Interactions of hydrophilic particles in hydrophobic media in the presence of a hydrophilic immiscible liquid



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Abstract

Several food products consist of highly concentrated suspensions of particles in oil or fat media, such as peanut butter and other types of spreads. The addition of an immiscible secondary liquid to such suspensions, even in small quantities, leads to a transition from a liquid-like to a solid-like structure due to the agglomeration of the solid particles. Information about the agglomeration of solid particles can be derived from the determination of the interactions between particles and the parameters that affect them. Consequently, this agglomeration and spanning filling network formation could be used to create food products with a tailored structure, and as a result, assist in food product design.

The aim of this project is to explore the agglomeration of particles in fat-continuous suspensions on both macro and micro scales. For this purpose, model food systems were established as highly concentrated suspensions of crystalline sucrose or glass particles in vegetable oil. The effects of adding different secondary immiscible liquids (water, saturated sugar solution and glycerol) were evaluated. The particle network formed upon the addition of such secondary liquids was assessed by monitoring particle and agglomerate size using laser diffraction and also by means of analysing the flow behaviour of the samples. In addition, interaction forces between a particle and a surface mediated by a secondary immiscible liquid inside oil medium were measured using an atomic force microscope (AFM). The use of an AFM in viscous media such as vegetable oil and the creation of bridges composed of different liquids are both challenging tasks. Therefore, in this project, two methods for the formation of liquid bridges between particle and surface were developed. One was based in the creation of water bridges by saturating the oil medium through an increase in relative humidity, while the other consisted of using an inverted microscope to locate individual small droplets of secondary liquid dispersed in oil continuous phase.

Macroscale observation showed that there is an increase in apparent viscosity upon addition of a secondary liquid for the sugar and glass suspensions. This could be supported by the agglomeration of the fine solid particles, which are preferentially wetted by the hydrophilic secondary liquid, forming liquid bridges. Analogously, on a microscale, strong and long-ranged adhesion forces were measured between a glass particle and a glass and sugar surfaces in oil in the presence of water or glycerol as secondary liquids; which confirms the formation of liquid bridges. The measured forces upon separation were dominated by capillary attraction when a liquid of high interfacial tension and low viscosity such as water formed the liquid bridges. When a highly viscous liquid formed the bridge (glycerol), a dynamic viscous interaction contributed to the adhesion leading to a higher force, which was less dependent on the volume of the bridge.

Furthermore, the effect of material parameters, such as particle size, shape, concentration, interfacial tension and viscosity and wetting properties of the secondary liquid, on the network formation in suspensions and on the interaction forces of particles and surfaces in oil upon the addition of secondary liquids was evaluated. The apparent viscosity of the suspensions with added secondary liquid showed to be inversely proportional to the particle size and dependent on particle shape – irregular particles form stronger networks. The viscosity of the secondary liquid had a significant effect in dynamic situations. An increase in viscosity for suspensions with added viscous secondary liquid was only observed at high shear rates. Similarly, on a microscale, a steeper increase in adhesion force was observed for more viscous liquid bridges upon an increase in the separation speed of particle and surface. Moreover, the addition of lecithin showed very comparable results both on macro and micro scales. The stabilization of secondary liquid droplets by the surfactant led to decreased adhesion energies, explaining the lower viscosities in suspensions of particles with added glycerol containing surfactant.

Finally, this work and the information about the agglomeration process may be further applied in an industrial context in order to adjust the properties of a particle network, enabling the creation of tailored solid particle networks in food products.

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Table of Contents

Abstracti				
Acknowledge	nentsiii			
List of Publica	tions and Presentationsix			
Chapter 1 In	troduction1			
1.1 Objecti	ves & Scope of the project2			
1.2 Thesis	Outline			
Chapter 2 Li	terature Review			
2.1 Introd	uction5			
2.2 Interfa	cial phenomena6			
2.3 Intera	ctions of solid particles dispersed in a liquid9			
2.3.1 var	n der Waals attraction9			
2.3.2 Ele	ectrostatic interactions11			
2.3.3 Sol	vation or structural forces11			
2.3.4 Hy	drodynamic forces12			
2.3.5 Lic	luid bridges			
2.4 Adhes	ion19			
2.4.1 Co	ntact mechanics			
2.4.2 Ad	hesion hysteresis			
2.5 Interp	article forces and the macro-behaviour in suspensions			
2.5.1 Rh	eology of suspensions22			
2.6 Direct	measurement of interparticle forces27			
2.6.1 Ato	omic Force Microscopy (AFM)29			
2.7 Agglon	neration in dispersions of solid particles in liquid media – previous work . 31			
2.8 Conclu	isions			
Chapter 3 M	aterials & Methods			

3.1	Ma	terials
3.	1.1	Model food systems
3.	1.2	Hydrophilic particles
3.	1.3	Hydrophobic continuous phase42
3.	1.4	Hydrophilic liquid44
3.2	Me	thods45
3.	2.1	Preparation of suspensions
3.	2.2	Rheology45
3.	2.3	Particle size determination by laser diffraction46
3.	2.4	Interfacial tension
3.	2.5	Contact angle
3.	2.6	Atomic force microscopy49
3.	2.7	Scanning electron microscopy
Chapt	er 4	Network formation by agglomeration of particles52
4.1	Int	roduction52
4.2	Ma	terials & Methods
4.3	Re	sults and Discussion
4.	3.1	Network formation by agglomeration of particles
4.	3.2	Evaluation of agglomeration by laser diffraction57
4.	3.3	Flow behaviour of fat-based suspensions upon addition of a secondary liquid61
4.	3.4	
4.		Note on the elimination of slip with the use of serrated plates
	3.5	Note on the elimination of slip with the use of serrated plates
4.4	3.5 Co	Note on the elimination of slip with the use of serrated plates
4.4 Chapt	3.5 Co er 5	Note on the elimination of slip with the use of serrated plates
4.4 Chapt 5.1	3.5 Co er 5 Int	Note on the elimination of slip with the use of serrated plates
4.4 Chapt 5.1 5.2	3.5 Co er 5 Int Ma	Note on the elimination of slip with the use of serrated plates
4.4 Chapt 5.1 5.2 5.	3.5 Co er 5 Int Ma 2.1	Note on the elimination of slip with the use of serrated plates
4.4 Chapt 5.1 5.2 5. 5.	3.5 Co er 5 Int Ma 2.1 2.2	Note on the elimination of slip with the use of serrated plates
4.4 Chapt 5.1 5.2 5. 5. 5.	3.5 Co er 5 Int 2.1 2.2 2.3	Note on the elimination of slip with the use of serrated plates

5.	2.5	Surfactant addition79
5.3	Res	sults and Discussion
5.	3.1	Effect of particle size
5.	3.2	Effect of particle shape and density
5.	3.3	Effect of particle concentration
5.	3.4	Effect of the viscosity and wetting properties of the binder
5.	3.5	Effect of the addition of a surfactant92
5.4	Co	nclusions96
Chapt	er 6	Microscale study of particle agglomeration in oil-based suspensions
6.1	Int	roduction
6.2	Th	eory99
6.3	Ma	terials & Methods102
6.	3.1	Secondary immiscible liquid: water addition through relative humidity
in	lcrea	use102
6.	3.2	Secondary immiscible liquid: Different binders dispersed in oil103
6.4	Re	sults and Discussion105
6.	4.1	Forces in purified sunflower oil105
6.	4.2	Effect of relative humidity on the adhesion of a spherical glass particle and
fla	at gl	ass surface
6.	4.3	Effect of different secondary binding liquids on the adhesion of spherical glass
pa	artic	le and flat glass surface
6.	4.4	Saturated sugar solution as the secondary liquid123
6.5	Co	nclusions125
Chapt	er 7	Effect of material parameters on the surface forces 127
7.1	Int	roduction
7.2	Ma	terials & Methods128
7.3	Res	sults and Discussion
7.	3.1	Effect of viscosity and wetting properties on the bridge – glycerol and relative
h	umic	1ity
7.	3.2	Effect of the addition of a surfactant on surface forces in oil
7.	3.3	Sugar colloidal probe142

7.3.4 Sugar surface
7.4 Conclusions
Chapter 8 Conclusions & Future Work154
8.1 Macroscopic behaviour: Particle size and rheology154
8.2 Microscopic behaviour: AFM156
8.3 Parallels between macroscopic and microscopic behaviour
8.4 Future Work
Notation161
List of Figures164
List of Tables174
References 175
Appendix I. Interfacial properties measurement
I.1. Introduction
I.2. Materials186
I.3. Methods
I.4. Detailed Results
I.4.1. Interfacial tension
I.4.2. Contact angle189
Appendix II. Investigation to obtain smooth sugar surfaces
Appendix III. Calculation of forces due to liquid bridges between flat surfaces
III.1. Bridge behaviour for different liquids197
III.2. Volume of the bridge199
III.3. Effect of viscosity
III.4. Effect of contact angle 202
III.5. Effect of interfacial tension203
Appendix IV. Liquid bridges Mathematica [®] code205

List of Publications and Presentations

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Chapter 1

Introduction

Numerous food products consist of hydrophilic solid particles dispersed in a continuous fat/oil phase. Such examples of fat-continuous suspensions or pastes are spreads and confectionery products. In such products, texture, flow behaviour, stability and appearance are important attributes to the consumer.

The addition of an immiscible liquid in highly concentrated suspensions of particles in fat media leads to a transition from a liquid-like to a solid-like macroscopic structure. This phenomenon is attributed to the agglomeration of particles by liquid bridges, resulting in a space-filling network (Johansson and Bergenståhl 1992, Dedinaite, Claesson et al. 1998).

Agglomeration in suspensions has been used in industry mainly as means of purification or extraction of valuable components from bulk (Rossetti and Simons 2003). In the food industry, agglomeration in dispersions is often related with product instability and, is therefore undesirable. Oil-continuous systems are never completely free of water; they can either contain minute amounts as a result of an equilibrium with ambient relative humidity, or because it has been added to the system (Israelachvili 1985, Johansson and Bergenståhl 1992). These traces of water, for example, could lead to the aggregation of particles which would result in increased sedimentation, thus resulting in phase separation and formation of a cream layer and/or sediment (Walstra and Vliet 2008). However, if this agglomeration process driven by the addition of an immiscible liquid is fully understood, i.e. the interparticle interactions that are driving agglomeration are identified and their effect quantified, agglomeration can be used to create food products with a customized structure, to match products with consumer needs, and, therefore, assist in food product formulation and structural design.

Food suspensions have a large surface-to-volume ratio due to the small size of dispersed particles. In addition, particles in food systems are often densely packed so that numerous particle-particle interactions may occur during manufacture and storage (Walstra 2003). Therefore, the forces acting between the surfaces are of extreme importance for determining the behaviour of these systems and the adhesion mechanisms. Moreover, the interaction forces between particles play a vital role in material properties such as stability, structure, rheology and appearance.

In the absence of water (or any other polar liquid), the force that predominates between two particles in non-polar media, such as edible oils and fats, is a monotonic attraction, the London-van der Waals force. However, at very small separations (Angstrom-scale) the short-range repulsive solvation and structural forces become important. Electrostatic repulsion can be anyways considered negligible in non-polar media. Hydrodynamic forces on the other hand would become important when bringing two particles into contact because the liquid between them would represent a resistance and a contact could only be possible upon drainage of the film. In the presence of an immiscible (polar) liquid such as water, the formation of liquid bridges results in forces of magnitudes that would dominate over the ones previously mentioned (Claesson, Dedinaite et al. 1997, Liang, Hilal et al. 2007).

Thus, the formation of **liquid bridges** is the initial hypothesis supporting the transition of fat-based suspensions from a fluid-like to a solid-like behaviour upon the addition of a secondary immiscible liquid. In order to verify the initial hypothesis, the aim of this PhD project is to experimentally measure the adhesion forces between particles and surfaces in oil in the presence of water and other immiscible hydrophilic liquids, and finally build a comparison of these quantitative results with the network formation on a macroscopic level and the existent theory.

Another main challenge of this project is that food particles are not inert and can interact with the bridge materials. Sucrose, for example, is highly soluble in water, and its dissolution in the liquid bridges results in alterations in the bridges, leading to possible stronger interactions. Therefore, the focus lies on identifying the forces holding these particles together and forming a strong network.

1.1 Objectives & Scope of the project

The scope of this PhD project is to explore agglomeration mechanisms of water-soluble particles in model food fat-continuous suspensions. This will involve a study of the macroscopic network formation and the microscopic characterization of the interactions of solid surfaces in oil-continuous phase mediated by a liquid bridge.

Therefore, the objectives of this project can be summarized as follows:

• To explain the role of hydrophilic immiscible liquids in the creation of solid particle networks in fat-based systems;

- To experimentally measure interparticle forces in fat-based systems, in order to identify and characterize them, depending on particle and immiscible material characteristics;
- To compare the measured macro and micro interactions in terms of the existent theory to predict interactions forces between particles, giving emphasis to the contribution due to liquid bridges formation;
- To describe the dependency of the interparticle interactions and network formation on the following material parameters:
 - Viscosity of the liquid bridge;
 - Wettability of the three-phase system (solid particle/surface, oil continuous medium, secondary immiscible liquid);
 - Addition of surfactants and consequently interfacial tension;
 - $\circ~$ Particle size and shape.

1.2 Thesis Outline

In the framework of this thesis, the agglomeration of hydrophilic particles in hydrophobic media due to the addition of a secondary immiscible secondary liquid is investigated on both macro and micro scales.

In Chapter 2 the state of the art is reviewed. The fundamentals regarding interface phenomena, interactions of particles in liquids, rheology and methodologies to experimentally determine interaction forces are described. The previous work concerning the agglomeration of particles in suspensions is reviewed, citing works done on both a macro and micro scale. Finally, the research areas which merit further investigation, and that are covered by this work, are clarified.

In Chapter 3, the general materials & methods used throughout this thesis are described. Materials or methods that were used for very specific experiments are described in the relevant results chapters.

Chapters 4 to 7 correspond to the results and discussions of this present work.

In Chapter 4, the network formation in suspensions of glass and sugar particles in oil due the addition of a secondary immiscible liquid is described. This agglomeration process is investigated using different experimental techniques such as microscopy, laser diffraction (particle size distributions) and rheology (flow behaviour). In addition, the effect of adding different secondary liquids (water, saturated sugar solution and glycerol) is also discussed. In Chapter 5, the effect of material parameters on the network formation is evaluated. The influence of particle size, shape, concentration, viscosity of the secondary liquid (or binder) and the addition of a surfactant on the flow behaviour of oil-based suspensions are examined.

In Chapter 6, colloidal probe AFM is used to investigate the particle agglomeration in oilbased suspensions on a microscale by measuring the interaction forces of a particle and a flat surface. The spherical particle-flat surface geometry is used a model for interparticle interaction because of its experimental advantage in the creation of liquid bridges and also because it can be easily generalized to interactions between two spherical particles. Two methods for the measurements of forces between a particle (colloidal probe) and a flat surface mediated by a droplet of an immiscible secondary liquid in oil media are developed. The influence of two binding liquids with different properties (viscosity, interfacial tension and wetting characteristics) on the adhesion between a particle and a flat surface was then examined and discussed in terms of the forces acting between them.

In Chapter 7, analogously to the analysis presented in Chapter 5 for the macroscopic behaviour of sugar and glass suspensions in oil, the effect of material parameters on the surface forces are explored. The effect of the viscosity of the liquid bridge and the addition of a surfactant are measured using colloidal probe AFM. The use of a sugar colloidal probe and also the formation of liquid bridges between a glass colloidal probe and a sugar surface are also elucidated.

Finally, in Chapter 8 the conclusions of this work are summarized and parallels are drawn between the macro and micro behaviours, linking interparticle forces to the network formation. Recommendations for further scientific research are also proposed.

