withdraw particles as well as silicone oil from the droplet and that the applied external electric field tear off some of the particles located in the buckles.

By coalescing two droplets, a jammed shell can be obtained, as was seen in Fig. 4.4a. However, trying to deform the drop further did not lead to the creation of a tube, since the particles were too few compared to the surface area of the drop. Hence, it seems that the methods of an applied electric field or manually deformation by pipette tips are better off when starting with one droplet alone, containing particles both at the surface and within. This increases the chances of filling the surface area with particles, so that the droplet can stay in a stretched state as a tube rather than as a sphere.

The method in which a sinking object was used to obtain tubes, the combination of castor oil on top of silicone oil in a glass cell was tried. Even though the viscosities of the silicone oil were changed between 10, 100, 1000 and 10000cS and particles of different sizes were put into the castor oil, no tubes were created. This was due to that the surface particles favour the castor oil instead of the silicone oil (fluid I and II, respectively, in Fig. 2.2). A reason for this might be the superior polarity of the castor oil molecule, pulling more on the particles than the silicone oil does, so that the tube, made by the sinking object, collapses in on itself and thus breaks up into smaller drops. In the case of a working combination, with castor oil below the silicone oil, the latter including particles is drawn downwards into the castor oil, and the particles will seek to place themselves on the interface with more of their volume in the castor oil rather than the silicone oil. Thus, the silicone oil will expand a little, making it possible for a tube to be made. This wettability situation is illustrated in Fig. 2.2.

Before allowing an object to fall through the silicone and the castor oils, the interface between the two oils is filled with particles which have sunk to the bottom of the silicone oil. These are not entirely tidily located, which means that there is a lot of open space, to which particles can move if necessary. What was observed during the experiments done, was that tubes were longer the larger the particles. This can be the consequence of that larger particles are heavier and have a larger volume, since a larger force is then needed to move the particles to the side so that the object can come through the interfacial particle layer. Hence, larger particles will decelerate the sinking object to a larger degree than smaller particles do, giving the object extra time to be able to pull some more particles down with it. Bearing in mind that larger identical particles attract each other more than smaller (according to Fig. 1.1a) and that the energy of the particles is higher when it is moved away from the interface (see Eq. (2.3)), the object is decelerated even more and more particles are pulled downwards, following the sinking object. This is underlined through the Figures 4.7b and 4.8c with the results 1.1 cm and 1.9 cm, respectively, using a glass sphere of d=4 mm. Parallel to this, it is possible to see a correspondence between the size of the sinking object and the aspect ratio a. The values for the tubes presented in Fig. 4.8 increase with larger object sizes. Though the aspect ratios of the tubes presented in Figures 4.7a and 4.7b are close to each other in value, the calculation of the tube in Fig. 4.7c underlines that larger objects create longer tubes with higher values of a.

As is covered above, increased mass, and hence volume, of the particles make the tubes longer. It was observed that the length of the tubes corresponded with the relationship between the cross-sectional areas of the sinking object and the container. This means that longer tubes were obtained if the cross-sectional area of the object was large compared that of the container. Examples can be seen in Figures 4.8c and 4.8d. However, by comparing the results in Figures 4.8e and 4.8f, the longest tube can be found in the largest container. Reaching a certain cross-sectional area, the object now has an advantage when sinking in the largest container.

CS particles tend to stick to each other to a larger degree than PE particles do, so that the tubes obtained with CS are longer, if any are achieved. Another advantage is that the particles more easily stick to the sinking object, making it possible to bring more particles down into the castor oil below. Again, the size of the particles at the interface matters. The larger they are, the bigger the chance to obtain tubes. This can be observed through looking at the two Figures 4.6a and 4.6d, with CS85 and CS20, respectively, and a sinking object with d=3 mm. Barely any droplets were formed when even smaller particles of diameter 5 μm were tried. Though the tubes made with the larger CS particles are longer and have got a larger value of the ratio a than what was the case for tubes covered by PE particles (see for instance Fig. 4.7a), the particles on the interface between the castor oil and the tube are not very orderly placed, located in more than one layer (see Fig. 4.6c). This lack of order makes it difficult to find out whether the observed results are tubes (hollow) and not only a tail of particles caused by the sinking object, see Figures 4.6a, 4.6c and 4.9b. This is something that has to be further investigated in the future.

