Pickering Emulsions Prepared with Ultrasound

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Contents

Chapter 1

Introduction

An emulsion is a mixture of two immiscible liquids in which one of the phases is dispersed in the other phase and, in general, these systems are prepared by applying shear; one of the phases is broken up into droplets by this shear. Examples of emulsions are milk, mayonnaise, butter and cream. Actually, the name emulsion is derived from emulgére (latin) which means "to milk out" [1][2][3]. Apart from these food emulsions they are widely used in a variety of applications, such as in cosmetics and drugs. Oil droplets in water allow the transport of materials soluble in oil and the release of the components onto a specific target can be controlled when using emulsions. This approach is for example used in drug delivery [4].

Emulsions are an example of metastable colloids and they exhibit behavior similar to solid colloidal particles: Brownian motion, reversible phase transitions as a result of droplet interactions, and irreversible transitions that generally cause destruction of the emulsion. One difference is that the droplets are more fragile; they must be protected against destruction. There are two mechanisms of destruction: Ostwald ripening, in which the dispersed phase diffuses through the continuous phase resulting in a decreased number of droplets with larger sizes, and coalescence, in which two droplets coalesce when they collide due to rupture of the thin film formed between the adjacent droplets which ultimately leads to the recovery of two macroscopic phases; the emulsion is destroyed in this case. Therefore, surface-active species are generally used to increase the lifetime of emulsions. They cover the droplet surfaces and delay both Ostwald ripening and coalescence. Surfactants are often used as emulsifiers in emulsions [4].

Another class of emulsions stabilised by colloidal particles, called Pickering emulsions, have been studied since the beginning of the 20th century when it was first reported that colloidal particles are able to stabilise liquid-liquid interfaces. Thereafter, they have been used in industry frequently, such as in food, cosmetics and paint industry. There has been a renewed interest in these systems in the last decade, partly because new applications for these systems have emerged and partly because of their stabilisation mechanism against coalescence which defers from the stabilisation mechanism of surfactant stabilised emulsions. Many studies now focus on a better understanding of the mechanical and physicochemical properties of these particle stabilised emulsions [5][6].

In order for particles to be adsorbed onto a water-oil interface they need to be partially wettable by both phases. When the particles are sufficiently large, larger than a few nanometers, the particles are irreversibly adsorbed and Pickering emulsions are formed. The particles will usually reside with their largest part in the continuous phase, dispersing droplets of the other phase. The ratio between the two phases and the wetting properties of the particles determine the type of emulsion formed; either water droplets in oil or oil droplets in water will be stabilised [5][7]. The solid particles attached to the interface protect the interface from coalescing with another interface, they serve as a mechanical barrier [6]. A unique stabilisation mechanism occurring in some Pickering emulsion systems is droplet bridging where solid particles bridge the interfaces of two droplets on approach. A dense monolayer of particles is formed in between the droplets preventing the thin film of the continuous phase from draining. Coalescence of the two droplets is prevented in this way [5][6][8].

Until now, most studies on droplet bridging consist of experiments in which two flat interfaces were brought into contact or a flat interface was brought into contact with a particle-laden droplet surface. During these studies it has been observed that bridging only occurs in systems where water droplets are dispersed in a continuous oil phase. Indeed, bridging has never been observed in oil-in-water emulsions [6]. Fuller et al. showed that tightly-packed ring and disk shapes were formed by particles in the film between a droplet and a flat interface [8]. Adhesive forces between 2 isolated droplets, sharing a monolayer of colloids, have also been measured. A novel method for determining the contact angle has been developed after comparing the measured adhesive forces to modelled forces [9]. As far as is known there has been one study concerning water-in-oil emulsions where droplet bridging occurred. They characterised the microstructure and rheology of these systems, observing gel-like behavior of the emulsions. Confocal microscopy was used to investigate the microstructure, revealing a percolating network of solid particles. Particle volume fraction was found to be an important parameter, determining the rheological characteristics. This bridging behavior provides long-term mechanical stability and resistance to gravitational effects and this is already achieved at droplet volume fractions well below the random-close-packing limit. In this study ultrasound was used as emulsification method [5].

The method used for emulsifying the systems is crucial for the bridging behavior to occur. This might be due to the different timescales involved in droplet formation and stabilisation, which are influenced by the emulsification technique. When these times are changed relative to each other emulsion droplets will be formed with different properties [10].

During this research project a Pickering emulsion system has been studied that contained bridging droplets when ultrasound was used as emulsification technique. However, this behavior did not occur when the emulsions were prepared by using mechanical agitation. Therefore, emulsions prepared with either ultrasound or vortex mixing are compared. Subsequently, the emulsions prepared with ultrasound are studied in more detail and confocal microscopy is used to study bridging qualitatively. The volume fraction of colloidal particles is varied to check whether this parameter is indeed important

and the water content has been changed relative to the oil content in order to study the effect this has on the bridging behavior. Droplet bridging has not yet been analysed quantitatively, so the droplet clusters are measured in size in order to quantify bridging.

Chapter 2

Theory

2.1 Pickering Emulsions

Pickering emulsions have been studied for many years for their importance in practical applications, such as cosmetics, food, paint, pharmaceutical and oil industries [11]. Colloidal particles, with particle sizes ranging from 1 nm to 1 μm, stabilise the emulsion droplets by strong adsorption at the liquid-liquid interface. Pickering emulsions generally have higher stabilities against coalescence than conventional surfactant-stabilised emulsions because the adsorbed particles behave as a mechanical barrier [12][6].

In surfactant-stabilised emulsions the shape of surfactant molecules can induce cur-

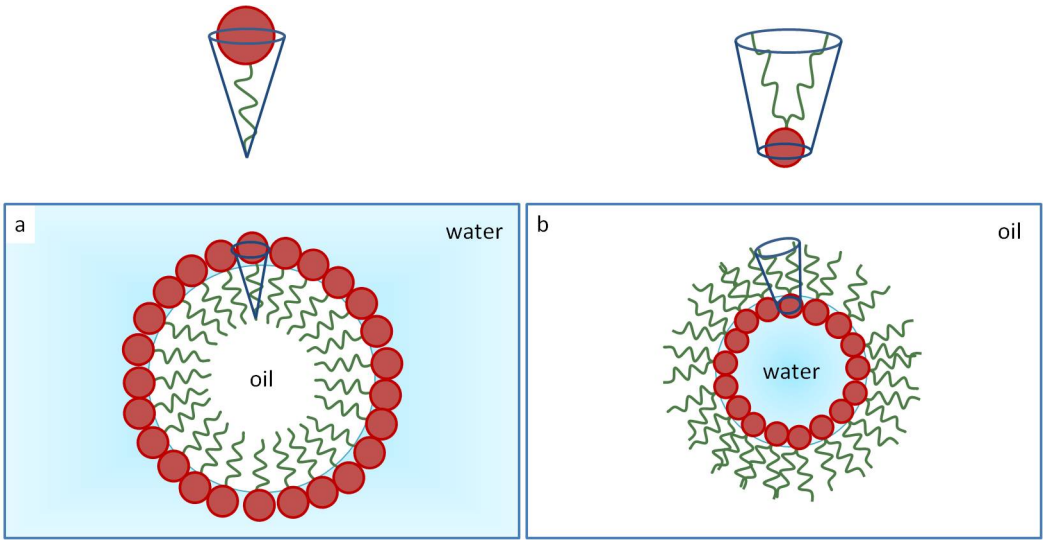

Figure 2.1: In surfactant-stabilised emulsions the type of emulsion formed depends on the shape of the surfactants. Surfactants with a relatively large headgroup form an oil-in-water emulsion (a) while surfactants with a relatively large tailgroup form water-in-oil emulsions (b).

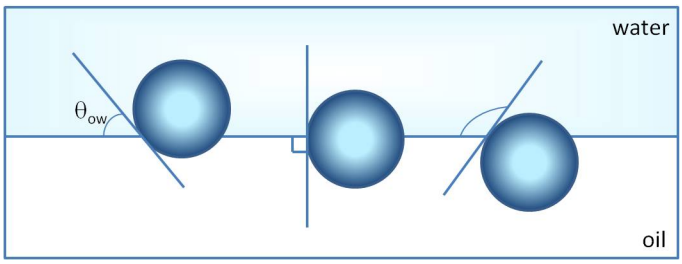

Figure 2.2: Position of a spherical colloid at a planar water-oil interface for a contact angle θ_{ow} of less than 90°(left), equal to 90°(centre) and greater than 90°(right).

vature. The way the droplet surface curves depends on the size of the head group relative to the size of the tail. Oil-in-water (o/w) emulsions are formed with surfactants consisting of a large head group compared to the tail group and water-in-oil (w/o) emulsions are formed with surfactants consisting of a large tail group compared to the head group [12]. A schematic representation of this dependence is shown in figure 2.1. In case of Pickering emulsions the contact angle the colloidal particle makes with the interface characterises the type of emulsion formed [13].