Chapter 2

Literature Review

In this chapter the literature relevant to the topic of interactions of particles in oil media with and without the addition of a secondary immiscible liquid is reviewed. The basics concerning interface phenomena, interactions of particles in liquid media and rheology of suspensions are considered. The techniques available to date for the direct measurement of interparticle forces are also exposed. Finally, a comprehensive review of the previous work regarding agglomeration of particles in suspensions due to the presence of a secondary liquid is presented.

2.1 Introduction

Wet agglomeration, or wet granulation, of powders refers to a particle size enlargement that occurs when individual primary particles adhere to each other due to the action of a liquid binder. This process has been extensively used in several industries, such as food, pharmaceutical and agrochemicals to improve characteristics of powders such as flowability, handling and ease of use (Simons and Fairbrother 2000).

A similar concept to wet agglomeration can be applied to suspensions, where a liquid constitutes the continuous phase instead of air. Agglomeration in suspensions of colloidal particles has also been studied, but mainly in the areas of industrial separation, such as to facilitate the filtration and recovery of fine particles or the purification of solutions. It consists of the addition of a second immiscible liquid to the suspension that preferably wets the solid particles and consequently holds the particles together by minute liquid bridges. By adjusting the conditions of this process, particles can be selectively agglomerated and removed from the suspension (Blandin, Mangin et al. 2003, Rossetti and Simons 2003).

Different terms have been used by authors to describe agglomeration in suspensions. '(Wet) spherical agglomeration' has been employed when agglomeration in liquid produces a dense spherical agglomerate (Smith and Puddington 1960, Kawashima, Furukawa et al. 1981, Kawashima, Cui et al. 1995, Rossetti and Simons 2003). If the recovery of solid particles in industrial separation processes is foreseen, usually 'selective agglomeration' is used, such as in the coal industry (Good, Badgujar et al. 1994, Vega, Martinez-Tarazona et al. 1995). Terms like 'flocculation' and 'coagulation' have also been widely used in relation to agglomeration in suspensions (Bilgen and Wills 1991).

When the suspensions are highly concentrated, the agglomeration of particles by a second immiscible liquid results in a macroscopic change in the flow behaviour of the suspension: a transition from a non-elastic liquid-like behaviour to a highly-elastic solid-like behaviour is observed (Johansson and Bergenståhl 1992, Dedinaite, Claesson et al. 1998, Koos and Willenbacher 2011).

A similar effect is also observed in food products. For example, the increase in water content in chocolate during processing leads to a dramatic increase in chocolate viscosity, which has been related with the agglomeration of sugar particles (Beckett 2009).

Agglomeration in food suspensions, however, has not been deeply investigated. Numerous food particles are composed of polar molecules and are thus water-soluble (Palzer 2011). Therefore, depending on the immiscible binding liquid that is added to food suspensions, particle interactions will be affected by solid dissolution.

2.2 Interfacial phenomena

In the process of agglomerating particles in suspensions, multi-component systems are created, with the different structural elements constituting different phases. The phases in these systems are separated by a narrow region – the interface or surface. The presence of this phase boundary has important consequences on the particle interactions in the suspension and therefore, defining the interface phenomena becomes essential.

In systems of two immiscible liquids, the interfacial energy is known as the free energy change necessary to expand the interfacial area between those two liquids in contact by unit area. This derives from the fact that any system has a tendency to minimize their free energy and, therefore, at an interface, free energy is accumulated. The surface (or interfacial) tension (γ) is equivalent to the surface free energy. It is the property of the surface of a liquid that allows it to resist an external force per unit length (or similarly work per unit area), and hence its importance in liquid-liquid and capillary systems (Walstra 2003). From the terminology point of view, in this thesis, interfacial tension is used for liquid/liquid systems, and surface tension for liquid/air ones.

When three different phases (oil, water, and solid) are in contact, three distinct phase boundaries exist with a contact line where the three phases meet. From this we can define the contact angle (Figure 2-1). The contact angle gives important information about the behaviour of the three-phase system and the wettability of the solid particle surface.

Surface (or interfacial) tensions and contact angles are bulk properties and both serve as an index of the relative forces of intermolecular attraction. They are closely related, but the surface tension is a property of the interface between two phases, while the contact angle describes the edge between two-phases where they meet a third phase (Hiemenz and Rajagopalan 1997).



Figure 2-1. Contact angle between a three-phase (liquid-liquid-solid) system. Interfacial tensions between phases are indicated.

At thermodynamical equilibrium, there is a balance of forces in the contact line, and consequently a proportion of interfacial tensions. The relationship between interfacial tensions and contact angle is given by the Young's equation (Equation 2-1) (Young 1805):

$$\gamma_{WO} \cos\theta = \gamma_{SO} - \gamma_{SW}$$

Generally, if the contact angle is lower than 90°, the liquid wets the surface and the surface is lyophilic (hydrophilic if the liquid is water).

The wetting state is derived from the three interfacial tensions and the extent of the spreading of a liquid (in this case, water) on a solid surface is given by the spreading pressure or coefficient (Π_s) (Equation 2-2):

$$\Pi_s = \gamma_{SO} - \gamma_{WO} - \gamma_{SW} = \gamma_{WO} (\cos\theta - 1)$$
Equation 2-2

For $\Pi_s < 0$, partial wetting occurs and a finite contact angle θ is obtained and given by Equation 2-1. If $\gamma_{SO} \ge \gamma_{WO} + \gamma_{SW}$, the Gibbs free energy of the system could decrease andcomplete wetting together with the formation of a stable film are obtained. In addition, in systems which are not in perfect thermodynamic equilibrium, Π_s could also be positive (Hiemenz and Rajagopalan 1997, Butt and Kappl 2006, Bonn, Eggers et al. 2009).

Equation 2-1

The topography of the solid surface has a significant impact on the contact angle and, therefore, when determining the contact angle this should be taken into consideration since real solid surfaces may differ significantly from ideal smooth ones. Figure 2-2 shows the impact the surface roughness has on the contact angle, and that the actual contact angle (θ_{ac}) can be relatively different than the apparent one (θ_{ap}), i.e. the contact angle as observed by eye or measured with a standard optical goniometer, depending on the scale of the roughness.



Figure 2-2. Contact angle on different surfaces; (a) ideally smooth surface (given by Young's equation); (b) actual contact angle(θ_{ac}) and (c) apparent contact angle(θ_{ap}) (adapted from Charles-Williams (2007)).

Different models have been developed to describe the effect of surface roughness on the contact angle.

The Wenzel equation (Equation 2-3) can be used for surfaces with low degree of roughness, i.e. if the roughness is below the wavelength of light.

$$\cos\theta_{ap} = R_{rough}\cos\theta$$

Equation 2-3

Where R_{rough} , the roughness ratio, corresponds to the ratio between actual and apparent areas and is always equal or larger than one. From this, one can conclude that surface roughness results in a decrease and increase the apparent contact angle for lyophilic ($\theta < 90^{\circ}$) and lyophobic ($\theta > 90^{\circ}$) sytems, respectively (Wenzel 1949).

Another model developed by Cassie (1948) takes into consideration surface heterogeneity (Equation 2-4), where the apparent average contact angle can be determined by sum of the contact angles in each region (θ_i) multiplied by the respective surface area ratio (f_i).

$$\cos \theta_{ap} = \sum_{i=1}^{n} f_i \cos \theta_i$$
 Equation 2-4

Surface roughness and other phenomena such as surface heterogeneity, presence of dissolved that can adsorb to the three-phase line, line tension and surface deformation can also lead to contact angle hysteresis, where the advancing contact angle differs from the receding angle. Advancing angles refer to the contact line advancing over the solid, i.e. the liquid spreading over the surface; while receding angles refer to the opposite effect, when for example the droplet is removed from the surface (Adamson and Gast 1997).

2.3 Interactions of solid particles dispersed in a liquid

Highly concentrated solid suspensions, such as those discussed throughout this work, have a large surface-to-volume ratio because of the small size of the particles. Consequently, the surface forces play a crucial role in these systems and in the adhesion mechanisms driving agglomeration. Therefore, it is important to define the interaction forces acting between solid particles in liquid.

The interaction forces between particles described here are focused on systems where the medium is a non-polar liquid (in this case, more specifically vegetable oils) and also where particles are rigid, i.e. forces originating from elastic or viscoelastic properties of the surface are not taken into account.

Interactions between particles suspended in liquid are frequently described by the theory from Deryagin, Landau, Verwey and Overbeek which is known as the DLVO theory. Following this theory, the interaction between particles is composed of an attractive and a repulsive part – the London-van der Waals and electrostatic double layer forces, respectively (Walstra 2003).

2.3.1 van der Waals attraction

The van der Waals forces between molecules arise from dipole- dipole interactions. Three interactions contribute to the total force between molecules: induction force (Debye interaction), orientation force (Keesom interaction) and dispersion force (London interaction). For macroscopic solid particles, the London dispersion forces are dominant; therefore, in this work, those are the forces considered when van der Waals forces are mentioned (Israelachvili 1985, Butt and Kappl 2010).

When the particles are the same, van der Waals forces are always attractive and they are assumed to be dominant in oil-continuous systems (Johansson and Bergenståhl 1992, Liang, Hilal et al. 2007).

There are two main approaches to calculate van der Waals forces; a microscopic (or Hamaker) approach and a macroscopic (or Lifshitz) approach. In the Hamaker approach, the van der Waals forces between macroscopic bodies are described as a pairwise summation of the forces between all molecules in an object. In this theory, however, the influence of neighbouring molecules with permanent or induced dipoles is not taken into account. This simplification is acceptable for gases as a media. On the other hand, this assumption is not true for condensed media such as liquids or solids, and therefore, this approach cannot be easily extended to particles interacting in a medium (Liang, Hilal et al. 2007, Butt and Kappl 2010).

The interaction energy (or potential) between bodies of different geometries can be calculated on the basis of the pairwise additivity, and some examples are given in Table 2-1.

Geometry	van der Waals Interaction Energy	Observations	
Sphere- Sphere	$V_{VdW}(D) = -\frac{A_H}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$	$f R_1 \mbox{ and } R_2 \mbox{ are the} \ radius \mbox{ of each} \ sphere, \mbox{ and } D \ll \ R_1, R_2$	Equation 2-5
Sphere- Surface	$V_{VdW}(D) = -\frac{A_H R}{6D}$	R is the sphere radius, the surface is infinitely thick and D ≪ R	Equation 2-6
Two sur- faces	$V_{VdW}(D) = -rac{A_H}{12\pi D^2}$ per unit area	the surfaces are infinitely thick	Equation 2-7
Two plates	$V_{VdW}(D) = -\frac{A_H}{12\pi D^2} \left[1 - \frac{2}{(1+H/D)^2} + \frac{2}{(1+2H/D)^2} \right]$ per unit area	H is the thickness of the plates	Equation 2-8

Table 2-1. van der Waals interactions free energies between bodies of different geometries (Israelachvili 1985, Butt and Kappl 2010).

Where A_H is the Hamaker constant and D is the distance between the bodies

The van der Waals attractive force is given by the derivative of the interaction energy over the distance between the bodies (Equation 2-9) (Israelachvili 1985):

$$F_{VdW} = -\frac{dV_{VdW}}{dD}$$
 Equation 2-9

In the Lifshitz theory, the aforementioned difficulty with the pairwise additivity assumption is overcome. In this approach the atomic structure is disregarded, large bodies are treated as continuous media and forces are obtained from bulk properties such as refractive indexes and dielectric constants. It is important to point out that this theory simply changes the way the Hamaker constants are calculated, and interaction energies previously described in the Hamaker approach (Table 2-1) remain valid in this continuum theory (Israelachvili 1985, Liang, Hilal et al. 2007).

From the Lifshitz theory, different approaches to calculate the Hamaker constant have been derived. One estimation of the Hamaker constant is through the difference in refractive indexes for two identical particles 1 interacting across a medium 2 (Israelachvili 1985):

$$A_{H} = \frac{3}{4} k_{B} T \left(\frac{\varepsilon_{1} - \varepsilon_{2}}{\varepsilon_{1} + \varepsilon_{2}}\right)^{2} + \frac{3h' \nu_{e}}{16\sqrt{2}} \frac{(n_{1}^{2} - n_{2}^{2})^{2}}{(n_{1}^{2} + n_{2}^{2})^{3/2}}$$
 Equation 2-10

Where k_B is the Boltzmann constant (1.38065 × 10⁻²³ J K⁻¹); T is the temperature (Kelvin); ϵ is the dielectric constant of each media; h' is the Planck constant (6.62607 × 10⁻³⁴ J s); v_e is the adsorption or resonance frequency (which can be assumed to be 3 × 10¹⁵ Hz) and n is the refractive index of each media (Johansson and Bergenståhl 1992).

2.3.2 Electrostatic interactions

In a medium with high dielectric constant such as water solid particle surfaces can get charged creating an electric field which attracts counter ions. The layer formed around particles composed by charges and counter ions is called electric double layer. Electrical double layer forces (F_{elet}) are generated by the fact that particles would be charged and they are usually repulsive. In non-polar liquids the electrical double layer is conventionally taken as negligible because the low solubility of ions in such media results that a double layer cannot be readily formed (Liang, Hilal et al. 2007).

2.3.3 Solvation or structural forces

Although the DLVO theory adequately explains long-range interparticle interactions, it fails to describe interactions when particles come closer to few nanometres distances. At very small distances between particles the discrete molecular nature of the solvent becomes more important and short-range forces are generated, which can deviate considerably from what is predicted by continuum theories. These short-range forces are usually referred to as solvation or structural forces. They can be monotonically repulsive, monotonically attractive or even oscillatory (Liang, Hilal et al. 2007).

The continuous media structure at the interface is usually different than in the bulk. When two particles approach each other, each layer of molecules of the continuous media is squeezed out of the gap. These molecular ordering and packing as a function of distance results in solvation forces (Israelachvili 1985).

Claesson et al. (1997) measured forces between two mica surfaces in anhydrous oil using a surface force apparatus (see Section 2.5 for information about SFA). They used triolein, a triacylglycerol composed by three oleic acid molecules. They observed strong repulsive oscillation forces located at distances of 60-50 Å and 30-20 Å. These forces are explained as structural forces related with the packing of the triolein molecules, as shown in Figure 2-3. Triacylglycerols are relatively long, flexible molecules and, therefore, at small distances solvation forces can become considerable.



Figure 2-3. Proposed layering of anhydrous triolein molecules between hydrophilic mica surfaces: (a) separation of 60-50 Å and (b) 30-20 Å. The calculated length of the triolein molecule was approximately 27 Å (Claesson, Dedinaite et al. 1997).

It is important to point out that solvation forces and the ones from the DLVO theory are generally not additive. The structural forces could be rather interpreted as the continuum forces at small separations taking into consideration the molecular properties of the medium (Israelachvili 1985).

2.3.4 Hydrodynamic forces

If one considers particles inside a liquid medium, the hydrodynamic effects have to be taken into consideration. When a particle approaches another particle, liquid is driven out of the gap between them. Similarly, when the particles are separated, liquid is squeezed into the opening gap. In both cases, a force occurs: the hydrodynamic force (F_{hydyn}) . In the first case (particles approaching) the force is long-range repulsive and in the second case (particles separating) the force is long-range attractive (Butt and Kappl 2010).

For a simple case of a sphere of radius R moving with a velocity v towards a planar surface, the hydrodynamic (repulsive) force that the sphere has to overcome is equal to (Butt, Cappella et al. 2005):

$$F_{hydyn} = 6\pi\eta v \frac{R^2}{D}$$
 Equation 2-11

where η is the viscosity of the liquid and D the distance between the sphere and planar surface.

2.3.5 Liquid bridges

If an immiscible liquid is added to an oil-continuous system, a liquid meniscus can form between particles when they get close to each other and the secondary liquid preferentially wets the particles. If one considers two particles connected by a liquid bridge inside fat media, when these particles are separated, two forces contribute to the adhesion: a static capillary (or meniscus) force and a dynamic viscous force.

A schematic of the dimensions of a liquid bridge between two flat plates is shown in Figure 2-4.



Figure 2-4. Scheme of the dimensions of a liquid bridge formed between two flat plates (Cai 2008).