Comparing the two figures 4.8a (obtained with glass sphere of diameter d=3 mm) and 4.9a (obtained with a metal sphere of diameter d=2 mm), both of which utilizing PE90-106, one can see that a certain amount of friction between the object and the surrounding fluids is needed if the object is to be able to pull particles with it from the interface. The velocity with which the object passes through the layer of particles at the interface will also matter. The quicker the objects sink through the interface (little friction), the less particles would be pulled at by the object, as was observed for metal spheres.

The stability of the tubes obtained varied with the type of particle used. Tubes covered by PE particles stayed stable for days, as opposed to those made with CS particles on the surface. The CS particles started to grow into lumps of particles and consequently started sinking due to the extra acquired mass, thus the tubes collapsed.

Chapter 5

Conclusion

Some different methods were applied to achieve the goal of producing tubes out of a silicone oil drop suspended in castor oil. It was found that the application of an electric field over a glass cell was unpredictable, since the deformations (stretching and rotation) are occurring in every direction. This great uncertainty did not, however, discourage fairly acceptable results. The most optimal tube obtained was the one with a length of 9.0 mm and an aspect ratio a=5.2, due to the relatively constant radius of the tube.

Furthermore, tubes were made by using pipette tips to manually stretch the droplets into tubes after having withdrawn some of the silicone oil originally situated in the droplet. Quite respectable results were obtained here, as well. Both Figures 4.3b and 4.3c show tubes of good values of lengths l and the ratio a, with the latter tube being the most preferable due to its fairly constant radius.

Coalescing two tubes before withdrawing silicone oil from the droplet was not an optimal method to obtain tubes, since the surface area of the coalesced drop was not jammed with particles. No results were obtained, see Fig. 4.4.

The longest tubes were obtained through the method of letting an object fall through a test tube containing two immiscible fluids. Allowing a manually formed plasticine object of diameter d=6.5 mm fall into a container of square base area of sides 1.40 cm, a tube of length l=4.0 cm was made. For smaller sinking objects no tubes were obtained with this container, but by using a container of a smaller base area, fairly good results were obtained also with smaller objects. In Fig. 4.8e the longest tube obtained in the test tube is shown, with its length of 2.9 cm and a ratio a=25. Though the lengths of the tubes are quite satisfying, their diameters are not, since they are not constant along the length of the tube. Thus, it can be fair to discuss whether these stretched droplets are to be called tubes compared to the results obtained with an external electric field or by pipette tips. The lengths of tubes obtained by using CS85 was good, but more work has to be done to determine whether they are hollow or not and hence can be called tubes.

It seems to be a correlation between the horizontal cross-sectional areas of the objects and the containers. The larger the object, the longer the tubes can be made. More friction between the object and the fluids gives the opportunity of creating longer tubes, so does larger particle sizes.

Chapter 6

Further work

Results obtained in this project are indicating relationships between variables taking part in process of making tubes. To further underline these findings, more work needs to be done.

Making tubes by applying an external electric field to a droplet or manually trying to deform it with pipette tips, initial droplet volumes could be changed. In this way, perhaps it could be possible to find out whether the volume of the initial droplet is significant for the length of the tubes obtained.

The concentration c of surface particles in the silicone oil (in all methods looked at in this project) might matter if long tubes are the desired outcome. This project did not reveal any correspondence between c and the length of the tubes, since the concentration was not changed throughout the experiments.

As for the method in which an object is sinking in a test tube or a taller container of a square base area, there are perhaps some adjustments that can be done to obtain longer tubes. By allowing an object to fall through a layer of CS85 in a longer test tube of the same diameter (0.85 cm) as was used in this project, the tubes might break loose from the particle layer at the interface of the two oils and the object lying at the bottom, thus giving an indication of how long the tube could be if floating freely in the castor oil. Also, it needs to be determined whether they are hollow, and therefore might be called tubes, or not. For all particles in question in this project report, cross-sections of objects could be increased even further compared with the cross-sections of the containers, thus hopefully obtaining longer tubes. Another factor that could be changed is the friction between the object and the oils, keeping mass and volume of the spherical objects the same throughout the experiments.

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