Figure 2.2 shows a colloidal particle at the interface at a contact angle θ_{ow}, which determines how the particle adsorbs at the interface when spherical particles are assumed. Generally, Hydrophilic particles make contact angles smaller than 90°, while hydrophobic particles make contact angles greater than 90°. The larger area of the particle surface will reside in its favourable phase which can induce curving of the interface. The favourable phase becomes the continuous phase which contains dispersed droplets of the unfavourable phase. Therefore, more hydrophilic particles tend to form o/w emulsions and more hydrophobic particles tend to form w/o emulsions. However, particles with a too high or too low wetting angle will not adsorb at the interface and will stay dispersed in their favourable phase, so partial wetting of the particle surface by both oil and water is required, leading to typical contact angles of around 90°. Examples of o/w and w/o emulsions are shown in figure 2.3. The stabilisation processes of surfactant-stabilised emulsions and colloid-stabilised emulsions have different mechanisms although both type of emulsions have comparable parameters to determine the type of emulsion formed. The type of emulsion formed may also depend on the ratio between the volumes of both liquids; the liquid with the smallest volume generally becomes the dispersed phase [12][13].

The driving force for particle adsorption to the interface is the reduction of the liquid-liquid interface. Therefore, a spherical colloidal particle is most strongly adsorbed at the water-oil interface if the contact angle is 90°; the particle then covers the largest possible area of the interface [12]. The energy required to remove a particle from the interface is highest in this case and the particles are effectively irreversibly adsorbed, provided that the particle sizes are in the colloidal range. In comparison, surfactants have the tendency to adsorb and desorb at relatively fast timescales compared to colloids due to their smaller sizes. Hence, their energy of detachment is much smaller. The energy

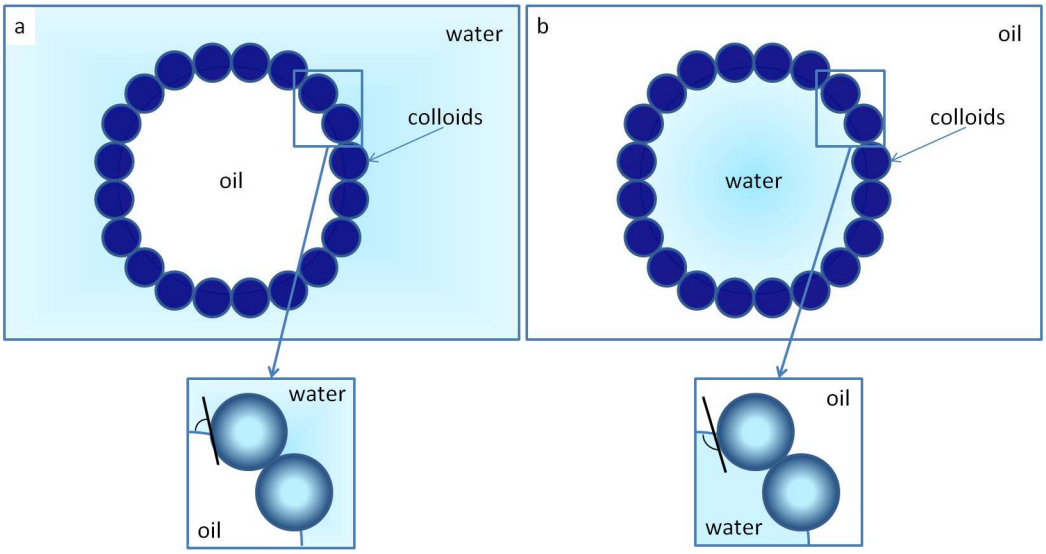

Figure 2.3: Spherical colloids at the interface of water and oil. More hydrophilic particles form o/w emulsions (a) and more hydrophobic particles form w/o emulsions (b).

required to remove a solid particle from the interface is given by equation 2.1

$$-\Delta_{int}G = \pi r^2 \gamma_{ow}(1 \pm \cos\theta_{ow})^2 \tag{2.1}$$

with contact angle θ_{ow} and surface tension γ_{ow} [13]. The sign inside the bracket depends on the phase from which the colloid is removed. The energy for removing a particle falls rapidly at degrees below or above 90°. Therefore, the energy of detachment is quite small for θ_{ow} between 0 and 20° or between 160 and 180° and stable emulsions are not formed. The colloid will detach and reside into the water phase when too small angles, below 90°, are present and the colloid will detach into the oil phase when too large angles, above 90°, are present. The stability of a Pickering emulsion depends on many parameters, e.g. particle size and shape, particle concentration, the surface properties of the particles and the interactions between the particles [13].

An increase in particle concentration generally results in a decrease in droplet size as a larger interfacial area can be stabilised when more particles are present and smaller droplets have a higher area to volume ratio. Hence, a larger total interfacial area is present when the system contains smaller droplets. This general idea holds at a qualitative level and the mean droplet diameter is estimated by equation 2.2.

$$D = \frac{6\phi_v V}{A} \tag{2.2}$$

Where ϕ_v is the volume fraction of the dispersed phase and $\frac{A}{V}$ is the interfacial area per unit volume of emulsion, which depends on the volume fraction of particles [14]. A limit in the decrease in droplet size is often present, set by the technique used for emulsification [13][15].

The amount of dispersed phase is another important parameter, which is linked to the amount of particles by considering the total amount of created interface. When the volume of the dispersed phase is decreased smaller droplets are stabilised when the same volume fraction of particles is used. A similar total interfacial area is stabilised in this way. Again the lower limit in droplet size is established by the used emulsification technique, combined with the properties of the system [14].

Apart from these properties determined by the system the formation and stabilisation of emulsion droplets also depends on the method used for preparing the emulsions.

2.1.1 Effect of emulsifying method

The formation of emulsions is a very complex process and despite many previous studies there is still a lack of understanding of the physical behavior of these systems [16][17]. Oil, water, emulsifiers and energy are needed for the formation of an emulsion; in case of Pickering emulsions the emulsifiers are colloidal particles. The composition of the system together with the method used for preparing the emulsion determine the type of emulsion, the volume fraction of droplets, the droplet size and its size distribution. The properties of the prepared emulsion, notably physical stability, are determined by these variables. Therefore, knowledge of the mechanisms behind emulsion formation are important [15].

Various processes occur during emulsification, such as droplet break-up, adsorption of the emulsifier and droplet collision, which may or may not lead to droplet re-coalescence. These processes all have their own characteristic timescale, depending on the way of processing [10]. A schematic representation of these processes is shown in figure 2.4 and the characteristic timescales involved are also shown.

Droplet break-up is commonly achieved by mechanical agitation of immiscible liquids and the quality of the formed emulsion can be characterised by looking at the droplet size and its distribution [16]. The formation of small droplets is an energy consuming process due to the Laplace pressure of the droplets p_L, which depends on the size of the droplet and the interfacial tension. This dependence is shown in equation 2.3

$$p_L = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R} \tag{2.3}$$

where γ is the interfacial tension between water and oil and R_1 and R_2 are the principle radii of curvature of the droplet. For a spherical droplet of radius R the equation becomes $\frac{2\gamma}{R}$. The Laplace pressure is defined as the difference between the pressure inside and outside the droplet and this difference will increase when a large droplet deforms and breaks up into smaller ones. In addition, The Laplace pressure is larger for droplet break-up of smaller droplets as the radii of curvature are smaller, see equation 2.3. To break up droplets into smaller ones agitation is generally used to transmit stress to the surrounding liquid and more vigorous agitation is needed when a higher Laplace pressure needs to be opposed. Hence, the smaller the droplets, the more intense the agitation should be to disrupt them and the higher the energy input should be to accomplish this [10][15].

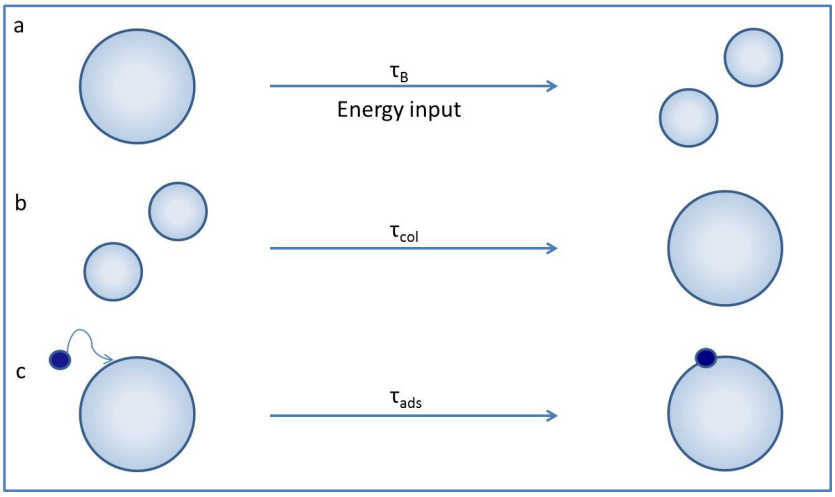

Figure 2.4: Simplified schematic of various processes occurring during emulsification: droplet break-up (a) with a characteristic timescale τ_B, droplet collision possibly leading to droplet coalescence (b) with the characteristic timescale τ_{col} and adsorption of colloids (c) with the characteristic timescale τ_{ads}.