2.3.5.1 Capillary or Meniscus forces

Static capillary forces have been widely studied, mainly theoretically but also experimentally. The majority of studies have concentrated on liquid bridges with air as a continuous phase (Fortes 1982, Lian, Thornton et al. 1993, Simons, Seville et al. 1994, Willett, Adams et al. 2000, Adams, Johnson et al. 2002, Butt and Kappl 2009), but also research in systems of particles in the presence of immiscible liquids has been carried out (Mason and Clark 1965, Christenson 1985, Rossetti and Simons 2003, Gogelein, Brinkmann et al. 2010).

The meniscus formed between two particles causes an attractive force. This is a result from both the interfacial tension of the liquid around the contact line pulling the particles together and the pressure deficiency inside the bridge resulting from the curvature of the bridge (known as Laplace pressure). The Laplace pressure (ΔP) attracts the particles towards each other and is given in Equation 2-12, known as the Young-Laplace equation.

$$\Delta P = \gamma_{LL} \left(\frac{1}{r_1^*} - \frac{1}{r_2^*} \right)$$
 Equation 2-12

where γ_{LL} is the interfacial tension between the liquid phases, and r_1^* and r_2^* are the two curvature radii of the liquid bridge which are perpendicular to each other.

In extreme cases, the resulting capillary force can be zero or even repulsive for specific meniscus geometries associated with imperfect wetting (Lian, Thornton et al. 1993). These cases, however, are not considered in the present work.

Solving the curvature term in the Laplace equation analytically is not straightforward, therefore, several numerical approximations have been proposed. The toroidal (or circular) approximation assumes the curvature of the bridge as arcs of a circle (Fisher 1926). This has been generally accepted as a good approximation (Lian, Thornton et al. 1993). The Laplace pressure given by the toroidal approximation can be re-written (Equation 2-13):

$$\Delta P = \gamma_{LL} \left(\frac{1}{r_1} - \frac{1}{r_2} \right)$$
Equation 2-13

where r_1 and r_2 are the radii of curvature as per the toroidal approximation, and are shown in Figure 2-4.

The use of the toroidal approximation to calculate the Young-Laplace equation and consequentely the capillary force between a sphere and a plane is discussed in more detail in Chapter 6. The capillary force is given by Equation 2-14:

$$F_{cap,gorge} = 2\pi\gamma_{LL}r_2 + \pi r_2 \Delta P$$
 Equation 2-14

where the first term corresponds to the interfacial tension contribution and the second one to the Laplace pressure input.

Equation 2-14 considers the capillary force at the neck of liquid bridge, i.e the narrowest part of the meniscus ('gorge method'). Alternatively, one could calculate the capillary force at the three-phase contact line where the force is actually transmitted to the particle, known as 'boundary method'. The difference in the forces calculated by the two methods as well as the errors due to the assumptions regarding bridge geometries have been shown to be small (Willett, Johnson et al. 2007). The equation for the 'boundary method' is explained in more detail in Section 6.2.

From the equations above and geometrical relations, one can determine the variables that the capillary force is dependent upon (Equation 2-15; thorough explanation is given in Section 6.3.1).

$$F_{cap} = f(\gamma_{LL}, \theta, r_1, r_2, D)$$
 Equation 2-15

where θ is the contact angle between the three-phases and D the distance between the particles/surfaces.

Moreover, the type of contacts between particles, i.e. particle dimensions and shape significantly affect the magnitude of the capillary forces (Tselishchev and Val'tsifer 2003).

Capillary condensation in immiscible liquids

The term capillary condensation is a defined concept in a gaseous environment. It is described by the Laplace-Kelvin equation (Equation 2-16), which states that the vapour pressure depends on the curvature of the liquid surface and, consequently, condensation of vapour into capillaries can occur for pressures even below the saturation pressure (Butt and Kappl 2009).

$$R_g T ln \frac{P}{P_0} = \gamma V_m \left(\frac{1}{r_1^*} - \frac{1}{r_2^*} \right)$$
Equation 2-16

Where R_g is the molar gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature, P is the actual vapour pressure of the curved bridge, P_0 is the saturation vapour pressure over a planar liquid surface, γ is the surface tension and V_m is the molar volume of the liquid.

Capillary condensation can also occur between particles (or into capillaries) in immiscible liquid mixtures. For example, if hydrophilic particles, oil and a small amount of water are mixed, the water tends to form menisci between the particles, resulting in particle agglomeration.

For the case of immiscible liquids forming a liquid bridge, the Kelvin equation can be rewritten in terms of activity (a), i.e. the effective concentration of the species in equilibrium with the bulk phase (where activity = 1 for saturation) as shown in Equation 2-17 (Adamson and Gast 1997):

$$RT\ln a = \gamma_{LL} V_m \left(\frac{1}{r_1^*} - \frac{1}{r_2^*} \right)$$
Equation 2-17

For a bridge of a liquid B in a bulk liquid A, the activity $a = \frac{c_B}{c_B^0}$. Here, c_B is the concentration of molecules of liquid B in the A-rich phase, c_B^0 is the saturation concentration, V_m is the molar volume of molecules B in the B-rich phase, and γ_{LL} is the interfacial tension between liquids A and B (Butt and Kappl 2010).

For the case when water forms the bridge, Christenson (1985) modified Equation 2-17 so that the activity is equal to the degree of saturation of water in non-polar liquids, or simply the water activity a_w . Hence, in the Kelvin equation for water condensing from a non-polar immiscible liquid, $a = a_w$. This is a useful relationship, since the concept of water activity is often present in food technology. Water activity is related to the *free water* (unbounded water molecules) in a food product. It is defined as the vapour pressure in the headspace of the product divided by the vapour pressure of pure water, for a given temperature; and is equal to relative humidity of air in equilibrium with the sample (Walstra 2003).

♦ Effect of roughness

The previously mentioned equations for capillary bridges consider perfectly smooth particles. However this is rarely true for real particles, and even for apparently smooth surfaces, asperities of few nanometres may exist. The extent of roughness on the particle surface has a direct effect on the formation (Figure 2-5) and magnitude of meniscus bridges, usually having a lowering effect (in particular at low vapour pressures). When particles approach one another, the more prominent asperities contact each other rather than the surface (Butt and Kappl 2009). Some approximations in the calculation of capillary forces taking surface heterogeneity effect into account have been developed (Butt 2008), and also the possible splitting of liquid bridges which would also affect the magnitude of the meniscus force due to multiple liquid bridges formation (De Souza, Brinkmann et al. 2008).



Figure 2-5. The effect of roughness on the formation of capillary bridges at different water activities (or vapour pressure of condensing liquid) (adapted from Butt and Kappl (2009)).

• Liquid bridge formation in a multi-particle system

In a system containing several particles such as suspensions, depending on the amount of secondary liquid present, different states can be reached, as identified by Newitt and Conway-Jones (1958) and shown in Figure 2-6. These states were described for granulation of particles in air driven by a liquid binder; however, the same concept can be easily conveyed to suspensions.



Figure 2-6. Liquid states depending on the saturation of liquid binder (adapted from Hapgood and Rhodes (2008)).

In a pendular state, the amount of liquid binder present is enough to form liquid bridges that are separate and independent from each other. As the saturation is increased (i.e. the ratio of secondary liquid to voids – in case of air – or continuous phase for suspensions), some voids are completely filled with the secondary liquid, however there are still some areas filled with air (or continuous phase). In a capillary state all the voids are occupied by the secondary liquid which forms menisci, resulting in a cohesive interaction among the outer particles. Finally, the saturation of liquid reaches a point where the particles become immersed in the secondary liquid and there is no interparticle cohesion (Newitt and Conway-Jones 1958, Mitarai and Nori 2006, Hapgood and Rhodes 2008). Such states were also described by Schubert (1975) who proposed a relationship of the tensile strength of agglomerates as a function of the liquid saturation, as shown in Figure 2-7.



Figure 2-7. Tensile strength as a function of liquid saturation. S_p and S_c correspond to the liquid saturation points where the states are changed from pendular to funicular and from funicular to capillary, respectively (adapted from Schubert (1975) and Hapgood and Rhodes (2008)).

2.3.5.2 Viscous forces

Although on one side the static contribution to the liquid bridge (F_{cap}) has been extensively discussed, the dynamic part has not been deeply researched. However, in industrial processes, for example, the dynamic effect becomes highly significant due to viscous dissipation of energy (Ennis, Li et al. 1990).

The dynamic contribution is related to the rate-dependent attractive effect from the viscosity of the liquid when the particles are separated within a short time. For infinite long separation times, the viscous forces could be taken as negligible. However, in real cases infinite separation times are non-existent.

This hydrodynamic viscous contribution can be obtained by integrating the pressure generated inside the meniscus over the whole cross-sectional area of the meniscus (Equation 2-18). The pressure generated in the liquid bridge can be calculated based on the Reynolds' lubrication equation, which is a simplification of the Navier-Stokes equations for fluid flow. The Reynolds' lubrication equation with cylindrical coordinates is given in Equation 2-19 (Hocking 1973, Cai and Bhushan 2007, Butt and Kappl 2010). This simplification only applies within the lubrication limit and considers steady-state flow i (i.e. velocity is constant) and also that the pressure inside the meniscus consists of horizontal pressure gradients (i.e. pressure is constant in the vertical plane). The pressure difference (ΔP) in Equation 2-18 can be obtained by integrating Equation 2-19 (result for sphere – flat surface shown in Section 6.2) (Ennis, Li et al. 1990, Cai 2008):

$$F_{vis} = 2\pi \int \Delta P' r \, dr$$
 Equation 2-18

$$\frac{\partial}{\partial r} \left(r D^3 \frac{\partial P}{\partial r} \right) = 12 \eta r \frac{\partial D}{\partial t}$$

Where D is the distance between particle and surface or two flat surfaces and η is the viscosity of the liquid bridge.

And from this, one can determine what the viscous forces are dependent upon (Equation 2-20):

$$F_{vis} = f(\eta, v_s, r_1, r_2, D)$$
Equation 2-20

where r_1, r_2, D are indicated in Figure 2-4, v_s is the velocity at which the two bodies are separated.

Equation 2-19

2.3.5.3 Resultant liquid bridge total force

Upon separation of two particles connected by a liquid bridge, the capillary force acts to attract and prevent particle separation while the viscous forces act to hinder particles motion. Therefore, both static and dynamic contributions oppose particle separation.

Finally, considering the two contributions to the liquid bridge, the static and dynamic ones, the liquid bridge force can be approximated as addition of both of them (Equation 2-21):

$$F_{\text{bridge}} = F_{\text{cap}} + F_{\text{vis}} = f(\gamma_{LL}, \theta, \eta, v_s, r_1, r_2, D)$$
Equation 2-21

The liquid bridge can be characterized in terms of the dimensionless capillary number (Ca) as shown in Equation 2-22:

$$Ca = \frac{v_s \eta}{\gamma}$$
 Equation 2-22

The capillary number represents a ratio between viscous and surface tension forces and, therefore, the relative magnitudes of the terms in Equation 2-21 are directly related to Ca. Highly viscous liquid bridges correspond to large Ca numbers, so that viscous forces become significant or even predominant as compared to the capillary forces (Mazzone, Tardos et al. 1987).

2.4 Adhesion

When agglomeration comes into play, attractive forces obviously have an important role. These attractive forces lead to adhesion between particles which result in a particle network formation and thus the aforementioned agglomerates.

Hence, the adhesion force is considered as the maximum force needed to separate the particles again and it depends on the strength of the attractive interaction, the minimum distance and contact area between the particles (Butt and Kappl 2010).

From the previous discussions about interaction forces, one can conclude that the adhesion force is a combination of the different contributions as shown in Equation 2-23:

 $F_{adhesion} = F_{VdW} + F_{elet} + F_{hydyn} + F_{cap} + F_{vis}$

Equation 2-23

2.4.1 Contact mechanics

The adhesion force between a rigid spherical particle and a flat surface can also be expressed in terms of the work of adhesion (W_{adh}), which corresponds to the free energy necessary to separate unit areas of the two surfaces. This relation is known as the Derjaguin approximation (Equation 2-24) (Butt and Kappl 2010).

$$F_{adhesion} = 2 \pi R_{eff} W_{adh}$$

Equation 2-24

Where R_{eff} is the effective radius and for sphere-flat surface contact it is equal to the particle radius ($R_{eff} = R$).

However, particles and surfaces are usually not strictly rigid, and they can deform elastically due to attractive surface forces or if they are subjected to a load force. Different theories have been developed to explain the contact mechanics between particles and surfaces. In the absence of surface forces, the Hertz model explains the elastic contact between spheres while the theory described by Johnson, Kendall et al. (1971), known as the JKR model, takes surface forces within the contact area into account (Figure 2-8).

In the JKR model, when two spheres are pressed against each other with a load force, they will flatten and reach a contact radius as shown in Figure 2-8 once mechanical equilibrium is reached. The adhesion force between two spheres with radii R_1 and R_2 according to JKR is expressed in Equation 2-27 (Johnson, Kendall et al. 1971). This theory is particularly suitable for soft materials, short-ranged forces and large spheres (Butt and Kappl 2010)..

$$F_{adhesion} = \frac{3}{2} \pi W_{adh} \frac{R_1 R_2}{R_1 + R_2}$$
Equation 2-25

For non-adhering surfaces or very high load forces, the JKR theory becomes equivalent to the earlier Hertz theory (Israelachvili 1985).

Another theory, developed by Derjaguin, Muller et al. (1975), also called DMT model, assumes the elastic contact as given by the Hertz theory and attractive surface forces acting in the zone around the contact, and not within the contact area as the JKR model. The additional load generated by those surface forces outside the contact area, known as cohesive zone, can be determined using the Derjaguin approximation (Equation 2-24). This theory is well suited for hard materials, long- ranged forces and small spheres (Butt and Kappl 2010).



Figure 2-8. Schematic of the contact between a sphere and a flat surface (a) rigid surfaces; (b) elastically deformable surfaces under external compressive load F in the absence (Hertz model) or presence (JKR model) of surface forces; (c) elstic adhering sphere upon tensile load (-F) before disconnection from surface (Israelachvili 1985). In this figure, R corresponds to the radius of the particle, K is the elastic moduli, a is the contact radius, δ is the central displacement or indentation, γ is the surface energy.

2.4.2 Adhesion hysteresis

In an analogous way to hysteresis explained for interfacial phenomena (Section 2.2, contact angle hysteresis), a contact area may also have different values for the work of adhesion for loading versus unloading. The theories mentioned in the previous Section (2.4.1) consider perfectly smooth surfaces. However, the presence of roughness can considerably affect the adhesion. Rough hard elastic materials will present lower adhesion than smooth ones because the reduced interaction caused by the real area of contact being smaller with increasing roughness. On the other hand, rough soft viscoelastic materials can deform upon adhesive contact and flow into the roughness cavities, so that they can have real contact areas which are even larger than the ones for smooth surfaces and predicted by the JKR or DMT models (Israelachvili 1985, Butt and Kappl 2010).

2.5 Interparticle forces and the macro-behaviour in suspensions

The macro-behaviour of suspensions is the first and more obvious indication of the strength of interparticle forces. Rheology is the study of flow and/or deformation of a material when exposed to an exerted force. In suspensions, this flow behaviour is strongly related to interparticle forces as well as to the volume fraction of particles and the particle shape and size (Tadros 2011).

2.5.1 Rheology of suspensions

2.5.1.1 Rheology fundamentals

In classic rheology, two ideal materials can be defined: an elastic solid and a viscous liquid. The elastic solid has defined shape and, when subjected to an external force will, respecting some limits, return to the original shape upon the removal of this force. On the other hand, a viscous liquid will flow irreversibly upon shear (Macosko 1994).

One way to study of rheology of fluids is by subjecting the material to a continuous deformation at a constant rate. If the material is confined between two parallel plates, if the upper plate is rotated, the material will begin to flow and generate a velocity profile which is the shear rate. The force required to achieve a certain relative deformation (strain) is the shear stress (Barnes, Hutton et al. 1989).