This imposed stress can be shear or extensional stress, where shear stress deforms the droplets by preserving the volume while extension or compression do not. The break-up of droplets occurs at the critical capillary number Ca, which is defined as the ratio between the imposed stress σ and the Laplace pressure p_L. This dependence is shown in equation 2.4 [18].

$$Ca = \frac{\sigma}{p_L} = \frac{\sigma R}{\gamma} \tag{2.4}$$

The capillary number typically has a value of Ca = 0.1 - 0.5. Apart from this capillary number, the ratio p of the viscosity of the dispersed phase, η_d, to the viscosity of the suspending phase, η_s, is another key parameter for droplet break-up. This ratio is shown in equation 2.5 and p should not be too large for droplets to break up into smaller ones. When η_d is very high the droplet is more difficult to deform [18].

$$p = \frac{\eta_d}{\eta_s} \tag{2.5}$$

The emulsifier plays several roles in the formation and stabilisation of emulsion droplets. Colloidal particles adsorb onto a water-oil interface due to the decrease in unfavorable interfacial area between water and oil. When the droplet surface is covered with colloids there exists a mechanical barrier against coalescence. Hence, it is important to have knowledge of the timescale in which adsorption of colloids occurs, notably relative to the timescale for droplet collision [6].

Generally, uncoated droplets will coalesce when they collide and consequently coalescence will occur frequently during emulsification since droplets collide frequently during

emulsification. Emulsifiers are needed to prevent re-coalescence between droplets which have just been formed [15][6]. The relation between the timescale for particle adsorption and the timescale for droplet collision may give information about the amount of coalescence occurring during emulsification. This relation is defined in equation 2.6

$$\kappa = \frac{\tau_{ads}}{\tau_{col}} \tag{2.6}$$

where τ_{ads} is the timescale for particles to adsorb onto the liquid-liquid interface and τ_{col} is the timescale for droplets to meet each other. When $\kappa >> 1$ coalescence will occur frequently as more collisions can occur before a considerable amount of particles is adsorbed onto the water-oil interface. The coalescence rate will increase even more when the volume fraction of the dispersed phase is increased, due to an increase in the collision rate between droplets [15].

To summarise, three processes have been introduced each with a characteristic timescale: droplet break-up, adsorption of solid particles and droplet collision. These processes occur numerous times during emulsification and each timescale is small, e.g. a microsecond [15].

The droplet size of emulsions is thus influenced by the amount of re-coalescence occurring in the system and this phenomenon depends on several factors, which may be correlated to one another. An important parameter, next to the different timescales of the various processes, is the residence time of the emulsion droplets in the zone of emulsification. This time depends on several factors, such as the technique of emulsification and the used volume of the system. The residence time is also influenced by the amount of energy put into the system; the number of collisions between droplets is increased when the energy input is increased and the droplets leave the emulsification zone faster. When the droplets leave the emulsification zone they should leave it under turbulent condition hereby increasing the collision time and preventing droplets from coming into close proximity. The collision time can be increased even further by using a very small amount of the dispersed phase; droplet encounters will occur less frequent [19][20].

To recapitulate, the occurrence of re-coalescence is influenced by both the used emulsification technique and the properties of the system [19].

2.1.2 Mechanical agitation

The most important variable, when using different methods for emulsification, is the mechanism by which droplets are disrupted. External forces generally act on the continuous phase. When a static mixer or rotor stator is used these forces are created by mechanical agitation and there is an unbounded flow because the walls of the sample are relatively far away from most droplets; any droplet is surrounded by a large amount of continuous phase. The frictional (or viscous) forces cause shear stresses which act on the interphase between the continuous phase and the dispersed droplet. These stresses act primarily in the direction of the interface and can be generated by either laminar or turbulent flow, depending on the scale of the apparatus and the liquid viscosity [15].

The residence time of the droplets in the shear zone is relatively long when using a rotor stator or static mixer because the complete volume is mechanically agitated and hence the shear stresses are acting on interphases present in the total volume of the sample. The droplets spend a considerable amount of time under shear stress and, therefore, the colloids have more time to adsorb onto the formed droplets resulting in a low number of coalesced droplets [15].

Another important parameter which varies between different emulsification techniques is the maximum power input possible when using a certain method. Rotor stators or static mixers are not able to put much energy into the system. A power input of about 1 Watt is generally used when using these types of mechanical agitation which is considered to be low compared to the power input when using other techniques; the limit in droplet size is quite large, compared to the limit when using other emulsification methods [15].

2.1.3 Ultrasound emulsification

Preparing emulsions by using ultrasound is a very efficient method compared to emulsification techniques such as mechanical agitation. Ultrasound probes generally emit ultrasound waves with frequencies between 16 and 100 kHz and only powerful ultrasound has the ability to interact with matter, necessary for emulsification [21]. The mechanisms of droplet disruption and the main influencing parameters are not yet fully understood, but acoustic cavitation is considered to be the essential mechanism of droplet break-up when ultrasound is applied [21].

Cavitation only occurs in a restricted region, close to the ultrasound probe where the sound is emitted [20]. Cavitation bubbles develop at nuclei, i.e. micro-bubbles in the liquid, on dust particles or on the wall and these cavitation bubbles implode [21]. This causes intensive shock waves in the surrounding liquid and liquid jets of high liquid velocity are also formed. Li and Fogler ([22][23]) proposed a 2-step mechanism for the formation of emulsions: first, the dispersed phase is erupted into the continuous phase due to a combination of Rayleigh-Taylor instability and interfacial waves. Subsequently, the cavitation effect breaks up droplets, in the vicinity of the imploding bubble, into smaller ones. Hence, shock waves have a strong effect on the system, disrupting and mixing it, which causes formation of small droplets and the most influential parameters are those affecting cavitation phenomena [22][23].

Comparing ultrasound emulsification with methods using mechanical agitation has been done using several systems and it can be concluded that smaller droplet sizes are generally formed when using ultrasound which implies that less emulsifier is needed to prepare droplets of comparable sizes. In addition, the prepared emulsions, processed with ultrasound, are more stable and may exhibit different properties [24]. It is still not fully understood why the use of ultrasound results in the stabilisation of smaller droplets; this is probably caused by several differences between the methods. Ultrasound generally has a higher power input than mechanical agitation leading to smaller droplets when using ultrasound if there are enough emulsifiers present to cover this additional interfacial area.

Another reason for the differences in properties of the formed emulsions might be

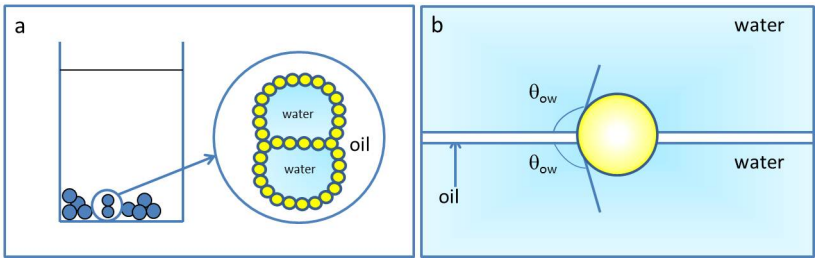

Figure 2.5: Droplet bridging: a schematic representation (a) and the position of a colloid when it bridges two droplets together (b).

the difference in residence time using either ultrasound or mechanical agitation. The residence time of the droplets at locations where they are broken up into smaller ones is shorter when using ultrasound, because cavitation phenomena are restricted to a small volume near the ultrasound probe [20]; once the droplets leave this region they will not break up into smaller ones anymore and re-coalescence may occur frequently, but can be diminished if emulsifiers have adsorbed onto the droplet surfaces and if the number of collisions between the droplets is decreased by decreasing the amount of dispersed phase. When mechanical agitation is applied, the residence time of the droplets in the region where droplet break-up occurs is longer. The solid particles have more time to cover the surface of the droplets hereby stabilising them against coalescence.

2.2 Droplet bridging

A unique phenomenon occurring in some Pickering emulsion systems is droplet bridging. Colloids protruding from a droplet surface can simultaneously adsorb to another interface, bridging two droplets. The bridges consist of monolayers of colloidal particles and the droplets are only separated by a thin film of the continuous phase. [8] A schematic representation of this behavior is shown in figure 2.5. There are several requirements for droplet bridging to occur and one of them is also shown in figure 2.5; the contact angle θ_{ow} should be satisfied on both sides of the thin film [5]. Another requirement for droplet bridging is that the droplets should collide with each other. However, if the rate of collisions is too high relative to the adsorption rate of colloids the particles will not be attached to the interface yet and particle bridges cannot be formed; the droplets will just re-coalesce, forming larger ones. Therefore, the relation between the timescale for adsorption and the timescale for collisions, κ, is of great importance [15].

Droplet bridging might act as a stabilisation mechanism against coalescence and it has been observed that the mechanical stability of the emulsion is increased when droplets are bridged together. Droplet coalescence is halted by the particles which hinder drainage of the inter-droplet film. [8] The rheology of such systems has been studied by Lee et al. ([5]) and appeared to be gel-like. Droplet bridging has been studied to some extent, but most studies concern two flat interfaces brought into contact or one

droplet brought into contact with a flat interface. Studies of Pickering emulsions in which droplet bridging occurs are scarce and there is still a lack of understanding [5].

One of the consequences of droplet bridging is the formation of smaller droplets when using the same amount of stabilisers compared to emulsions in which droplet bridging does not occur. The colloids are stabilising twice as much interface when they bridge interfaces together. Consequently, more interface can be stabilised by a similar number of solid particles. Pickering emulsions that contain bridged droplets also have another feature; the droplet surfaces flatten at places where droplets are bridged together by a monolayer of particles due to the contact angle being satisfied on both sides of the bridging particles. This flattening of the droplet surfaces is shown in figure 2.6, which is a confocal image of a Pickering emulsion containing bridged droplets [5].

2.2.1 The mean diameter over volume (the DeBroukere mean)

In this thesis the Debroukere mean (D_{43}) is determined for the mean droplet sizes and the mean cluster sizes. This mean is used because the simple mean does not accurately reflect where the mass of the system lies, while D_{43} does take this mass into account [25]. The equation for the DeBroukere mean is shown in equation 2.7 [26][4]

$$D_{43} = \left(\frac{\sum_i^n n_i D_i^4}{\sum_i^n n_i D_i^3} \right) \tag{2.7}$$

where D_i is the diameter of droplet i and n_i is the i_{th} droplet of a total of n droplets. The standard deviation σ in this mean diameter over volume can be determined from the polydispersity P as is shown in equation 2.8 [4].

$$P = \frac{1}{D_{43}} \frac{\sum_i^n n_i D_i^3 |D_{43} - D_i|}{\sum_i^n n_i D_i^3} = \frac{1}{D_{43}} \times \sigma \tag{2.8}$$

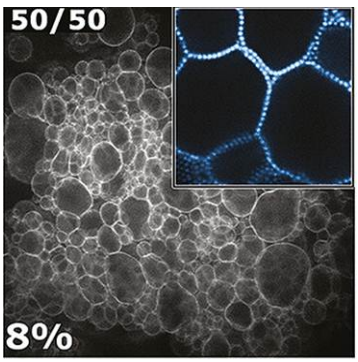

Figure 2.6: The surface of droplets flattens at places where droplets are bridged together by a monolayer of colloidal particles. [5]

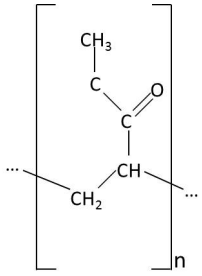

Figure 2.7: The structure of PMMA.

2.3 The system

Polymethylmethacrylate (PMMA) particles of two particle sizes are used as emulsifiers in this study. PMMA is a polymer of methylmethacrylate and the structure is shown in figure 2.7.

The solid particles are sterically stabilised by poly-12-hydroxystearic acid (PHS) and synthesised following Bosma et al. [27]. The PMMA is labeled with 4-chloro-7-nitrobenzo-2-oxa-1,2-diazol (NBD), a fluorescent dye which is excited when a wavelength of 488 nm is applied. This dye was chemically linked to the PMMA during synthesis. The particle radii of the particle batches used in this thesis are 315 nm and 1.1 μm. These particles were cleaned by 8 washing cycles using hexane. Subsequently, they were dried using an oven under vacuum at about 40 °C. Hence, the particles were stored as dry powders.

n-dodecane was used as received (Sigma-Aldrich, $\geq 99\%$) and water was distilled and passed through a Millipore Milli-Q RG system (resistivity 18 M$\Omega \cdot$ cm).

Chapter 3

Experimental

3.1 System preparation

The dried PMMA colloids were dispersed in dodecane using an ultrasonic bath for 30 min followed by about 10 s of vortex mixing after which water was added to the dispersion. The sample composition was typically: 0.1 to 9 vol-% of PMMA, 90:10 dodecane:water volume ratio, unless noted otherwise, where the dodecane volume was set at 3 mL. Subsequently, the emulsions were prepared using either vortex mixing for (3-10)×1 min, waiting 5 min in between cycles, or an ultrasonic probe for 10×6 s waiting 15 s in between cycles while changing the location of the probe in the sample.

The influence of the water vol-% was studied by varying the dodecane/water volume ratio from 90:10 to 99.9:0.1. To summarise, six sequences have been prepared and the sample compositions and the methods of emulsification of these sequences are shown in table 3.1.

Particle size	vol-% PMMA	dodecane:water	Emulsification method
315 nm	0.1-9	90:10	US
315 nm	0.5-7	90:10	VM
1.1 μm	0.5-7	90:10	US
1.1 μm	0.5-6	90:10	VM
315 nm	1	90:10 - 99.9:0.1	US
1.1 μm	2	90:10 - 99.9:0.1	US

Table 3.1: Sample compositions of the sequences of emulsions prepared in this study. Either utrasound (US) or vortex mixing (VM) is used for emulsifying the systems.

3.2 Optical microscopy

Apparatus: Olympus BX50 with Qimaging Micropublisher 3.3 RTV (camera)
A sample of the prepared emulsions was put on a microscopy slide and a coverslide was

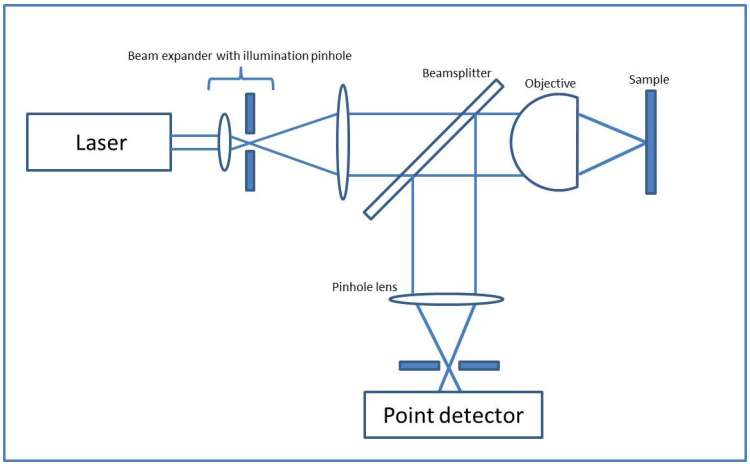

Figure 3.1: Simplified schematic of a confocal scanning laser microscope (CSLM).

put on top of this. The transferring of this small sample was done by using a pipette or a spatula depending on whether the droplets were clustered. The samples are studied at several magnifcations, varying from a 5× to a 50× magnifcation, and the microscope was calibrated before the samples were analysed.

3.3 Confocal microscopy

3.3.1 Theory

The basic principle of confocal scanning laser microscopy (CSLM) is illuminating and imaging an object point by point through a pinhole. A laser beam is used as illumination source and the beam is focused on a pinhole acting as a spatial filter. The light passing through the pinhole arrives at a microscope objective where it forms a diffraction-limited spot on the sample. The reflected beam is then deflected to a separate detector pinhole by a beamsplitter. This technique is called confocal because the objective lens is used twice, both for illuminating and for imaging the sample. The sample or illumination beam must be raster scanned since only one point is illuminated at a time and hence the image is built pixel by pixel. The scanning time of one spot generally takes about 10 seconds, so imaging a sample may take a considerable amount of time [28][29].

CSLM differs from standard optical microscopy in the sense that their depth of focus is shallow (vertical resolution of about 0.5 μm), hence, this technique is capable of accurate height and thickness measurements and of obtaining cross-sectional images. Confocal microscopes generally have a motorised stage which enables the study of the sample in the z direction; two-dimensional sections can be imaged at different depths in the sample, up to a maximum depth of about ten to hundreds of microns [29]. One of the major advantages of the CSLM is that a defocused image disappears rather than becoming blurred which happens when using a standard microscope. Another advantage

of using this technique is that the details of an image are not obscured by details from layers above or below the region of interest. Fluorescent material can be imaged using CSLM when a laser beam is used with a wavelength that excites this fluorescent material. Due to the excitation this material will fluoresce at a longer wavelength than that of the incident light and this fluorescent light passes a filter which eliminates the incident light and hence the fluorescent regions in the sample are imaged [28][29].

In summary, there are several basic requirements for the CSLM, like point illumindation, point detection, a confocal lens system and a method of scanning the image. A schematic representation of this technique is shown in figure 3.1 [28].

3.3.2 Sample preparation and used properties CSLM

Apparatus: Zeiss Observer.Z1 inverted microscope in conjunction with a Zeiss LSM700 scanning system

A sample of the prepared emulsions was put on a thin coverslide and the sample was prevented from drying by placing another, smaller, coverslide on top of the sample. Transferring the small sample from the emulsion onto the coverslide was again achieved by using either a pipette or a spatula, depending on whether the droplets were clustered. A 63× oil immersion objective was used and the confocal microscope was already calibrated. A laser beam with a wavelength of 488 nm was used as incident light source.

3.4 Sample preparation for cluster size analysis

The emulsions prepared with ultrasound form clusters of droplets. The sizes of these clusters have been analysed by transferring these clusters carefully with a spatula to a petridish, where the system is diluted by adding dodecane, the continuous phase, until the clusters were visible individually. The cluster sizes have been measured using the following method. The clusters of the emulsions are carefully transferred to a petridish, where the emulsion is diluted by adding more of the continuous phase. Pictures of these systems have been taken and these pictures are converted into 8-bit grayscale images after which the scale has been set (Analyze → Set Scale) and the images have been 'thresholded'. The option 'Analyze Particles' is then used for measuring the cluster areas with a lower limit of 0.1 mm^2 and no upper limit. A few options are checked, i.e. the 'show outlines' and the 'Display Results' boxes. After clicking OK, each measured area is outlined and the results are shown in a data window. These areas are then converted to diameters assuming that all clusters have circular areas. This procedure is summarised in figure 3.2.