Figure 2-9. Velocity or deformation profile (shear flow) between an upper rotating plate and a lower fixed plate separated by a defined gap. The upper plate moves with a speed v in the x direction (adapted from Barnes, Hutton et al. (1989)).

When the relationship between the stress (σ) and the shear rate ($\dot{\gamma}$) is linear, the material is said to be Newtonian (Equation 2-26). The proportionality constant, the shear viscosity (η), expressed this resistance to flow in Newtonian fluids:

Equation 2-26

 $\sigma = \eta \, \dot{\gamma}$

However, most liquids have a viscosity that is dependent on the shear rate. Those liquids are denominated non-Newtonians and several models have been developed to characterize their behaviour.

2.5.1.2 Non-Newtonian models

Characteristic shear stress curves as a function of shear rate for different types of fluids are shown in Figure 2-10. Power law fluids can be either shear thinning or shear thickening. Their behaviour is described by Equation 2-27 where n is the power law index and is smaller than 1 for shear thinning fluids, where the apparent viscosity decreases with increasing shear rate, and is bigger than 1 for shear thickening fluids, which present an opposite behaviour (increase of viscosity with the shear rate).

$$\sigma = \eta \dot{\gamma}^n$$
 Equation 2-27

Many materials can behave as a solid for small stresses and start to flow when the stress exceeds a critical value, which is known as the yield stress (σ_y). When the shear stress increases linearly with the shear rate above the yield value, the fluid is known as a Bingham fluid (Equation 2-28).

When the flow above the yield value has a shear thinning behaviour, the Herschel-Bulkley model can be used (Equation 2-29). Finally, in suspensions with a yield stress a semiempirical model has been developed and commonly used to describe the flow of paints, blood and food products such as chocolate. This is the Casson model, which is obtained when n=1/2 in Equation 2-30 (Mewis and Wagner 2012).

$$\sigma = \sigma_y^B + \eta \dot{\gamma}$$
Equation 2-28
$$\sigma = \sigma_y^{HB} + \eta \dot{\gamma}^n$$
Equation 2-29
$$\sigma^n = \sigma_y^n + \eta \dot{\gamma}^n$$
Equation 2-30

The yield stresses for each model are given a unique notation - σ_y^B , σ_y^{HB} and σ_y^n correspond to the yield values for the Bingham, Herschel-Bulkley and Casson models, respectively.



Figure 2-10. Flow curves (shear stress as a function of shear rate) for different systems (adapted from Tadros (2010))

Other models have been described but since they are not relevant to this work, they are not given here.

2.5.1.3 Time dependence: Thixotropy

In many food products, the relation of shear stress and shear rate is dependent of the time, which is known as thixotropy (or anti-thixotropy/rheopectic). This behaviour is caused by changes in the structure of the materials and it is highly related to the handling history of the material. The characteristic behaviour of a thixotropic sample can be obtained when such material is first subjected to an increasing shear rate followed by a decreasing shear rate. A clear hysteresis loop is observed. A thixotropic material show a decrease in viscosity on the second shear rate ramp while with a rheopectic material (anti-thixotropic) the opposite happens, as shown in Figure 2-11.



Figure 2-11. Typical hysteresis loop observed for materials with time-dependent flow behaviour - thixotropic and rheopectic samples (adapted from Barnes (2000) Barnes, Hutton et al. (1989))

2.5.1.4 Viscoelasticity

Many materials in food products are neither purely elastic or purely solid, i.e. they can combine properties of viscous liquid with those of elastic solids and are known as viscoelastic materials. Such materials can be described by the complex shear modulus (G*) which expresses the stiffness of the material and is given by Equation 2-31. Through a generalization of Hooke's law, Equation 2-37 can be defined at the linear viscoelastic region, i.e. at sufficiently low strains.

$$G^* = G' + i G''$$
 Equation 2-31

$$\sigma = \mathbf{G}^* \gamma_{st}$$

Where G' corresponds to the elastic or storage modulus, G" is the viscous or loss modulus and γ_{st} is the strain (relative deformation). G' measures the energy which is stored in the material during deformation while G" corresponds to the energy that is lost in the form of heat (Macosko 1994).

G' and G" can be determined by subjecting the material to an oscillatory motion, i.e. once as oscillatory strain (γ_{st}) is applied to those materials, the resulting stress (σ) may be shifted in frequency with respect to the strain. In general, for viscoelastic materials this phase shift (δ) is between 0° and 90° and is related to G' and G" as shown in Equation 2-33 (Mewis and Wagner 2012).

$$\tan \delta = \frac{G'}{G''}$$
Equation 2-33

Equation 2-32
Oscillatory experiments may be used in suspension rheology for different applications, such as the non-destructive analysis of the microstructure at low strains or the identification of space-filling networks which could behave as a solid (Mewis and Wagner 2012).

2.5.1.5 Suspension rheology

The addition of a particle to a liquid results in a disturbance of the fluid flow. This hydrodynamic alteration is strongly dependent on the volume fraction of the particles and also causes a deviation from a Newtonian behaviour. It is noteworthy to point out that in colloidal susspensions (particles smaller than 1 μ m) interparticle interactions can become large and result in a considerable effect on viscosity (Macosko 1994).

For a suspensions of hard spherical particles in a Newtonian fluid, Einstein derived an equation that relates the viscosity of the suspension (η) with the continuos liquid phase viscosity (η s) and the volume fraction of particles (ϕ) (Equation 2-34):

$$\eta = \eta_s \left(1 + \frac{5}{2} \phi \right)$$
Equation 2-34

Einstein's equation is valid for low particle volume fractions ($\phi \ll 0.1$). For more concentrated suspensions, it was found experimentally a divergence from Einstein's equation once the particles get closely packed.

The Krieger-Dougherty relation (Krieger 1972) provides a good expression for the viscosity of the suspension in terms of the volume fraction considering this divergence at close packing (Equation 2-35):

$$\eta = \eta_s \left(1 - \frac{\phi}{\phi_{max}}\right)^{-2.5 \phi_{max}}$$
Equation 2-35

Where ϕ_{max} is the maximum packing volume fraction and is expected to be between 0.49 and 1. It has been suggested that the maximum packing at low shear rates is 0.63 and at high shear rates 0.71 (Macosko 1994).

In addition, from computational calculations it has been determined that the maximum volume fraction for randomly closed packed monodisperse hard spheres is 0.64. For highly polydisperse hard spheres the value for the maximum volume fraction can approach 1 (Mewis and Wagner 2012).

2.6 Direct measurement of interparticle forces

The direct measurement of interparticle forces is demanding because a sensitive determination of forces with a precise definition of distance in the nanometre scale is necessary due to the short-range nature of the forces.

Different instruments have been used for interparticle force measurements, but here emphasis is given to the surface force apparatus (SFA) and the atomic force microscope (AFM), which can also be used in to measure forces in liquid media.

The surface force apparatus principle was first developed by Tabor, Winterton and Israelachvili in early 1970s (schematic in Figure 2-12). It is capable of measuring the interaction force acting between two surfaces while they are moved towards and subsequently apart from one another. The surfaces are composed of two mica sheets arranged in crossed cylinder geometry, which is mathematically equivalent to sphere on flat surface contact (Figure 2-12c). Mica, a type of clay mineral, is usually used because it is atomically flat, easy to handle and optically transparent. During the measurement one surface is kept fixed, while the moving upper surface is held by a cantilever spring, and its deflection can be converted into force according to Hooke's law. The distance between the plates is given by optical interferometry, in which a beam of white light is shone through the mica sheets producing interference fringes. The distance between the fringes is directly related to the spacing between the mica pieces (Figure 2-12b). The limitation of the SFA is related to the substrate that can be used to mimic particles. They have to be thin, smooth, semitransparent sheets and also malleable to be positioned in the cross cylinder geometry. Therefore, the majority of studies with the SFA are limited to mica (or mica with modified surface) as surfaces (Claesson, Ederth et al. 1996, Dedinaite, Claesson et al. 1997, Hodges 2002, Butt and Kappl 2010).



Figure 2-12. Schematic of the surface force apparatus (SFA): (a) The measuring chamber with the detail of the arrangement of the silvered mica sheets; (b) Optical interferometry - the white light passes through the mica sheets and the interference fringes (FECO) are analysed in a spectrometer, resulting in the distance H between the sheets; (c) The crossed-cylinder arrangement of the mica sheets (Claesson, Ederth et al. 1996, Dedinaite, Claesson et al. 1997).

Some other specific (purpose-built) instruments have been used by other authors to measure interparticle forces, such as the MASIF (measurement and analysis of surface interactions forces) and the MFB (micro-force balance). The MASIF instrument is a bimorph SFA in which the sphere-sphere geometry and opaque materials can be used. A bimorph consists of two piezoelectric plates bonded together with the polarization directions facing each other, and in the MASIF this is used to act as a pressure sensor (Claesson, Ederth et al. 1996, Hodges 2002). The MFB developed by Simons and Fairbrother (2000) is composed of micromanipulator micropipettes which can hold particles. One micropipette is held static while the other calibrated micropipette with another particle can be brought in contact with the static particle. Forces are measured by the deflection of the flexible micropipette. The whole system is coupled with a video camera where the distance between particles and the bridge curvature can be obtained by image analysis.

F

2.6.1 Atomic Force Microscopy (AFM)

The first atomic force microscope was developed in 1986 by Binnig, Quate and Gerber with the objective of imaging surface topography. However, because of its construction and improvements made over the years, the AFM has many more capabilities, including force-versus-distance measurements with high sensitivity (Binnig, Quate et al. 1986).

In an AFM (Figure 2-13), a cantilever tip, which is attached to a piezo-translator, is moved towards the sample in the normal direction. The basic idea of the AFM lies in the fact that local attractive or repulsive forces between the sample and tip result in a deflection of the cantilever spring, which can be measured by an optical laser technique. The laser beam is positioned on top of the cantilever and its reflection is detected by a photodiode which calculates the deflection signal based on the deflection of the cantilever (Z_c). In turn, the piezo-translator gives the position (Z_p) of the base of the cantilever (Butt and Kappl 2010).



Figure 2-13. Scheme of an AFM setup (adapted from Butt, Cappella et al. (2005)).

A force-distance measurement can then be converted from the measured values of the detector signal and piezo position. The separation (D*) between the tip and sample (or between particles in particle-particle experiments) is given by the sum of the piezo position and cantilever deflection as given in Equation 2-36.

$$D^* = Z_p + Z_c$$
 Equation 2-36

The force is obtained based on Hooke's law by multiplying the spring constant of the cantilever (k_c) by the cantilever deflection (Butt, Cappella et al. 2005):

$$= k_c Z_c$$
 Equation 2-37

As from the description of the AFM system, one can notice that the cantilever and its properties are of importance. Cantilevers are usually made of silicon and silicon nitride, but other materials and also different shapes and forms can be found for different applications. Stiffer cantilevers are less sensitive but more resistant to hydrodynamic drag, for example. The important characteristics of a cantilever are its spring constant and its resonance frequency. They can be theoretically calculated from material properties and cantilever dimensions. However, more precise calibration techniques are available nowadays such as the cantilever spring constant determination by thermal oscillations (or thermal noise method) (Hodges 2002).

A schematic of a force-distance measurement with the AFM is shown in Figure 2-14. In Figure 2-14(a) the deflection of the cantilever as measured by the photo-detector (detector signal) is plotted as a function of the piezoelectric translator position on approach and retraction of the cantilever from the surface. Figure 2-14(b) is derived from (a) using Equation 2-36 and Equation 2-37. In Figure 2-14(c) each step of the AFM measurement is explained (Butt and Kappl 2010).



Figure 2-14. Scheme of an AFM force measurement adapted from Butt and Kappl (2010).

One critical aspect of the AFM is the determination of zero distance. In contrast to the SFA where the separation distance and forces are calculated directly through the interference fringes, in the AFM the separation distance is indirectly calculated based on the piezo translator position. Modern AFMs have systems that calibrate the piezo expansion taking into account hysteresis and ageing of the component. However, the fact that distance is not measured directly can lead to ambiguities when adsorbed layers are present or if particles are considerably deformable (Claesson, Ederth et al. 1996).

2.6.1.1 Colloidal probe technique

One of the biggest advantages of the AFM is that particles of interest can be used as the tip (or probe) independent of their shape. This became possible with the colloidal probe technique. In a colloidal probe a particle is attached to a tipless cantilever, and then particle-particle or particle-surface force-distance measurements can be performed.

There are different techniques to attach particles to tipless cantilevers. Among them are gluing and sintering particles to cantilevers. In the case when glue is used, care must be taken so that the glue is insoluble in the liquid media used in the experiments. Also, it should be rigid enough so that its deformation does not affect the measurement. An epoxy type of glue is usually used in AFM colloidal probe experiments (Kappl and Butt 2002).

2.7 Agglomeration in dispersions of solid particles in liquid media – previous work

Previous studies have followed the degree of agglomeration in suspensions on a macroscale by either evaluating their flow behaviour (rheological measurements) or assessing the sedimentation behaviour. Sedimentation tests relate the volume of the sediment (or its density) with attraction or repulsion between particles. High sediment volumes (small sediment density) are related to strong attraction between particles, characteristic of agglomerated systems.

Early works from Bloomquist and Shutt (1940), Kruyt and van Selms (1943), Eggleton and Puddington (1954) and Van Kao, Nielsen et al. (1975) showed that the addition of minute amounts of an immiscible liquid, water, to suspensions of glass beads in different nonpolar liquids (benzene, toluene, aniline, different alcohols, carbon tetrachloride and polybutadiene) resulted in agglomeration. Bloomquist and Shutt (1940) reported the data in terms of sedimentation volume and also stated that while in some cases the sedimentation volume is proportional to the increase of water in the system (e.g. benzene); in other cases the flocculation only occurs once saturation of the organic liquid (alcohols) with water occurs. Kruyt and van Selms (1943) and Van Kao, Nielsen et al. (1975) have evaluated the agglomeration by the flow behaviour of the samples, which changed from Newtonian to shear thinning behaviour. They related this observation with the presence of liquid bridges between particles. Eggleton and Puddington (1954) and Howe, Benton et al. (1955) reported increased sedimentation volume and yield with the presence of water and a strong dependence of the agglomerates stability on temperature which in turn influences the interfacial tension. Also, they have calculated and experimentally observed that, for the same concentration of solid particles, the yield value is inversely proportional to the radii of the spheres.

In the area of industrial separation or wet spherical agglomeration, several authors have separated the agglomerates formed by the addition of a secondary liquid to the suspensions by sieving and evaluated the extent of granulation (Kawashima, Furukawa et al. 1981, Kawashima, Cui et al. 1995, Takase 2009).

Johansson and Bergenståhl (1992) showed a significant increase of sediment volume (50%) of sugar dispersions in oil (solid particles fraction (ϕ) of 10 %wt) as the water content of the samples was increased from 0 to 1 %wt. Subsequent reduction in the volume of the sediment containing higher amounts of water (above 1 %wt); sugar dissolves and separates from the oil forming a lump. Their work (Johansson and Bergenståhl 1992, Johansson and Bergenståhl 1992, Johansson and Bergenståhl 1992, Johansson and Bergenståhl 1992, also thoroughly analysed the effect of several different emulsifiers (such as phospholipids, monoolein, polyglycerol, sorbitan, etc.) on the rheology, colloidal forces and sedimentation volumes of sugar and fat dispersions in oils.

Ziegler, Garbolino et al. (2003) found that the increase in water activity (or relative humidity at equilibrium) resulted in a lower sediment density and slightly higher yield stress (without surfactant) in suspensions of sugar and cocoa particles in medium chain triacylglycerol (TAG) oil. In addition, they have also reported that the sediment density was increased by addition of lecithin, indicating a reduction in the attraction between particles. Lecithin was shown to be effective in reducing the size of the agglomerates formed by capillary condensation forces at high water activities. The multilayers of lecithin on the surface of the particles formed a lubricating film that lowered the yield stress. Polyglycerol polyricinoleate (PGPR) formed a loosely packed monolayer on the particle surface.