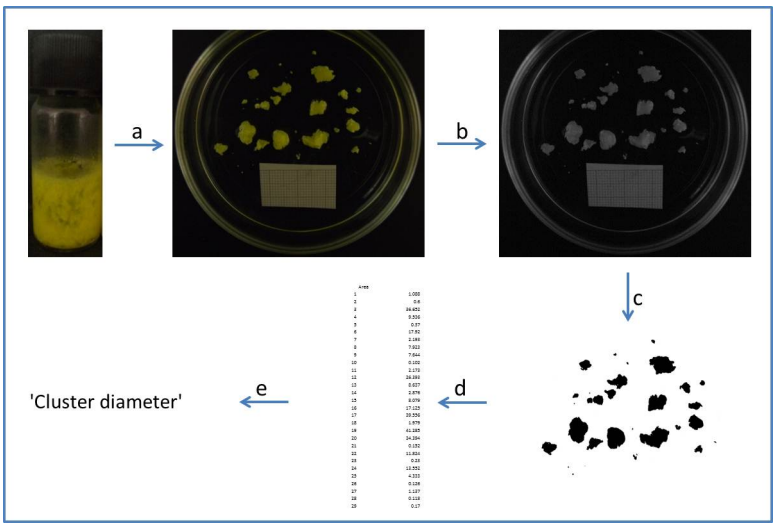

Figure 3.2: The procedure for area measurements using Image J. After transferring the clusters onto a petridish a picture has been taken (a), which is converted to a 8-bit grayscale image (b) and this image is 'thresholded' (c). Subsequently, the areas are measured (d) and the cluster diameters are determined from these areas (e).

Chapter 4

Results and discussion

4.1 Emulsifications

Redispersing PMMA particles of both size batches in dodecane results in yellow turbid dispersions. After adding water and emulsifying the samples with either vortex mixing (VM) or ultrasound (US) emulsions are prepared. Some examples of the prepared emulsions are shown in figure 4.1 and the emulsions prepared with VM differ from the emulsions prepared with US.

When VM is used emulsion droplets are formed which sediment within minutes, leav-

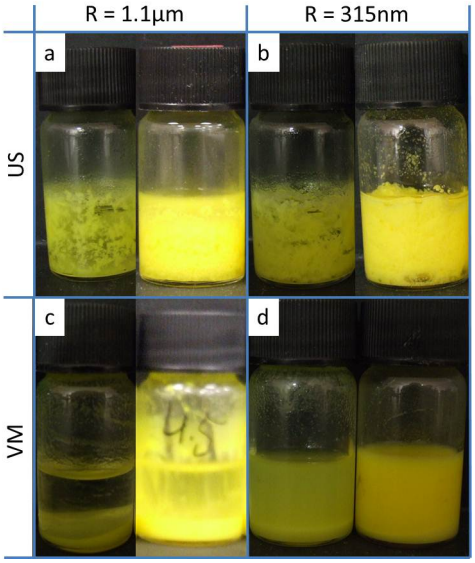

Figure 4.1: Prepared emulsion stabilised by particles of 2 sizes: R = 1.1 μm (a, c) and R = 315 nm (b, d), using either ultrasound (a, b) or vortex mixing (c, d). Two emulsions are shown of each type, where the left sample contains a smaller vol-% of PMMA than the right sample.

ing behind a clearer upper phase which may still contain some excess colloidal particles, depending on the used volume fraction of PMMA. By contrast, when US is used as emulsification method clustering of emulsion droplets is observed during emulsification.

In the next part of this thesis, the emulsions prepared with US will be compared to the emulsions prepared with VM. Subsequently, the emulsions prepared with US will be studied in more detail on the influence of the vol-% of PMMA and of the oil:water volume ratio, see section 4.3.1 and section 4.3.2 respectively.

4.2 Influence of emulsification method

The way an emulsion is prepared is a very important and complex parameter, which is hard to control. The difference between using VM or US for this particular system has not yet been studied in detail. In this section the emulsions prepared with these two methods are compared, both qualitatively and quantitatively. First, results from optical and confocal microscopy are shown. These results are discussed and subsequently the measured droplet sizes are given and discussed.

4.2.1 Optical microscopy

The emulsions are studied with the optical microscope and some pictures of emulsions prepared with VM and US are shown in figure 4.2. These pictures give a representative impression of the prepared emulsions.

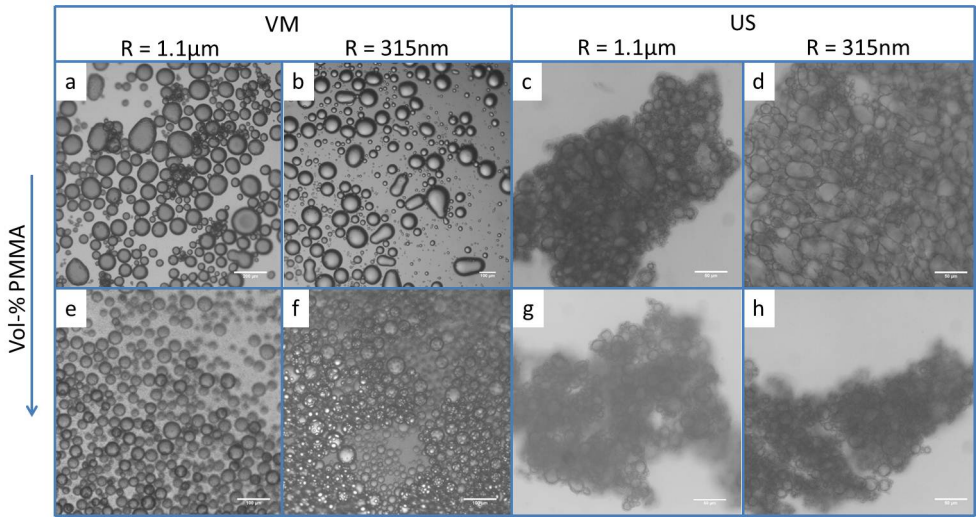

Figure 4.2: Optical microscopy images of emulsions stabilised by particles of 2 sizes: R = 1.1 μm (a, c, e, g) and R = 315 nm (b, d, f, h) prepared with vortex mixing (a-b, e-f) and ultrasound (c-d, g-h). The volume fraction of PMMA is increased going down in the figure.

Again, a clear difference is observed between emulsions prepared with VM and US; clusters of emulsion droplets are formed when US is used whereas separate droplets are present, which do not cluster, when using VM. Increasing the volume fraction of colloids results in a decrease in droplet size as can be seen in the optical microscope images. This qualitative result can be explained by considering the total amount of interfacial area that can be covered by the solid particles. When more particles are used they are able to cover more interfacial area, hence smaller droplets can be stabilised.

4.2.2 Confocal Microscopy

The emulsions are also studied qualitatively using confocal microscopy, which leads to more insight in the mechanism behind the clustering of droplets when ultrasound is used as method for emulsification. Some confocal images of the prepared emulsions are shown in figure 4.3. The images shown in this figure are representative for the prepared emulsions; other samples gave comparable images.

The confocal images of the emulsions prepared with US again show clustering of droplets while the images of the emulsions prepared with VM show separate droplets which are not often clustered or touching each other. Clustering in the samples prepared with US appears to be the result of a unique phenomenon: droplet bridging. The monolayers of PMMA particles are visible in the confocal images and the droplet surfaces are flattened at places where bridging occurs. This behavior is clearly observed in the emulsions containing larger colloids; these larger fluorescent PMMA particles can be observed individually. Droplet bridging also occurs in the emulsions containing PMMA with R = 315 nm, although colloids can not be observed individually in these samples.

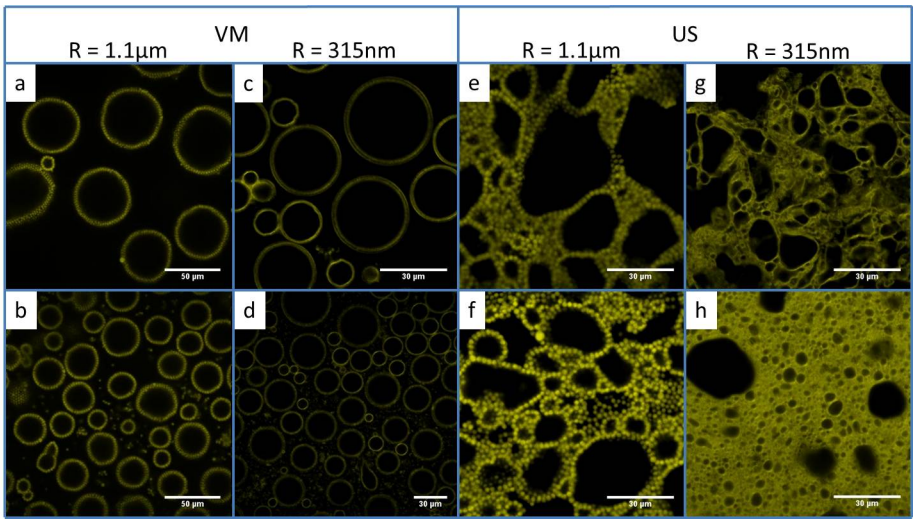

Figure 4.3: Confocal microscopy images of emulsions stabilised by particles of 2 sizes: R = 1.1 μm (a-b, e-f) and R = 315 nm (c-d, g-h) prepared with vortex mixing (a-d) and ultrasound (e-h). The volume fraction of PMMA is increased going down in the figure.

The droplets in these systems have flattened surfaces and the angle where the bridge stops also indicates droplet bridging.

4.2.3 Droplet size analysis

The droplet sizes have been measured from images taken with the optical microscope, using ImageJ. The mean over volume D_{43} has been determined from these droplet sizes and the results are shown in figure 4.4. A theoretical possible mean droplet size has been calculated and these values are also shown in the graph.

It can be concluded that the droplet size decreases with increasing vol-% of PMMA particles in all systems. This can be explained by considering the total amount of coverable interfacial area. When more particles are present they can cover a larger interfacial area between water and oil and hence smaller droplets can be stabilised which will not re-coalesce if enough particles are present.

Another observation is that smaller droplets are stabilised when smaller colloids are used. Smaller particles have a larger area to volume ratio than larger ones and therefore, more interface can be covered by smaller particles if a comparable volume fraction of particles is used.

Comparing the systems prepared with VM and US, the droplet sizes are smaller when the latter emulsification method is used, which has already been observed in other studies. [24] This observation can be explained by several mechanisms, e.g. a higher power input of the used emulsification method, different mechanisms for droplet break-up and droplet bridging.

To improve understanding of the cause of this difference in droplet size due to different processing techniques the ratio between the droplet sizes has been calculated. Table 4.1 shows the various ratios of the droplet size measured with VM to the droplet size measured with US. This ratio remains constant when changing the vol-% of particles, except for a high volume fraction when using the smaller particles.

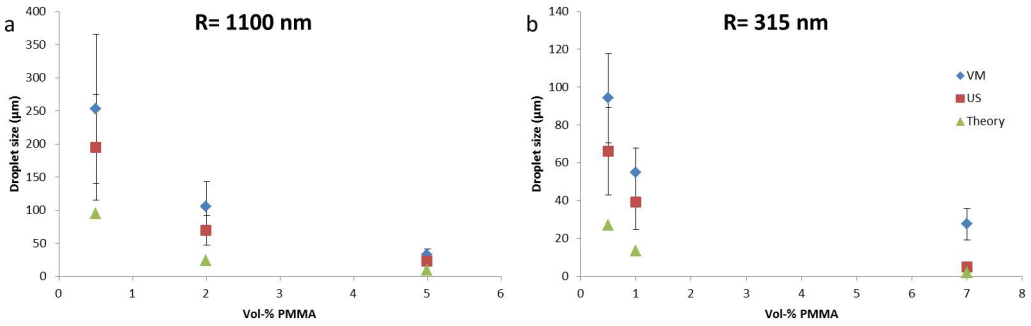

Figure 4.4: Graphs of droplet size d_{43} as a function of vol-% of PMMA for emulsions prepared by using vortex mixing (VM) or ultrasound (US) and the theoretically possible droplet size is added to the graphs (Theory). The droplets are stabilised by PMMA particles with R = 1.1 μm (a) or R = 315 nm (b).

R = 1.1 μm		R = 315 nm	
vol-% PMMA	$\frac{D_{43}(VM)}{D_{43}(US)}$	vol-% PMMA	$\frac{D_{43}(VM)}{D_{43}(US)}$
0.5	1.3 ± 0.8	0.5	1.4 ± 0.6
2	1.5 ± 0.7	1	1.4 ± 0.6
5	1.4 ± 0.6	7	5.6 ± 2.8

Table 4.1: Ratio between the droplet sizes of emulsions prepared with vortex mixing (VM) and ultrasound (US).

First, the emulsions prepared with the smallest volume fraction of PMMA are discussed. In these emulsions almost no freely dispersed PMMA particles were present in dodecane after emulsification. Hence, (almost) all particles are adsorbed onto droplet surfaces and comparable droplet sizes are predicted, because a comparable amount of particles is able to stabilise a comparable amount of interfacial area. However, the formation of smaller droplets when using ultrasound has already been mentioned in literature [24]. The mechanism responsible is not understood yet, but in this particular system droplet bridging is one of the causes as a certain fraction of the particles stabilises twice as much interface.

A limit in minimum droplet size is reached in the samples, prepared with VM, containing a high volume fraction of PMMA, like the emulsion containing 7 vol-% of PMMA particles with R = 315 nm. The upper phase of the emulsion is opaque and still contains many excess PMMA particles not involved in droplet stabilisation. This presence of excess PMMA is one of the causes for the larger ratio between VM and US when comparing the droplet sizes of each system. Whereas many excess PMMA particles, not adsorbed at liquid-liquid interfaces, are present in the emulsion formed by VM, no excess particles are present in the emulsion formed with US. All PMMA particles are involved in droplet stabilisation in the latter case, so more interfacial area is stabilised and therefore smaller droplets are stabilised. Furthermore, droplet bridging is also occurring in the emulsions prepared with US so the smaller droplet size is caused by at least two mechanisms in this case.

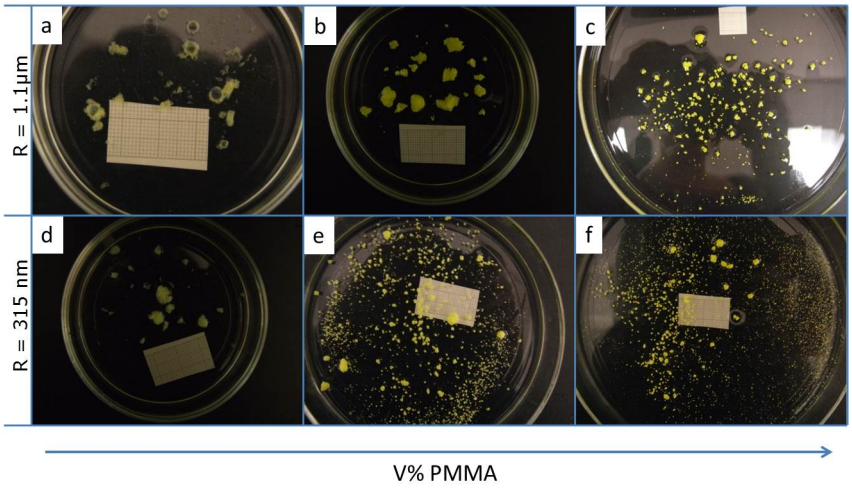

Figure 4.5: Pictures of droplet clusters from emulsions prepared with ultrasound and stabilised with particles of 2 sizes: R = 1.1 μm (a-c) and R = 315 nm (d-f). The volume fractions of PMMA are: 0.1 (a,d), 1 (b), 2 (e), 5 (c) and 7 vol-% (f).

4.3 Ultrasound emulsification

4.3.1 Influence of vol-% PMMA

In order to quantify the amount of bridging occurring in the emulsion systems prepared with ultrasound the sizes of the droplet clusters are determined using the method explained in section 3.4. Figure 4.5 shows some pictures of the clusters present in emulsions with increasing volume fractions of PMMA. This figure reflects the general picture of the influence of vol-% of PMMA on cluster size; cluster size decreases when increasing the amount of PMMA. It became increasingly difficult to transfer the clusters without disrupting them when less PMMA was used. At some point, around 1 vol-% of PMMA and below, it was impossible to transfer the clusters without breaking them and the analysis of the cluster sizes became impossible. This can be observed in the image containing 0.1 vol-% of PMMA where large water droplets are visible which are formed after disrupting the original clusters.

Figure 4.6 shows the droplet and cluster size as a function of volume fraction of PMMA for emulsions stabilised by particles of either R = 1.1 μm or 315 nm. Both the droplet and the cluster size decreases with vol-% of PMMA. Again, the region where it became increasingly difficult to measure the cluster sizes is shown (starting around 1 vol-% and below) and within this region the difference in cluster size does not change significantly anymore although in reality the cluster size still increases. Plotting the cluster size as a function of droplet sizes shows that the cluster size increases with droplet size. This could be due to several causes, e.g. droplets with larger diameters contribute more to the total volume, but other mechanisms involving droplet bridging may also cause this difference in cluster size. The region where cluster sizes could not

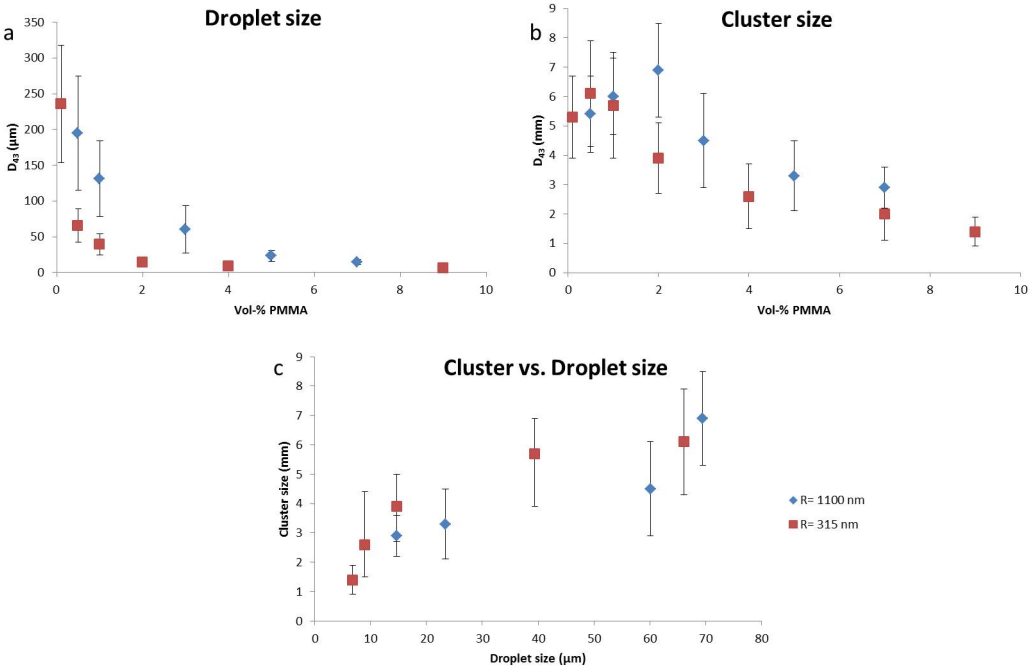

Figure 4.6: Graphs of droplet (a) and cluster size (b) as a function of vol-% of PMMA and the cluster size is also plotted as a function of the droplet size (c).

be measured accurately anymore is not shown in this graph.