Yucel and Coupland (2011) used a different technique, ultrasound attenuation measurements, to characterize the agglomeration of sugar particles in vegetable oil with addition of water (< 1 %wt). They observed an increase in ultrasonic attenuation upon water addition which they related to the agglomeration of particles.

Killian and Coupland (2012) have investigated the agglomeration of sugar crystals in oil ($\phi = 50$ %wt) by using a water-in-oil emulsion. The agglomeration was experimentally analysed by submerging the whole system in hexane and evaluating the formation of a sugar network (or 'skeleton'). The water-in-oil emulsions were made with two emulsifiers (PGPR and lecithin). PGPR generated more stable emulsions with smaller droplets which resulted in a stronger sugar skeleton retention compared to lecithin.

Cavalier and Larché (2002) studied the flow behaviour of calcite suspensions in dioctylphthalate (ϕ = 11 %vol) upon the increase in water activity. They have reported that an increase of over an order of magnitude for the yield stress and storage modulus and a lower increase of the loss modulus for water activity (a_w) values between 0.1 and 0.3. Above a_w = 0.3, a plateau was reached with no further changes in the rheological parameters.

McCulfor, Himes et al. (2011) also reported a large increase in viscosity and change in the flow to a highly shear thinning behaviour upon addition of small amounts of water in suspensions of glass spheres (38-45 μ m) in mineral oil (ϕ = 10-25 %vol). They related these observations to the formation of water bridges between particles. They also showed that the viscosity of the dispersion goes through a maximum with the increase in the amount of water and that it is inversely proportional to the particle size. They investigated the effect of two hydrophobic surfactants (Span 80 and Arquad 2HT) and reported that the addition of both resulted in a reduction in the viscosity of the dispersions with added water by reducing or preventing liquid bridge formation.

More recently, Koos and Willenbacher (2011) have studied the agglomeration in suspensions of different solid particles (hydrophilic and hydrophobic glass, hematite, PVC, silica, calcium carbonate, cocoa solids and plastisols) with volume concentrations (ϕ) of 10 to 30 %. They showed that particle agglomeration in suspensions occurs when an immiscible secondary liquid is added; which is supported by an increase in viscosity and yield stress. This secondary liquid can be either wetting the particles ("pendular state") or not wetting ("capillary state"). The existence of liquid bridges in both capillary and pendular state has also been shown with fluorescence microscopy. In a study from the same group, similar suspensions were analysed and a model to explain the cluster and network formation using Surface Evolver was developed. They showed that the formation of capillary suspensions relies on three steps: (1) well-distributed droplets of secondary fluid are created through high-shear mixing; (2) these droplets quickly become surrounded by solid particles forming structures of small particle numbers (seed groupings); and finally, (3) these structures merge to form large particle number networks (Koos and Willenbacher 2012). On another study, Koos, Johannsmeier et al. (2012) evaluated the effect of particle size and interfacial tension on the flow behaviour of similar pendular and capillary suspensions. They observed that the decrease in particle size would result in an increase in the strength of capillary suspensions which is proportional to the reciprocal particle radius. At sufficiently high shear rates, the network is destroyed for suspensions of all particle sizes; however, the larger particles were more sensitive to shear showing a faster viscosity decrease. They showed that the strength of the network is proportional to the interfacial tension and decreasing the interfacial tension by increasing the temperature resulted in

lower viscosities. The addition of surfactants resulted in a decrease of two orders of magnitude in the yield stress as the number of capillary bridges was decreased. The rate of reduction was dependent on the type of surfactant.

Dittmann, Koos et al. (2013) used the same concept with of "capillary suspensions" to agglomerate ceramic powder dispersed in paraffin oil with saturated sucrose solution (ϕ = 15-25 %vol). They exploited the fact that crystallized sucrose bridges form between the particles to hold the particles together. This strong particle network formed by capillary suspensions yields a high open porosity; the suspension could be heated to remove the continuous phase. The remainder (connected ceramic particles) was then sintered to produce ceramic materials.

Hoffmann, Koos et al. (2014) evaluated the agglomeration of model food suspensions consisting of native and hydrophobized corn starch granules or cocoa particles dispersed in sunflower oil (ϕ = 33-35 %vol) with the addition of water as a secondary liquid. All the systems studied were in the "capillary state", since the particles (starch and cocoa) were poorly wetted by the secondary liquid (water). The addition of small amounts of water to such suspensions resulted in the increase of the yield stress by several orders of magnitude. They have also found that the increase in the viscosity of the secondary liquid by adding PEO (polyethylene oxide) to water did not result in any significant changes to the yield stress. They proposed that the network state is energetically favourable and dependent on the diffusion of the secondary liquid.

Imaging and microscopy have also been used to characterize the agglomeration in suspensions. By imaging the suspensions and considering the solid particles and continuous phase had the same refractive index, Kohonen, Geromichalos et al. (2004) and Fournier, Geromichalos et al. (2005) managed to image the liquid bridges and determine packing characteristics and distribution of number of liquid bridges per sphere. This procedure, the index matching technique, is very powerful as it enables the imaging of liquid bridges; however, it can be complicated to find solid particles and continuous phase with the same refractive index and also desired properties. In their studies glass particles and a mixture of toluene and 11.9% diiodomethane were used and water was chosen as the binding liquid. Kohonen, Geromichalos et al. (2004) established a critical relative volume of added water (in relation to the total volume of the solid pack) of 0.03% below which no bridges are formed due to the trapping of liquid on the microscopic rugosities of the spheres. Above this value, bridges were reported to increase rapidly at first, followed by a flat plateau. They also described a number of approximately 6 and 6.5 bridges per particle (coordination number) for loose and dense packing, respectively. Finally, they suggested that only about half of the gaps that are smaller than the rupture distance are bridged by liquid, which showed the hysteretic nature of bridge rupture and reformation cycles.

Gogelein, Brinkmann et al. (2010) used confocal microscopy and bright field imaging to evaluate the formation of liquid bridges between glass spheres in a 2.6-Lutidine system saturated with water. The liquid bridges were formed upon heating which resulted in phase separation of water-lutidine system. They calculated the magnitude of the forces based on the geometry of the bridges to be in the order of nano Newton.

Also recently, Heidlebaugh, Domenech et al. (2013), through images of the macroscopic suspensions and microscopy, have reported the strong aggregation or separation of several ternary particle/liquid/liquid mixtures for the cases where the particles are fully (or almost fully) wetted by one fluid, and/or the wetting fluid volume fraction is comparable to the particle volume fraction. If the secondary liquid was present in excess, they described a phase inversion in the system where oil droplets became encapsulated in the aqueous phase and creaming was observed. When the particles are partially wetted by both fluids, the formation of a strong pendular network was observed at all compositions. This is shown in the morphological map and ternary composition diagrams in Figure 2-15.



Figure 2-15. Morphological map and ternary composition diagram (in volume fraction) for the system glass particles/mineral oil/water. In the schematic drawing, the glass particles are represented by glass circles while the mineral oil is given in pink and the water in light blue-grey (adapted from Heidlebaugh, Domenech et al. (2013)).

Focusing on a microscale approach, the direct measurement of the magnitude and range of forces due to the formation liquid bridges has been widely studied in systems where air constitutes the continuous phase (Lian, Thornton et al. 1993, Simons, Seville et al. 1994, Willett, Adams et al. 2000, Adams, Johnson et al. 2002, Butt and Kappl 2009).

Christenson (1985) was among the first to measure the capillary condensation in systems of immiscible liquids using a SFA. His setup consisted of mica surfaces interacting in different organic media (cyclohexane, OMCTS, n-octane) and capillary condensation was driven by the increase in water activity. He observed repulsive short-range oscillatory solvation forces at low water activities, which decreased in magnitude and range with the increase in a_w . At $a_w \ge 0.8$ strong attractive forces resulted in the complete disappearance of the repulsive solvation forces. Similarly, another study from the same group showed that when the surfaces are brought together at a_w of 0.9 a strong increase in force happened when the spontaneous condensation of water occurs, pulling the two surfaces together. This force was shown to be not due to the force in the liquid (water) but rather due to the formation of a liquid-liquid interface with negative curvature (Laplace pressure) (Christenson, Fang et al. 1989).

Dedinaite et al. (1997, 1998, 1999, 2000) and Claesson, Dedinaite et al. (1997) have studied mica (hydrophilic) interactions in triacylglycerols (triolein) and also the influence of water content on these interactions with the SFA. They identified that a layer of triolein is strongly adsorbed between the hydrophilic mica surfaces due to strong structural forces, and as a result the surfaces cannot be brought closer than about 20 Å even under strong compressive forces. They have also identified very strong adhesive forces when the relative humidity (and therefore the water content in the oil phase) was increased, suggesting the formation of liquid bridges between the hydrophilic liquid mica sheets. However, as already mentioned, because of the limitations related with the SFA, their work was limited to mica surfaces. In addition, they have studied the effect of two surfactants to those interaction forces: PE (phospholipid phosphatidylethanolamine) and PGPR (polyglycerol polyricinoleate). They have showed that the addition of the surfactants resulted in a repulsive force between mica surfaces in triolein – PE turned the mica surfaces non-polar by adsorbing on them while PGPR adsorption resulted in a long-range steric repulsion. Upon the saturation of such systems with water ($a_w=1$), the formation of reversed phospholipids with PE results in a strong repulsive barrier. On the other hand, when PGPR is present in the system at a_w=1, a water bridge is formed, completely removing the steric repulsion effect.

Rossetti and Simons (2003) have developed a method which they called the Micro Force Balance to measure the magnitude of forces due to the formation of liquid bridges between glass spheres (80-130 μ m) in water mediated by silicon oil (kinematic viscosity of 10^{-4} m²/s). They have shown that as the particles are separated from each other, the profile of the bridge changes from convex to concave due to the formation of a neck, which progressively stretches resulting in the rupture of the liquid bridge. During the separation of the particles, the thinning of the bridge neck and concomitant decrease in Laplace pressure (due to the increase in pressure inside the bridge) results in a decrease in force. Also, they discussed viscous forces and showed that in their system, those were negligible (low capillary number).

As discussed in Section 2.6.1, the invention of the AFM enabled the direct measurement of interparticle forces using of different particles and systems. Butt (1994) and Ducker, Xu et al. (1994) were the pioneers in using the colloidal probe technique with the AFM to study interactions at deformable surfaces by measuring the force between a silica particle and an air bubble in aqueous solution. Similar experiments between a solid particle and an air bubble were reported by other authors (Fielden, Hayes et al. 1996, Ecke, Preuss et al. 1999, Preuss and Butt 1999, Assemi, Nguyen et al. 2008). They have registered repulsive forces when a hydrophilic silica particle approached an air bubble in aqueous solution, while strong long-ranged attractive forces were observed for hydrophobic particles. It was also found that in the presence of surfactants, a repulsive force could be measured on the approach of a hydrophobic particle and the bubble.

The number of experimental AFM studies which would be relative to suspensions, i.e. measuring the interaction of a particle at a liquid/liquid interface, have been more limited, if compared to the numerous works evaluating the interaction of a particle at a liquid/air interface. Interactions of particles and droplets of organic liquids in aqueous solutions were described by some authors (Mulvaney, Perera et al. 1996, Hartley, Grieser et al. 1999, Aston 2001, Aston and Berg 2001, Dagastine, Chau et al. 2005, Webber, Edwards et al. 2008). Mulvaney, Perera et al. (1996) and Hartley, Grieser et al. (1999) reported strong attractive forces between a silica particle and a decane droplet in water media at small separations, with the consequent jump of the particle towards the droplet. Such attractive forces were reported to disappear once a surfactant (sodium dodecyl sulphate; SDS) was added, lowering the interfacial tension. Aston (2001) related the stability of the thin film of continuous medium formed between particle and oil droplet to the hydrodynamic repulsion between rigid microspheres and deformable interfaces. They have identified two hydrodynamic drainage regimes: (1) Reynolds lubrication for thick films with slightly deformed drops, and (2) a wrapping film condition for an indented interface. Furthermore, they have observed improved film stability and force curves dependent on the probe speed and on the presence of surfactants (SDS) below the critical micelle concentration (CMC). Dagastine, Chau et al. (2005) reported the importance of non-DLVO forces when measuring the interaction between a silica colloidal particle and an organic droplet in different aqueous solutions. Webber, Edwards et al. (2008) also recorded repulsive electrical double layer forces due to the presence of surfactant (SDS) on the deformable tetradecane oil/water interface upon contact of a solid silica particle and found good agreement of experimental results with theory.

More recently, Banerjee, Mulder et al. (2012) have studied the interaction between a silica colloidal probe and a cellulose surface in hexane media saturated with water. They showed the existence of attractive adhesion forces and also that this interaction is dependent on the time that the surfaces are left in contact before separation. They hypothesized that the reason the measured adhesion force was lower than the expected theoretical capillary force was due to one or more bridges forming between the asperities of the surfaces.

2.8 Conclusions

In light of the presented literature review, important research areas have been identified, indicating interesting and novel research opportunities; which are aligned with the objectives and scope presented in Section 1.1.

On a macroscopic level, the thorough investigation of the particle network due to the formation of pendular liquid bridges in food model systems can provide the knowledge to manipulate and tailor the structure of foods. It has also been identified that investigating the factors affecting the network, such as particle size and shape, volume concentration, viscosity, wetting properties of the secondary liquid and addition of a surfactant merit further work.

On a microscale, the use of colloidal probe AFM in viscous media such as vegetable oils together with the formation of liquid bridges of an immiscible liquid constitutes a novel approach that can increase the understanding of the mechanism of formation and the strength of liquid bridges in these systems. The use of colloidal probe AFM has the advantage that different types of particles and surfaces can be used as well as size scales which are pertinent to food science applications.

Furthermore, drawing a direct link between the macroscopic network formation and the microscopic experimental determination of interparticle forces in model systems will provide a complete picture of the phenomena occurring and leading to the agglomeration of particles in oil media.

Chapter 3

Materials & Methods

Food products are mostly complex systems with several components; therefore, model food systems are used in this project in order to isolate the effects of bridge formation. In this chapter the general materials and methods used, their definition and motivations for use are discussed. Materials and methods used for specific trials are listed in each respective chapter.

3.1 Materials

3.1.1 Model food systems

The model suspensions used in this study consisted of either icing sugar (code 55437, British Sugar, United Kingdom) or glass particles (Spheriglass[®], code 20035, Potters Industries LLC, United Kingdom) suspended in high oleic sunflower oil (Type F, Sofinol Speciality Oils, Switzerland). The icing sugar contained less than 1.5 %wt of calcium phosphate as a free-flow (anti-caking) agent. The binder liquids (or secondary liquids) were deionized water, saturated sugar solution (67.47 %wt pure sucrose, Sigma-Aldrich, United Kingdom) or glycerol (Anhydrous, \geq 99.5 purity, Sigma-Aldrich, United Kingdom). The glass particles are used as a disperse phase due to their inert character.

3.1.2 Hydrophilic particles

Sucrose particles and glass particles were used as model hydrophilic food particles.

Sucrose $(C_{12}H_{22}O_{11})$ is a common disaccharide composed of glucose and fructose residues linked by a glycosidic bond (Figure 3-1). Sucrose crystallizes as an anhydrous monoclinic crystal which usually has a quite high purity (>99.9 %) even when commercially produced. A crystalline sucrose morphology is illustrated in Figure 3-2, where the eight most important faces are shown. Commercial sucrose is usually crystallized from solution, either using the evaporative or cooling method (Vaccari and Mantovani 1995).





Figure 3-1. Sucrose molecule conformation (α-D-glucopyranosyl-(1,2)- β -D-fructofuranoside) (Asadi 2007)

Figure 3-2. Sucrose crystal showing its eight most important faces (Vaccari and Mantovani 1995).