The size of the stabilising particles does not seem to influence the cluster size drastically; the difference in cluster size between clusters in emulsions stabilised by particles of R = 1.1 μm or R = 315 nm is insignificant.

Calculating the number of droplets per cluster may give more insight in the amount of bridging occurring in each system. This number has been calculated from the mean

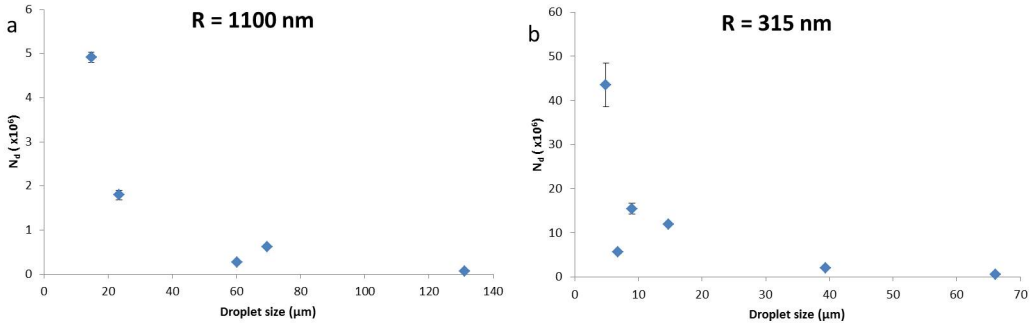

Figure 4.7: Number of droplets as a function of droplet size for emulsions stabilised by particles of R = 1.1 μm (a) or R = 315 nm (b).

cluster and droplet sizes, assuming a random packing of droplets ($\eta_p = 0.64$) [30] and the results are shown in figure 4.7. It can not be concluded that the number of droplets per cluster (N_d) decreases with increasing droplet size, because the results are alternating between large and small numbers. However, it can be concluded that N_d is larger when smaller particles are used as stabilisers. Smaller particles generally stabilise smaller droplets when a comparable volume fraction of stabilisers is used and hence more droplets per cluster are present if the clusters are not significantly differing in size which is observed in our ultrasound systems, see figure 4.6.

4.3.2 Influence of oil/water volume ratio

A requirement for the occurrence of bridging is that droplets meet each other. When droplets do not meet they can not cluster together by forming a monolayer of particles in between their surfaces. Decreasing the amount of dispersed phase generally leads to a decrease in droplet encounters and hence the amount of bridging is expected to decrease. This hypothesis is checked with experiments in which the volume fraction of water, relative to the volume fraction of oil, is decreased.

The prepared emulsions are shown in figure 4.8 and the samples containing less water differ from the samples containing 10 vol-% of water. Clustering of the droplets is decreased when the water volume fraction is decreased and the samples in which 0.1 vol-% of water is added have formed emulsions that do not contain any clusters. Fast

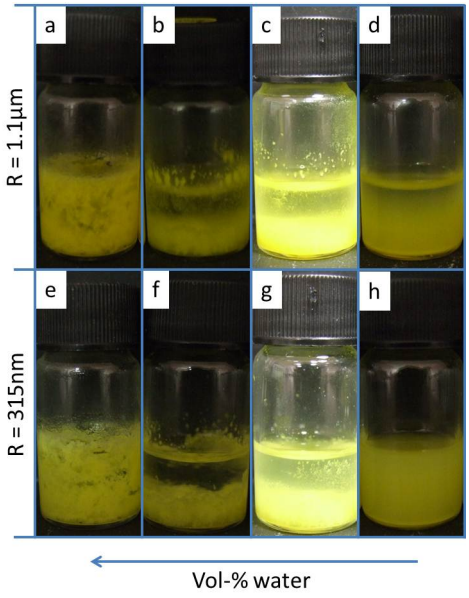

Figure 4.8: Emulsions prepared with ultrasound, stabilised by particles of R = 1.1 μm (a-d) or R = 315 nm (e-h). The volume fraction of water relative to the volume of oil is decreased going from left to right: 10 (a, e), 1 (b, f), 0.5 (c, g) and 0.1 vol-% (d, h).

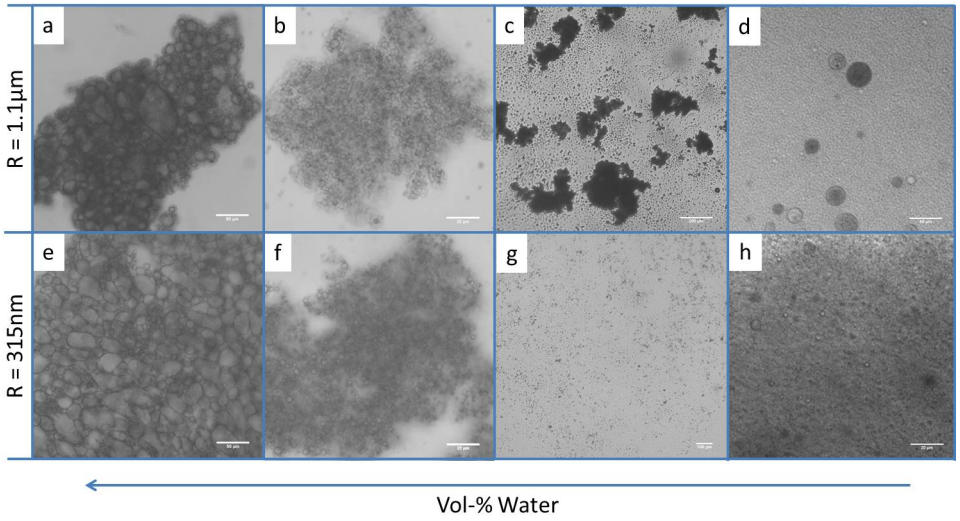

Figure 4.9: Emulsions prepared with ultrasound, stabilised by particles of R = 1.1 μm (a-d) or R = 315 nm (e-h). The volume fraction of water relative to the volume of oil is decreased going from left to right: 10 (a, e), 1 (b, f), 0.5 (c, g) and 0.1 vol-% (d, h).

sedimentation of droplets is observed in these samples and many excess PMMA is also present, observed by a slower sedimentation.

Figure 4.9 shows some bright field microscope pictures of emulsions prepared with varying water volume fractions. The droplet clusters in the emulsions decrease in size when this parameter is decreased until individual droplets are observed which do not cluster at all. These optical microscopy pictures confirm the conclusions drawn from looking at the emulsions themselves and a qualitative relation between volume fraction of water and cluster size is obtained.

This relation is also studied quantitatively using ImageJ as explained in section 3.4 and the results are shown in figure 4.10. It can be concluded that bridging indeed decreases when the amount of dispersed phase is decreased, confirming the conclusions drawn from previous results. When using a water volume fraction of 0.1 vol-% individual droplets are observed and clusters are not present in these emulsions; bridging is not occurring in these samples and the cluster sizes correspond to the sizes of the individual droplets.

4.4 Mechanism of droplet bridging

Some conclusions about the droplet bridging mechanism can now be drawn. As bridging does not occur in the VM emulsions it can be stated that the relations between the different timescales involved in emulsion formation are crucial. Especially the relation κ between the timescales of collision and adsorption of stabilising particles is crucial and this relation is different for VM and US, also depending on the residence time of droplets

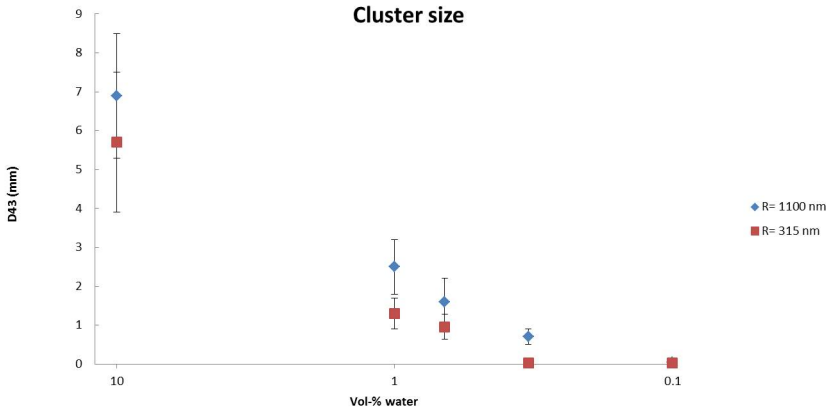

Figure 4.10: The cluster size as a function of vol-% of water (relative to the vol-% of oil) for emulsions stabilised by particles of R = 1.1 μm or R = 315 nm where the cluster size of the emulsions containing 0.1 vol-% of water is determined by measuring sizes of individual droplets.

in the shear zone.