Sucrose has eight hydroxyl groups, three hydrophilic oxygen atoms and fourteen hydrogen atoms which results in a sucrose elevated solubility in water driven by the its high capability of forming hydrogen bonds with water molecules. At room temperature (25°C) sucrose solubility is 66.47 %wt (2.0741 g of sucrose per gram of water) and it increases with temperature. The equilibrium phase diagram for sucrose-water is given in Figure 3-3. Sucrose does not dissolve in non-polar solvents and its solubility is much lower in nonaqueous solvents. Examples of sucrose solubility in different anhydrous solvents are (at 25 °C, weight percentages): 5.7 % in glycerol, 1.9 % in propylene glycol (Bubník and Kadlec 1995), 0.66 % in methanol and 0.05 % in ethanol (Peres and Macedo 1997).



Figure 3-3. Phase equilibrium diagram sucrose-water (Bubník and Kadlec 1995)

Sucrose solution viscosity is dependent on the concentration and is given in Figure 3-4. Close to the saturation point in water (around 60 %wt) the viscosity of sugar solutions are significantly increased.



Figure 3-4. Viscosity of sugar solutions – dependence on solids concentration at 25 °C (Reiser, Birch et al. 1995)

The types of sucrose used in this project are powdered crystalline sugar and crystal sugar. Crystal sugar, denominated granulated sugar by the sugar industry, was supplied by Sigma-Aldrich (purity \geq 99.5 %, United Kingdom). Powdered sugar (or icing sugar) consists of crystalline sugar grounded to very small particle sizes (produced by British Sugar, United Kingdom). Powdered sugar, in contrast to the sugar crystals, has a rather irregular shape. The median volume-based particle size (D_{50,3}) of powdered sugar is approximately 29 μ m and the particle size distribution is given in Section 4.3.2 (Figure 4-6). The density of icing sugar is 1.59 g/cm³ (Reiser, Birch et al. 1995).

The solid glass particles (Spheriglass®, code 20035, soda-lime glass of chemical composition SiO₂ < 75 %, Na₂O < 15 %, CaO < 10 %, MgO < 5 %) were supplied by Potters Industries LLC (United Kingdom). The median particle size (D_{50,3}) is approximately 41 μ m and the particle size distribution is given in Section 4.3.2 (Figure 4-6). The particles have a density of 2.52 g/cm³ (given by the supplier). In Chapter 5 the effect of particle shape and density is analysed, and for this purpose, irregularly-shaped glass grains (Potters Industries LLC, United Kingdom) and hollow glass particles (Ultra-fine hollow microspheres 110 P8, Potters Industries-EGM Division, United Kingdom). More specific details of these materials (glass grains and hollow glass particles) are given in Section 5.2.2.

3.1.3 Hydrophobic continuous phase

The fat used as the continuous phase was high-oleic sunflower oil (HOSO, Type F, refined, Sofinol Speciality Oils, Switzerland). Sunflower oil was chosen mainly because of the ease of handling (liquid at room temperature). The density of HOSO at 20 °C is about 0.91 g/cm³ (O'Brien 2004).

Vegetable oils consist primarily of a mixture of triacylglycerols (TAG), i.e. esters of glycerine with three fatty acids attached to the glycerine hydroxyl groups. The type and proportion of fatty acids in the TAG and the quantity of different TAGs will determine the chemical and physical properties of the oil or fat (Scrimgeour 2005). Traditionally, the terms 'oil' and 'fat' are used depending on the state of the material, liquid or solid, respectively. However, in this thesis, the two terms (oil and fat) are used interchangeably.

Fatty acids are carboxylic acids with a long aliphatic chain containing from 4 to 24 carbon atoms and up to three double bonds. Its structure is usually designated by the number of carbon atoms and number of double bonds (degree of unsaturation) in the following form: C number of carbons: number of unsaturations (O'Brien 2004).



Figure 3-5. Example of the chemical structure of a triacylglycerol molecule, formed by three fatty acids attached to a glycerol molecule (McClements 1999)

High-oleic sunflower oil refers to a variety of sunflower oil with high oxidative stability. It is mainly composed of the following fatty acids and respective quantities: 81.3 % oleic acid ($C_{18:1}$), 9.0 % linoleic ($C_{18:2}$), 5.4 % stearic ($C_{18:0}$), 3.7 % palmitic ($C_{16:0}$) (O'Brien 2004).

Commercially available oils may naturally contain certain amounts of minor components such as free fatty acids, phospholipids and tocopherols which may act as surfactants and considerably reduce the interfacial tension when adsorbed on the surface (O'Brien 2004). For this reason, purified oil was used as the continuous medium. The oil purification was aimed to reduce the effect of these surface-active agents on the interaction between particles. The purification process, based on the method described by Gaonkar (1989) and Babin, Dickinson et al. (2005), consisted of dispersing 5-10 % of activated magnesium silicate (Florisil[®], 100-200 mesh Sigma-Aldrich, United Kingdom) in the HOSO under agitation for at least 30 minutes followed by filtration. The effect of the oil purification on the interfacial tension with water is detailed in Appendix I.

Lecithin was used as a surfactant in some experiments. It was chosen because it is the most commonly used surfactant (or emulsifier) in the food industry. Lecithin consists of a mix of mainly four different phosphatides: phosphatidylethanolamine, phosphatidic acid, phosphatidyl inositol and phosphatidylcholine (Babin 2005). Phospholipids are amphiphilic molecules which are formed by a polar (hydrophilic) head and two aliphatic chains (lipophilic), as schematized in Figure 3-6. Such molecules have the ability to adsorb on the interfaces such as oil-water or sugar particles-oil. Their adsorption to the oil-water interface results in the lowering of the interfacial tension. After a complete packing of the molecules on the interface, a monolayer is obtained and no further decrease in interfacial tension is seen. When lecithin is present in an excess, studies have shown that they can aggregate forming micelles or bilayers in the continuous phase or hemimicelles on surfaces (Johansson 1995, Walstra and Vliet 2008). This occurs at a defined concentration, known as critical micellization concentration (CMC). The formation of reversed micelles have been suggested by Johansson and Bergenståhl (1992) as the reason that pure phospholipids have a worse ability to reduce viscosity in chocolate than lecithins.



Figure 3-6. Schematic examples of the structure of phospholipids as amphiphilic molecules and some of their possible configurations once associated into micelles, reversed micelles or bilayers (Adapted from Walstra and Vliet (2008) and McClements (1999)).

Commercial lecithin is generally extracted from vegetable oils, and in order to obtain specific characteristics, it can be purified by enzymatic hydrolysis, de-oiling or fractionation so that defined fractions of phosphatides are obtained (O'Brien 2004, Babin, Dickinson et al. 2005). The lecithin used in this project was in liquid form and is from sunflower origin (Topcithin[®] SF, Cargill, Netherlands). This lecithin consists of a mixture of triacylglycerols, phospholipids, glycolipids and a small amount of carbohydrates. The specification of the surfactant used as given by the supplier is given in Table 3-1.

General composition	Phospholipids concentration [%]	50
	Triacylglycerol (oil) content [%]	38
	Glycolipids	6
	Carbohydrates	5
	Moisture content [%]	1
Phospholipids breakdown composition	Phosphatidylcholine (PC) [%]	14-30
	Phosphatidylethanolamine (PE) [%]	8-24
	Phosphatidic acid (PA) [%]	2-7
	Phosphatidyl inositol (PI) [%]	13-17
	Minor phospholips [%]	6-12
General properties	Molar mass [g/mol] (Johansson and Bergenståhl 1995)	760
	Viscosity [Pa·s] at 25° C	7.6
	Density [g/cm ³] at 25° C	1.037

 Table 3-1. Specification of the lecithin used (Topcithin® SF) provided

 by the supplier (Cargill, Netherlands)

3.1.4 Hydrophilic liquid

Deionised water, saturated sugar solution and glycerol (anhydrous, purity \geq 99.5 %, Sigma-Aldrich, United Kingdom) were used as the immiscible secondary liquid. Saturated solution was prepared by dissolving pure sucrose (Sigma-Aldrich, United Kingdom) in deionized water until saturation at room temperature (25 °C) was reached (67.47 %wt) (Bubník and Kadlec 1995). Saturated sugar solution was used so that there is no dissolution of the sugar particles. Glycerol was used because not only is sucrose solubility very limited (5.7 %wt) but also the effect of viscosity in the bridges can be evaluated since glycerol has a relative high viscosity ($\eta_{glycerol} = 1420$ mPa·s) (CRC 1977).

3.2 Methods

3.2.1 Preparation of suspensions

Suspensions were prepared by dispersing the hydrophilic particles (either sucrose or glass particles) in high-oleic sunflower oil (HOSO). Due to the highly hygroscopic characteristic of the sucrose particles, they were oven dried at 45 °C overnight before making the suspensions. The suspensions were thoroughly mixed using a laboratory mixer (IKA, model RW16) for 5 min at 500-600 rpm. The volume fraction of the suspensions of glass and sucrose was maintained constant and equal to 0.40 (equivalent to a mass fraction of 0.54 for sugar suspensions and 0.64 for glass suspensions).

The amount of secondary liquid added was determined as the ratio (Vr) between the volume of secondary liquid ($V_{secondary \ liquid}$) and of the volume of particles in the whole suspension ($V_{particles}$):

$$Vr = rac{V_{secondary \, liquid}}{V_{particles}}$$
 Equation 3-1

The addition of the secondary liquid as a ratio of the volume of particles assures that the volume fraction of particles in the system is always constant. Trials were performed at room temperature (25 °C), unless stated otherwise.

3.2.2 Rheology

The flow properties of the suspensions were measured with a rotational rheometer (Kinexus, Malvern Instruments) using the serrated plates measuring system (upper plate with 25 mm of diameter, lower plate with 65 mm diameter and gap of 150 μ m between them; Figure 3-7). The serrated plates geometry was used because it reduces wall slippage, a phenomenon important in high solid fraction suspensions (Barnes and Nguyen 2001). In the suspensions tested, slip can be due to the liquid phase separating from the bulk of the sample to form a slip plane, or by a shear induced non-uniformity of particles near the surface of the plates. This thin diluted layer of the continuous phase near the wall of the plates will have a considerably lower viscosity than the suspension as a whole resulting in the slippage of the continuous phase the plates (Macosko 1994, Barnes 1995). By using serrated plates, it is possible to reduce and often completely eliminate slip because the serrations allow the stress to be applied over a larger area of sample and provide voids to accommodate any separating liquids (Barnes 1995).

Viscosity curves for sugar suspensions were measured using a shear rate step ramp ranging from 0.01 s^{-1} to 100 s^{-1} with 10 s integration time, so that steady-state could be obtained at each shear rate value. Measurements were repeated at least three times.



Figure 3-7. Serrated plates geometry used showing the detail of the serration.

3.2.3 Particle size determination by laser diffraction

In order to evaluate particle agglomeration in vegetable oil in the presence of a secondary liquid, the particle size distribution was measured (with and without secondary liquid addition). A Malvern Mastersizer S (Malvern Instruments, United Kingdom) was used; which principle lies on static light scattering/laser diffraction. The particles passing through the laser beam of the equipment will diffract light at an angle that is inversely proportional to their size. The Mie theory was used for the calculations of particle size distributions using the refractive indexes of sucrose ($n_{sucrose} = 1.5380$) and sunflower oil $n_{HOSO} = 1.4694$ (CRC 1977).

The Mie theory provides a rigorous solution for the calculation of particle size distributions. However, it makes some assumptions, such as that the optical properties of the particles and solvent are known, that the particles are spherical and homogeneous, and that the suspension is dilute (so that scattered light is not re-scattered by other particles) (Merkus 2009).

Because of the construction and theory behind the working principle of the Mastersizer the particle size of the concentrated suspensions cannot be measured directly – it is necessary to dilute them. Therefore, the concentrated suspensions were added to the liquid flow cell of the Mastersizer where they were diluted in the HOSO until an obscuration of 10-15 % was reached. The obscuration is the light intensity absorbed by the sample and it is related to the amount of sample in the system. The water addition was performed on the original concentrated suspensions, and then a sample of this was added to the

equipment for the measurement. The sample was scanned for approximately 60 s; this is equivalent to the set-up of 30000 sweeps of the laser per measurement (1 sweep = 2ms).

The results are given as logarithmic volume weighted particle size frequencies ($q_{3,lg}$) which are functions of the particle size interval width Δx_i (Sommer 2001):

$$q_{3,lg}(\overline{x_{l}}) = \frac{v_{i}}{\sum_{k=1}^{\infty} v_{k}} \frac{1}{\Delta x_{i}} \frac{\overline{x_{l}}}{\lg (\exp(1))}$$
Equation 3-2

where v_i is the volume of all particles in the size range from $\overline{x_i} - \Delta x_i/2$ to $\overline{x_i} + \Delta x_i/2$. Each measurement was repeated at least four times for each sample.

3.2.4 Interfacial tension

Two methods were used to measure the interfacial tension: the pendant drop method and the (Du Noüy) ring method.

The pendant drop method is based on the fact that the shape of a drop at equilibrium is determined by a balance between external forces (i.e. gravity and buoyancy) and interfacial tension. The drop hangs from a needle and its volume should be sufficient so that gravity deforms its shape. Images are then collected, and analysis of them with appropriate algorithms that solve the Laplace pressure equation in relation to the shape results in the interfacial tension (Figure 3-8). The advantage of the pendant drop method is that interfacial tension can be monitored for long periods of time. The pendant drop interfacial tensions were measured using a goniometer FTA125 (First Ten Angstroms, USA).



Figure 3-8. Typical pendant drop image for interfacial tension analysis

As mentioned in Section 3.1.4, glycerol can be used as an immiscible liquid in order to evaluate the effect of viscosity, and also because sucrose is poorly soluble in it. However, since the refractive indexes of glycerol and HOSO are very similar ($n\approx1.47$ for glycerol and HOSO at 20 °C), it is virtually impossible to determine the interfacial tension optically

through the pendant drop method. Therefore, the ring method was used. The ring method is based on measuring the force needed to detach a wire ring from a liquid-liquid interface. These measurements were performed at the Nestlé Research Centre in Lausanne.

As mentioned in Section 3.1.3, some minor components present in commercial oils can influence its surface tension. In order to evaluate the effect of these naturally present minor components, the commercial HOSO was purified. The purification process was done by dispersing 5-10% of activated magnesium silicate (Florisil®, 100-200 mesh) in the HOSO and leaving this dispersion under agitation for at least 30 min. The dispersion was then filtered using a Büchner funnel with a paper filter (Qualitative filter cellulose paper, grade 595, particle retention in liquid of 4 to 7 μ m, Whatman, UK) under suction. This method was suggested by Gaonkar (1989) and Babin (2005) as effective in purifying the oils.

After purification, the effect of the addition of surfactant to the oil phase was investigated. Lecithin was used since it is a very commonly used food surfactant. The surfactant, lecithin, was added in the oil phase and mixing was carried out for about 24 h in order to ensure full dispersion of the surfactant.

3.2.5 Contact angle

The contact angle was measured based on the sessile drop technique. It was measured using the goniometer FTA 125. A drop of water was placed on the surface (either glass or sucrose) inside an oil container as shown in the schematic in Figure 3-9. A high-speed camera captured several images; from which the advancing contact angle could be then determined by image analysis (in-built software).



Figure 3-9. Scheme of contact angle of the three-phase system

The contact angle of glycerol made with sugar and glass surfaces inside HOSO was also measured.

3.2.6 Atomic force microscopy

Atomic force microscopy (AFM) was used to measure the adhesion between surfaces (particle and flat surface). The principle behind the AFM technique has been explained in detail in Section 2.6.1.

An atomic force microscope (NanoWizard III, JPK Instruments, Germany) was used to measure force curves between a particles and flat surfaces inside oil medium over separation distance.

The use of AFM in unusual environments such as vegetable oil is challenging, therefore, three properties of the fluid should be considered. First, the transparency of the medium to the laser light used to measure the cantilever bending. The second property to consider was the refractive index of the medium and the third was the viscosity, since hydrodynamic effects could influence the motion of the cantilever. The vegetable oil (HOSO) was shown to be transparent to the laser and its refractive index is close enough to water (and to the other secondary liquids used) to enable the adjustable mirror to direct the reflected light onto the photodetector ($n_{water} = 1.33$ and $n_{oil} = 1.47$; (CRC 1977)). However, due to its high viscosity (if compared with water - $\eta_{water} = 1$ mPa·s; $\eta_{oil} = 67$ mPa·s), drag effects on the cantilever movements could be observed. This was reduced by using stiffer cantilevers and also evaluating the effect of speed.

The colloidal probe technique has the advantage that particles of choice can be used instead of commercially available cantilevers where material and shape are limited. The particle attachment was performed using the AFM and its integrated inverted microscope (Zeiss Axio-Observer A1). This was done by dipping a tipless cantilever into epoxy glue (Araldite® 2-components epoxy glue, 90 minutes curing time), and after the excess glue was removed from the cantilever (by bringing it into contact with a clean glass surface), a particle could be attached. An inverted microscope was used during this procedure in order to align the particle and the glue at the end of the cantilever tip. The cantilever with the particle was then left for at least 120 minutes to allow the glue to completely dry and harden before the measurements.

The rectangular AFM tipless cantilevers used were the ACT-TL (AppNano, non-coated silicon probe, nominal specifications: length 125 μ m, thickness 4 μ m, width 30 μ m, spring constant 37 N/m, resonance frequency 300 kHz) and the NSC12 (Mikromasch, non-coated silicon probe, nominal specifications: length 90 μ m, thickness 2 μ m, width 35 μ m, spring constant 14 N/m, resonance frequency 315 kHz).

In a force measurement, the colloidal probe (particle glued to the cantilever) was brought down towards the sample (called the "approach"). After contact, a set-point load force was applied (dependent on the experiment) and subsequently the colloidal probe was retracted from the surface ("retraction"). During this procedure, the vertical deflection of the cantilever was recorded versus the displacement in the vertical direction (normal to the surface). The force data could be obtained based on Hooke's law, i.e. by multiplying the deflection of the cantilever by its spring constant.

The cantilever spring constant and sensitivity were calibrated using the thermal noise method which is based on the cantilever fluctuations due to thermal vibrations of the environment (Hutter and Bechhoefer 1993). The spring constant was always calibrated after the attachment of the particle, since the extra mass at the tip of the cantilever could affect the deflection of the cantilever. The NaNoWizard III AFM has a thermal noise acquisition of up to 3.25 MHz; which enabled the calibration of the spring constant with the thermal noise method even when stiff cantilevers were used. Several force curves (at least 20) were collected for each position on the surface.

The colloidal probes produced and the cantilever measured spring constants and sensitivities are described in more detail in each results chapter (Chapter 6 and Chapter 7).

In order to perform force measurements inside oil medium, an AFM liquid cell was used (Biocell, JPK Instruments, Germany). In addition, the AFM has a purpose-built setup that enables the control of relative humidity in the liquid cell, where a Wetsys Humidity Generator from Setaram (France) is connected to the Biocell (Figure 3-10). In this unit, humidity and temperature could be controlled by heating a mixture of dry and humid air. The flow rate was set at 50 mL/min during equilibration time (around 2 hours) and reduced to 20 mL/min during the measurement to reduce noises and disturbances on the force-distance curves. The Biocell had a temperature control which assured constant temperature throughout the experiment and the connection of the Wetsys to the Biocell was done through a heated line in order to minimize water condensation in the pipework. The measurements were performed at 25 °C.



Figure 3-10. Purpose-built AFM setup consisting of a relative humidity and temperature control unit connected to the AFM.

3.2.7 Scanning electron microscopy

Scanning electron microscopy (SEM) was used in order to visually characterize the particles used and also the colloidal probes used for the AFM experiments.

The principle of SEM lies on scanning a surface with a focused beam of electrons and building a topographical image based on the signals that are detected based on the interaction of the beam of electrons and sample (Joy and Howitt 2003).

A CamScan Mk. II SEM (CamScan, United Kingdom) was used. Samples were sputtered with gold under vacuum prior to the insertion on the CamScan chamber. Scans were taken generally at a power of 20 kV, however, for the sugar particles a lower power (10-15 kV) was used due to the sensitive nature of the sample and the fact that a high power accelerated beam of electrons could result in localized high temperatures on the surface of the sample and consequently, change the topography of the sample.

Chapter 4

Network formation by agglomeration of particles

In suspensions of hydrophilic particles in oil (hydrophobic medium), the addition of a secondary immiscible hydrophilic liquid results in a change in the macroscopic behaviour which is related with the network formation by the agglomeration of the particles. In this chapter, this network formation is investigated in sugar and glass suspensions in sunflower oil using different techniques such as microscopy, laser diffraction (particle size distributions) and rheology (viscometry). In addition, the effect of adding different secondary liquids (or binders) is explored and analogies to wet granulation and spherical agglomeration phenomena are also drawn.

4.1 Introduction

In food products, attributes such as texture, appearance and mouth-feel are of utmost importance for the consumer and determine the acceptance of a product in the market.

As mentioned in Section 2.7, in highly concentrated suspensions such as the ones common in food products, the addition of a secondary immiscible liquid results in a rheological transition from a liquid-like to a solid-like structure. This phenomenon is attributed to the agglomeration of particles by liquid bridges, resulting in a space-filling network (Johansson and Bergenståhl 1992, Dedinaite, Claesson et al. 1998).

The majority of the works concerning agglomeration of solid particles in suspensions due to the presence of a secondary immiscible liquid have focused so far in the area of industrial separation where the concentration of particles in the suspension is relatively low (Blandin, Mangin et al. 2003, Rossetti and Simons 2003). In the food sector, the concentration of particles in suspensions is usually high, such as in peanut butter, spreads, purees, cake and biscuit doughs, among others. Therefore, highly concentrated model suspensions are used in this work.

4.2 Materials & Methods

The materials and methods used for this specific chapter are described in detail Chapter 3. A summary of the materials utilised is given in Table 4-1 and the properties of the liquids used are given in Table 4-2. The experimental methods used were described in detail in Section 3.2 and the preparation of the suspensions was detailed in Section 3.2.1.

Table 4-1. Summary of materials used for experiments in this chapter					
	• Icing sugar (British Sugar, UK, $D_{50,3}$ = 29 µm, ρ = 1.59 g/cm ³)				
Solid particles	• Spherical solid glass particles (Soda-lime glass, Spheriglass [®] , code 20035,				
	Potters Industries LLC, UK, $D_{50,3}$ = 41 µm, ρ = 2.52 g/cm ³)				
Continuous phase	• Purified high oleic sunflower oil (HOSO, Type F, Sofinol Speciality Oils,				
Continuous phase	CH)				
	Deionized water				
Secondaryliquid	• Saturated sugar solution (67.47 %wt pure sucrose (Sigma-Aldrich, UK) in				
secondary nquid	deionized water)				
	• Anhydrous glycerol (purity ≥ 99.5%, Sigma-Aldrich, UK)				

Table 4-2. Liquid properties (25 °C).								
Liquid		Density, ρ [kg/m ³]*	Interfacial Tension with HOSO, γ [mN/m]**	Dynamic vis- cosity, η [mPa·s]***	Contact angle with a glass surface inside HOSO, θ [°]**			
Continuous media	HOSO	919		65				
Secondary liquids	Water	998	26	0.9	39			
	Saturated sugar solution (67.47 %wt sucrose)	1327	25	206	40			
	Anhydrous glycerol	1250	17	840	64			

* Density was measured with a liquid pycnometer.

** Measured using the drop method (pendant drop for interfacial tension, sessile drop for contact angle) with a goniometer (FTA125, First Ten Angstroms, USA)

*** Viscosity was determined experimentally with a rotational rheometer (Kinexus, Malvern Instruments, UK) using the cone and plate system (4° / 40 mm) and shear rate table ranging from 0.1 s⁻¹ to 100 s⁻¹. All the four fluids showed Newtonian behaviour.

The SEM micrographs of the particles used are given in Figure 4-1, and, as it can be observed, the glass particles have a spherical shape while the sugar particles (icing sugar) are highly irregularly shaped. From Figure 4-1 (b) one can also notice that the sugar particles have a wider range of sizes (shown later in the particle size distribution in Figure 4-6 and Table 4-3).



Figure 4-1. SEM micrographs of the hydrophilic particles used: (a) solid glass spheres (b) icing sugar.

4.3 Results and Discussion

4.3.1 Network formation by agglomeration of particles

Suspensions of sucrose and glass particles in oil (HOSO) with different amounts of water added are shown in Figure 4-2.



Figure 4-2. Effect of water addition on fat-based suspensions - transition from a fluid-like to a solid-like behaviour is visible (weight percentages of water added are specified above each sample)

Both suspensions with sugar and glass particles showed similar behaviour with the transition from a fluid-like to a solid-like state upon the addition of water (Figure 4-2). This phenomenon supports the hypothesis that liquid water bridges are bringing the particles together. The observed agglomeration of particles suggests the presence of adhesion forces in between them. Glass particles were used in order to mimic sugar particles in order to be able to evaluate whether the adhesion forces are dependent on the particle material properties or not. It is important to point out that samples with sugar as the suspended solid had a lumpy appearance after the addition of water. This is probably related to the fact that the sugar particles are partially dissolving in the added water, creating a viscous concentrated sugar solution around the particles which bridges them. Moreover, if enough time is given, recrystallization of the saturated solution bridge could occur, creating very strong large individual agglomerates in the suspension.

Similarly, in Figure 4-3, a similar transition in the suspensions is observed upon addition of anhydrous glycerol. This indicates that the liquid bridges can form with secondary liquids other than water as long as they are immiscible with the continuous phase and wetting the particles.



Figure 4-3. Effect of glycerol addition on fat-based suspensions

The samples above were stored at room temperature (25 °C) for 1 day and no visual changes in texture could be observed. The glass particles in the sample with no added water or glycerol sedimented after storage. This sedimentation was not observed, or was observed to a lower extent, upon water or glycerol addition. As one can observe in Figure 4-4, the addition of glycerol results in a smaller separation of oil and particles, indicating that the adhesion bonds create a network that holds the particles in suspension.



Figure 4-4. Glass suspensions in oil with different amounts of added glycerol after 1 day storage at room conditions. The amount of added glycerol is stated below each picture and it corresponds to Vr (as stated in Equation 3-1).

However, for suspensions with higher concentrations of secondary liquid, the particles agglomerated strongly, releasing and separating some of the oil from the suspension. For

sugar suspensions this phenomenon was observed for Vr above 0.1 and for glass suspensions for Vr of 0.5. This behaviour can be related to the states of saturation of the secondary liquid in the suspensions as shown in Figure 2-6 and in Figure 2-7 (Section 2.3.5.1). When secondary liquid is added, cohesive pendular bridges are formed and the particles are held in suspension. However, when the secondary liquid is added in excess, a capillary or droplet state is reached and all the space between the particles is filled with the secondary liquid resulting in the expulsion of the continuous phase (oil separation).

Optical micrographs of the suspensions (Figure 4-5) show the presence of water liquid bridges between particles dispersed in an oil continuous phase (Figure 4-5 (b) and (d)). The water was coloured with red erythrosine (Erythrosine B, dye content 90%, Sigma-Aldrich, United Kingdom). The visible liquid bridges give evidence of the agglomeration of particles and consequent particle network formation.



(a) Glass-in-HOSO

(b) Glass-in-HOSO with 0.02 water



(c) Crystalline sucrose-in-HOSO Figure 4-5. Glass and sugar suspensions in sunflower oil (HOSO) with and without added water. Water was coloured with erythrosine and was added to the suspensions at Vr=0.02.

It is important to point out that the particles used for the above micrographs (Figure 4-5) are larger (in size) than the ones used in the other experiments (Sections 4.3.2 and 4.3.3).

Larger particles were used in order to enable the visualization of the bridges with an optical microscope.

4.3.2 Evaluation of agglomeration by laser diffraction

In order to analyse the agglomeration of sugar and glass particles in vegetable oil in presence of water, the particle size was measured (with and without the addition of water) using laser diffraction (Section 3.2.3).



Figure 4-6. Volume weighted logarithmic size frequency $(q_{3,lg})$ for glass and sugar suspensions in oil, with and without water addition (ratio of water is given as Vr).

Particle size measurements (Figure 4-6) show an increase of particle size for the sugar suspensions upon water addition, with the particle size distribution (PSD) shifting in the direction of larger size classes and a median particle size ($D_{50,3}$) greater by approximately 40 % (Table 4-3). This supports the hypothesis that the sugar particles are agglomerating because of the presence of water.

In the case of glass particles, however, the increase in particle size upon addition of water is not observed (Figure 4-6). The hypothesis is that sugar partially dissolves in the water bridge leading to an increase of the local viscosity within the bridge, thereby strengthening it. Moreover, the sugar particle's irregular shape can lead to the formation of numerous liquid bridges, which would also result in stronger adhesion. Therefore these bridges form a stronger network which is not destroyed during the particle size measurement by the impeller of the dispersion unit of the instrument. In the case of glass particles, water bridges are also formed (Figure 4-5), however, they might be ruptured during the dilution and mixing in the dispersion unit of the apparatus.

-	water addition ($D_{10,3}$, $D_{50,3}$ and $D_{90,3}$ are given in μm).					
	Sugar		Gla	ass		
	Vr=0	Vr=0.02	Vr = 0	Vr=0.02		
D _{10,3}	8.1 ± 0.9	23.1 ± 1.2	26.1 ± 0.5	25.9 ± 0.2		
$D_{50,3}$	28.9 ± 3.5	55.4 ± 3.4	40.8 ± 0.2	40.6 ± 0.2		
$D_{90,3}$	95.5 ± 16.7	145.3 ± 12.4	61.2 ± 1.0	61.0 ± 0.3		

Table 4-3. Percentile PSD parameters for sugar and glass suspensions in HOSO with and withoutwater addition ($D_{10,3}$, $D_{50,3}$ and $D_{90,3}$ are given in μ m).

The effect of water addition is shown in detail in Figure 4-7. The increase in the added amount of water results in a relative increase of agglomerate size.



Figure 4-7. Effect of water addition on the particle size distribution of sugar in oil suspensions

The effect of glycerol addition to sugar suspensions in HOSO was also analysed (Figure 4-8).



Figure 4-8. Effect of glycerol addition on the particle size distribution of sugar-in-oil suspensions

In a similar manner to the sugar suspension with added water, the addition of glycerol resulted in an increase in agglomerate size relative to the amount of liquid addition. Glycerol addition, however, showed a subtle increase in agglomerate size for Vr up to 0.02 and a more drastic increase for Vr=0.05. The difference in behaviour between the two immiscible liquids could be related to the sugar dissolution into the water bridge changing the agglomerates formation.

The effect of viscosity of the binding liquid in the formation of agglomerates was evaluated by comparing the effect of the addition of water (low viscosity; Table 4-2) and glycerol (viscosity three orders of magnitude higher than water; Table 4-2) to glass suspensions in HOSO (Figure 4-9). As already observed in Figure 4-6, the addition of water in glass suspensions showed no agglomerates due to bridge rupture by the instrument impeller (also in Figure 4-9). However, the addition of glycerol resulted in a shift of the particle size distributions to larger sizes, indicating the presence of agglomerates that resisted the impact with the impeller, the shearing action of the liquid leaving the impeller blades, as well as due to the laminar flow within the tubes that lead to the laser beam presentation area.



Figure 4-9. Comparative effect of water vs. glycerol addition in glass-in-oil suspensions

Finally, by measuring the particle size of the same sample over longer periods of time, the effect of the impeller was identified. Glass suspensions in HOSO with added glycerol (Vr=0.1) were measured three times each, which correspond to the different runs in Figure 4-10. The more time the samples were left in the instrument under agitation to promote a continuous flow, the smaller the amount and size of agglomerates.



Figure 4-10. Effect of prolonged impeller mixing on the particle size distribution of glass bead suspensions in oil with Vr=0.1 glycerol added. The different runs correspond to the approximate time the sample has been mixed (run $1 \approx 1$ min; run $2 \approx 2.5$ min; run $3 \approx 4$ min).