The droplets in the US emulsions leave the emulsification zone fast because this zone is very small whereas the droplets in the VM emulsions are kept under shear during the entire emulsifying period. The colloidal particles have more time to adsorb onto the droplet surface in the latter emulsion before the droplets collide, stabilising their entire surfaces against re-coalescence. Particles in the US emulsion, conversely, have less time for adsorption and hence the droplets may not be fully covered when they collide. The droplets may, however, have enough particles on their surface for a different mechanism of stabilisation to occur: colloids form monolayers of particles in between the droplets in order to prevent re-coalescence.

This hypothesis is confirmed by experiments in which the volume of water was decreased relative to the amount of dodecane. When a smaller volume is dispersed, less droplets are present and when they leave the emulsification zone they will not collide with each other as frequently anymore because of the large dodecane volume. This decrease in water volume thus results in an increase in collision time. The colloids now have more time to adsorb onto the droplet surfaces before the droplets collide and this coverage may now be sufficient for stabilising the droplets against re-coalescence. The bridging mechanism is not occurring anymore in this case.

This might be the mechanism of droplet bridging in our system. However, more studies are needed to confirm this hypothesis and to improve the knowledge of the mechanisms of emulsion formation, especially when ultrasound is used as technique for emulsification.

Chapter 5

Conclusion

In this thesis emulsions prepared with either ultrasound or vortex mixing are compared. These emulsions differ on several aspects. First, it has been observed that the droplets are clustered when the former method is used while separate droplets, which do not cluster, are present if the latter method is used.

These emulsions have been analysed qualitatively by using both optical and confocal microscopy. It is concluded that droplet bridging is the cause for the clustering in the US emulsions; particle monolayers are observed between droplets. The droplet sizes of these emulsions have been analysed quantitatively and some trends are observed: the droplet sizes decrease with increasing vol-% of PMMA particles and with decreasing PMMA particle size. The droplet sizes of the US emulsions are smaller than the droplet sizes of VM emulsions.

These results can all be explained considering the amount of coverable interfacial area and the possible amount of interfacial area which can be covered by the colloids. The smaller droplet size using ultrasound as emulsification technique is caused by several mechanisms which differ for the two techniques, of which droplet bridging is known to be one of the mechanisms, next to the possible minimum droplet size which depends on the energy input and thus on the used technique.

The bridging behavior is studied quantitatively by measuring the sizes of the droplet clusters. It can be concluded that the cluster size decreases with increasing volume fraction of PMMA. It is not yet understood if this is exclusively due to the smaller droplet sizes or if the bridging mechanism is also one of the causes.

Finally, the volume fraction of dispersed phase was decreased, relative to the volume fraction of the continuous phase. This decrease results in a decrease in cluster size and eventually, bridging was not occurring at all, when a very small water vol-% was used. Separate droplets were observed in this sample. This decrease in bridging is due to an increase in collision time and hence colloids have more time to adsorb, stabilising the droplets.

Chapter 6

Outlook

The mechanisms of droplet bridging and emulsion formation using ultrasound are still not fully understood. More research is needed to get more insight in the timescales of the various processes taking place in these systems. The study of these systems under confinement might confirm the hypothesis made in this thesis, which stated that the particles in the US system do not have enough time to cover the prepared droplets sufficiently before the droplets encounter each other again. The expectation is that droplet bridging does not occur when the system is emulsified under confinement, as a larger part of the total volume will be under shear and hence droplets are repeatedly broken up until the surface is sufficiently covered for droplet stabilisation to occur.

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Appendix A

Additional experiments

Several additional experiments have been done after finishing the studies discussed in this thesis in order to get more insight in the mechanism of droplet bridging. First, the residence time of the droplets in the shear zone was increased by using smaller total volumes in smaller bottles. The exact properties of the used emulsion systems are shown in table A.1 and the emulsification time was adjusted from 6×5 s of emulsification with 15 s of rest in between the cycles to 30 s of emulsification. These changes in emulsification time/pulses were not of great influence on the prepared emulsions. The decrease in total volume did not result in a decrease of clustering; the cluster sizes of these samples were comparable to the cluster sizes of the emulsions prepared in the original bottles and the original volumes. This can be explained by the fact that the used volume and used bottles were still too large; the droplets were still thrown out of the zone of emulsification resulting in a clustering which was visible about 5 seconds after emulsification was started. During some emulsifications part of the clusters were driven upwards. This upper layer sometimes stayed static and these droplets exhibit a less amount of time under shear. It might be insightful to analyse the difference in cluster size between the clusters in this upper layer and between the clusters of the lower part.

The opposite situation was also tested: the total volume of the system and the total volume of the used bottle were increased and a magnetic stirrer was used in these

Vial diameter	Oil volume	Water volume	vol-% PMMA	Particle size
1.1 cm	1 mL	0.01 mL	2-vol%	1.1 μm
1.1 cm	1 mL	0.1 mL	5-vol%	1.1 μm
1.1 cm	1 mL	0.01 mL	1-vol%	315 nm
1.1 cm	1 mL	0.1 mL	7-vol%	315 nm
2.7 cm	15 mL	1.67 mL	3-vol%	1.1 μm
5 cm	30 mL	3.34 mL	3-vol%	1.1 μm
2.7 cm	15 mL	1.67 mL	4-vol%	315 nm
5 cm	30 mL	3.34 mL	4-vol%	315 nm

Table A.1: Properties of the prepared emulsions

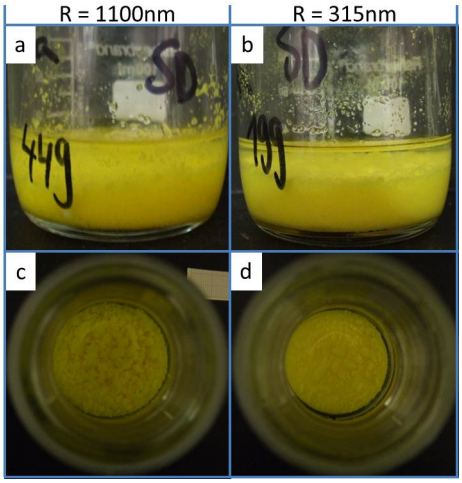

Figure A.1: Clusters present in the prepared emulsions containing 30 mL dodecane. The emulsions are stabilised by either 3-vol% of particles of R = 1.1 μm (a-b) or 4-vol% particles of R = 315 nm (c-d). The total oil volume was either 15 ml (a,d) or 30 mL where the larger volumes were prepared in larger bottles.

systems. The used properties are again shown in table A.1 and figure A.1 shows the clusters present in the prepared emulsions containing 30 mL dodecane. Larger clusters are present in the upper part of these emulsions, which might be due to several causes. The stirring bean, for example, does not break up these clusters. Another cause might be that these clusters have a very short residence time in the zone of shear and therefore, after they have left this region, form more bridges in between droplets due to fewer particles on the droplet surface while the droplets in the lower part spend a longer time under shear and hence bridging occurs less often between droplets in this region.

The cluster sizes in these samples thus defer in size depending on the region they are in and it might be insightful to check this quantitatively. Figure A.2 shows the clusters of the samples containing either 15 mL or 30 mL dodecane and it can be seen that fewer large clusters are present in the 15 mL oil samples. The formed clusters in the samples containing 15 mL dodecane were partly broken up due to the stirring bean, resulting in a smaller final cluster size compared to the emulsions with a larger total volume. This difference in cluster size may again be caused by the two mechanisms already given; the stirring bean broke down part of the formed clusters and the region of shear is larger in these smaller volumes relative to the emulsions with larger total volumes.

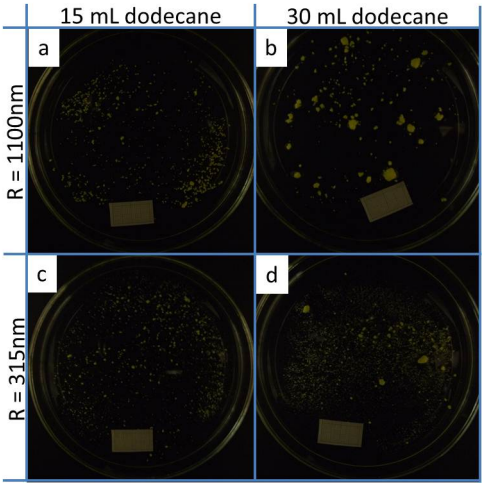

Figure A.2: Clusters present in the prepared emulsions with larger total volumes. The emulsions are stabilised by either 3-vol% of particles of R = 1.1 μm (a-b) or 4-vol% particles of R = 315 nm (c-d). The total oil volume was either 15 ml (a,d) or 30 mL where the larger volumes were prepared in larger bottles.