The effect of the addition of a secondary liquid (water, saturated sugar solution or glycerol) to the flow behaviour of glass and sugar suspensions in oil was assessed by means of viscometry (Figure 4-11 to Figure 4-16).

Firstly, the analysis of the steady-state apparent viscosity curves for sugar and glass suspensions without the addition of any secondary liquid shows that the glass suspension exhibit a behaviour similar to a Newtonian fluid while the sugar suspension exhibit a shear thinning profile for shear rates values from 0.1 to 10 s⁻¹.

The factors that influence the flow behaviour of suspensions are mainly: particle concentration, size, shape, interparticle forces and forces between particles and the continuous phase (Macosko 1994, Mewis and Wagner 2012). Comparing the glass and sugar suspensions, the particle concentration was the same (volume fraction of 0.4). The sugar particles are slightly smaller than the glass particles – the $D_{50,3}$ for sugar is smaller ($D_{50,3} \approx 29$ μ m for sugar and D_{50.3} \approx 41 μ m for glass), however, the particle size distribution for sugar has a larger span (Figure 4-6 & Table 4-3). Forces between particles and continuous media are expected to be comparable for both systems and, as discussed in Section 2.3, interparticle forces in oil medium are also negligible if compared to hydrodynamic forces. On the other hand, the sugar particles have an irregular shape due to the way they were produced (i.e. milling of sugar crystals; Figure 4-1 (b)) while the glass particles have a spherical shape (Figure 4-1 (a)). Consequently, for the case of no added binder liquid, those differences in particle shape can explain the observed pseudo-Newtonian behaviour of glass suspensions and shear thinning of the sugar suspensions for lower shear rates (0.1 to 10 s⁻¹). Additionally, the higher values of viscosities for sugar suspensions can be justified by both their irregular particle shape, slightly smaller and wider size distribution. At shear rate values above 10 s⁻¹, an increase in viscosity is observed for both the sugar and glass suspensions with no added secondary liquid. The increase in shear rate results in a strong association of the particle motion and the formation of local transient selforganized clusters lead to a shear thickening effect (Mewis and Wagner 2012).

Once the secondary liquid is added to the suspensions, a clear increase in viscosity is observed for both types of suspensions, with all the secondary liquids tested. In addition, glass suspensions start to demonstrate a more shear-thinning behaviour upon addition of secondary liquid (Figure 4-11 to Figure 4-17). Considering that the particle concentration, size and shape do not change upon the addition of the secondary liquid, one can conclude that the interparticle forces are responsible for the viscosity increase and change in shear behaviour. These forces are related with the formation of binder liquid bridges between the particles as the ones shown in Figure 4-5 (b) and (d). Water, saturated sugar solution
and glycerol are hydrophilic liquids (as given by the contact angles values < 90° as shown in Table 4-2). Therefore, the secondary liquids preferably adsorb on the glass and sugar particle surfaces, and due to the high solid concentration and consequent small distances between particles, liquid bridges could be formed.

For both glass and sugar suspensions, at lower Vr values, the viscosity at high shear rates reduces to values similar to the suspensions with no added secondary liquid. This suggests that the small bridges break when submitted to large shear stresses. For the glass suspensions, at Vr values above 0.002 (water) and 0.01 (saturated sugar solution and glycerol), the viscosity values are always superior to the viscosity of the suspension with no added secondary liquid, even at high shear rates. This, similarly to observations from Van Kao, Nielsen et al. (1975) and McCulfor, Himes et al. (2011), shows that the larger bridges together with the higher availability of secondary liquid, form a stronger network which can resist even higher stresses.

Considering the suspension of sugar particles in oil with added water as the secondary liquid, as the water concentration increases, the sugar dissolves into the bridge, which then becomes a sugar solution. When the water content approaches a certain value (from Figure 4-11 and the pictures in Figure 4-2, above Vr=0.05), the sugar dissolves and separates from the oil forming a lump as seen in the picture (Vr=0.1) in Figure 4-2. Due to this oil-phase separation it was not possible to measure the viscosity curves for Vr>0.05. Similar behaviour was observed by Johansson and Bergenståhl (1992) when evaluating the sediment volume of sugar suspensions in oil upon water addition. They observed an increase of sediment volume until a certain water concentration (1 %wt in their case), with a subsequent reduction in the volume of the sediment containing higher amounts of water. They correlate the sediment volume with an attraction between particles, with a higher volume (and lower density) indicating a greater attraction between particles. It is also important to note that at high shear rates (above 10 s⁻¹), slip due to centripetal artefactual effects can be noticed for the Vr=0.05 sample in Figure 4-11 and for the Vr=0.05 and 0.1 samples in Figure 4-13, despite measures taken to avoid it (i.e. the use of serrated plates rather than smooth parallel plates). Although this phenomenon is observed at high shear rates, the upward trend in viscosity upon addition of water or saturated sugar solution is nonetheless substantial.

In the case of glass particles, an increase in viscosity is also observed upon the addition of water (Figure 4-12). However, in contrast to the sugar suspensions, at a Vr of 0.1 neither a reduction in viscosity nor oil separation is observed. Glass, as an inert particle, does not promote any changes to the bridge composition and, therefore, more bridges are formed since there is no particle dissolution. This oil-phase separation is only observed for glass suspensions at much higher values of Vr (at Vr=0.5, for example), where the particles be-

come immersed in the water phase (comparable to the droplet state in granular media in the Schubert diagram, Figure 2-7, Section 2.3.5).

When a saturated sugar solution is used as the secondary liquid, the dissolution of sugar particles in the bridge is expected to be minimized. By comparing the flow curves shown in Figure 4-11 and in Figure 4-13, for the smallest addition of secondary liquid (Vr=0.001), there is no significant difference between the viscosity curves of the sugar suspensions with the addition of either water or saturated sugar solution; however, a difference between the two can be observed for larger amounts of secondary liquid. In the case where sugar solution is added as a secondary liquid, a gradual increase in viscosity with concentration is observed; the curves are sparser, while for water, the viscosity curves overlap. For the glass suspensions, a similar effect is observed for the two different secondary liquids (Figure 4-12 & Figure 4-14). This can be correlated to the dispersion of the secondary liquid in the suspension. The saturated sugar solution is two orders of magnitude more viscous than water (Table 4-2). Therefore, for the same volume of secondary liquid, different levels of mixing would be needed to achieve the same dispersion. In addition, it is important to point out that the indication that the saturated sugar solution minimized the dissolution of the sugar particles in the bridge is that at a Vr value of 0.1 it was still possible to measure the viscosity curve, which was very close to Vr of 0.05.

Finally, in the case where glycerol is added to the suspensions, a similar behaviour is observed for the glass suspensions with added saturated sugar solution (Figure 4-16) – a gradual increase in viscosity is seen upon glycerol addition. The viscosity of glycerol is much higher than water and saturated solution (Table 4-2), so it is hypothesised that its dispersion into the suspension also requires higher mixing levels. For the sugar suspensions a gradual increase in viscosity in relation to Vr is not observed to the same extent as saturated sugar solution (Figure 4-15).



Sugar suspension with added water

Figure 4-11. Steady state apparent viscosity curves for 40 %vol sugar in oil suspensions with different amounts of added water (given as Vr). At Vr=0.1, large phase separation was observed, therefore, the viscosity curve is not shown. Slip is observed for Vr=0.05 at high shear rate values.

Glass suspensions with added water



Figure 4-12. Steady state apparent viscosity curves for 40%vol glass in oil suspensions with different amounts of added water (given as Vr).



Sugar suspension with added saturated sugar solution

Figure 4-13. Steady state apparent viscosity curves for 40%vol sugar in oil suspensions with different amounts of added saturated sugar solution (given as Vr). Slip is observed for samples with Vr≥0.05 at higher shear rate values.

Glass suspension with added saturated sugar solution



Figure 4-14. Steady state apparent viscosity curves for 40%vol glass in oil suspensions with different amounts of added saturated sugar solution (given as Vr).



Sugar suspension with added glycerol

Figure 4-15. Steady state apparent viscosity curves for 40%vol sugar in oil suspensions with different amounts of added glycerol (given as Vr).





Figure 4-16. Steady state apparent viscosity curves for 40%vol glass in oil suspensions with different amounts of added glycerol (given as Vr).

One interesting aspect that should be pointed out is that it is visually perceptible that the increase in secondary liquid, be it water, saturated sugar solution or glycerol, results in a network that holds the glass particles in the suspension. The more secondary liquid is added, the more opaque the samples become (e.g. no oil on the surface for the suspension with water Vr of 0.05; Figure 4-2) and also there is significantly less separation of the particles from the oil due to sedimentation driven by gravitational forces (Figure 4-4).

Another way to analyse the viscosity increase upon the addition of secondary liquid is to plot the viscosity versus the amount of secondary liquid (Vr) for a specific shear rate, as shown in Figure 4-17 for 0.1 s⁻¹, 1 s⁻¹ and 10 s⁻¹. Those values of shear rates were chosen because they cover the typical range of shear rates of processes in food production, such as mixing $(10 - 1000 \text{ s}^{-1})$ and sedimentation/drainage $(0.1 - 10 \text{ s}^{-1})$ (Macosko 1994), and at such shear rates values, no slippage was observed. The difference in magnitude of the viscosity for the three values of shear rate is due to the shear thinning behaviour of the suspensions.

At the three values of shear rates plotted, the same pattern in viscosity increase is observed, i.e. a steep increase in viscosity directly after the secondary liquid is added (Figure 4-17). In addition, a viscosity plateau is reached in general for $Vr \ge 0.01$ in glass suspensions and at lower values (Vr > 0.002) for the sugar suspensions with the different secondary liquids. This plateau shows that a further increase in the amount of binder liquid present in the suspension does not cause any additional rise of the viscosity. It is important to highlight, as aforementioned, that for higher amounts of secondary liquid a strong agglomeration of the suspensions was seen followed by phase separation and deoiling. This whole profile of viscosity increase, followed by a plateau and consequent decrease due to de-oiling can be compared to the observations from Schubert (1975). He proposed a correlation between the tensile strength and the saturation of dry granular material (Schubert diagram, Figure 2-7, Section 2.3.5). Although there are differences in the stresses due to the applied normal forces in a tensile strength measurement from the shear forces in rotational viscometry, a qualitative comparison can still be built. When liquid is added, pendular bridges are formed and the viscosity of the suspensions is increased. Further addition of secondary liquid leads to the formation of more pendular and funicular liquid bridges and the increase in viscosity is still steep. Once the secondary liquid concentration starts to saturate the suspension, capillary bridges followed by the droplet state occur, with the consequent de-oiling in the suspension.

From Figure 4-17(b), one could argue that the curves for the glass suspensions with added saturated sugar solution do not show the mentioned plateau for the Vr values plotted. This plateau is reached, but for a higher value of Vr (Vr=0.1) as seen in Figure 4-14.



Figure 4-17. Apparent viscosity curves for glass and sugar suspensions in oil at different shear rates (0.1 s^{-1} , 1 s^{-1} and 10 s^{-1}), as a function of the amount of secondary liquid (water, saturated sugar solution and glycerol) added to the suspension.

From Figure 4-17 it is also observed that the magnitude of the viscosity for the suspensions with added glycerol is lower than for the suspensions with added water. In order to evaluate this observation, the viscosity curves for glass suspensions with added water and glycerol at Vr=0.001 and 0.02 are plotted together for comparison in Figure 4-18. At lower values of Vr (Vr=0.001), the viscosity curves for the suspensions with added water and glycerol are very similar in shape and magnitude. At higher values of Vr (Vr=0.02) and low shear rates, higher values for viscosities are observed for the suspensions with added water. For the glycerol, it is expected that a dynamic contribution due to its high viscosity will play a role. Since it is a dynamic contribution, it becomes more prominent at high shear rates. Taking into consideration that the interfacial tension between oil-glycerol is lower than between oil-water (Table 4-2), it is also consistent that glass suspensions with glycerol bridges would have a lower viscosity at low shear rates, where static contributions to the liquid bridge adhesion force will be dominant (Section 2.3). This will be discussed in more detail and on a microscale point of view in Chapter 6 and Chapter 7.



Figure 4-18. Apparent steady-state viscosity curves for glass suspensions plotted for different secondary liquids (water and glycerol) added to the suspension at two different concentrations (Vr = 0.001 and Vr = 0.02).

4.3.4 Note on the elimination of slip with the use of serrated plates

When measuring the flow behaviour of suspensions, one very important aspect that has to be taken into account is wall slip, since this could lead to misinterpretation of results. As mentioned earlier, in order to reduce (and possibly even avoid) slippage, serrated plates were used. The serrations (prominent rough patterns) provide space to accommodate any phase separation and also increase the area that the stress is applied on the sample. In order to verify if the serrated plates were actually minimizing slip, one can measure the viscosity curves at different gaps between the plates. Yoshimura and Prud'homme (1988) suggested a correction for wall slip in parallel plates by measuring the torque (or shear stress) at two different gap heights. In their results, slippage in an oil-in-water emulsion was present when measured with smooth parallel plates and it could be identified by the lower shear stress for the smaller gap height as a function of the shear rate. In the example shown in Figure 4-19 one can observe that the viscosity curves for different gaps coincide, showing the wall slip was not present. Only one example is plotted, but similar tests were performed for all the different samples and analogous results (i.e. inexistence of slippage) were observed.



Figure 4-19. Viscosity curves for 40 %vol glass-in-oil suspensions with added water (Vr=0.01) for different gap separation between the serrated plates.

Limited slippage was observed in specific cases, such as for sugar suspensions containing elevated amounts of secondary liquids at high shear rate (above 10 s⁻¹) as shown in Figure 4-11 and Figure 4-13 and discussed in the previous section (4.3.3). Although slippage was identified for such extreme circumstances, it was generally reduced by the use of serrated plates.

4.3.5 Note on the hysteretic nature of viscosity curves

The viscosity curves for glass and sugar suspensions in oil upon secondary liquid addition presented in Chapter 4 and also the ones which are later shown in Chapter 5 were measured while increasing and then decreasing shear rate. Those shear rate tables (a shear rate ramp with equilibrium time to get apparent steady-state viscosity) were collected for all samples, but only the ascending shear rate viscosity curves are plotted in the other chapters not to become exhaustive. In Figure 4-20, characteristic viscosity curves obtained upon increase and consequent decrease in shear rate for sugar and glass suspensions with added glycerol (Vr=0.02) are shown.

From the shape of the curves from both glass and sugar suspensions, a hysteresis loop is observed. This behaviour is characteristic of thixotropic samples, i.e. samples which flow behaviour is time-dependent and reversible. The hysteretic behaviour in thixotropic samples has been related to a spatial rearrangement of particles or molecules due to the applied stress or to a structural change in the system (Macosko 1994, Tadros 2010, Tadros 2011, Mewis and Wagner 2012).

During the increase in shear rate, the structure of the suspension breaks down hence the decrease in viscosity. However, when the shear rate is brought from a high value back down, the structure does not recover at the same rate it initially broke apart, hence the hysteresis loop and lower viscosity than the ascending shear rate viscosity curve. In addition, the rearrangement of irregular particles such as the sugar particles can result in an even stronger thixotropy. For this same reason, it was not possible to measure the yield stress, G' (elastic modulus) and G'' (loss modulus) for the suspensions presented in this work. Due to the rearrangement of the particles, it was also not possible to obtain a linear viscoelastic region in amplitude sweeps measurements (oscillatory mode).



Figure 4-20. Apparent viscosity for sugar and glass suspensions in oil with added glycerol (Vr=0.02) for increasing and decreasing shear rate ramps - hysteretic nature of the samples.

4.4 Conclusions

In this chapter, the agglomeration of hydrophilic particles in fat based systems was studied using suspensions of sucrose and glass particles in oil (HOSO) upon the addition of secondary immiscible liquids. Such systems are particularly interesting because they can be used as a model to investigate processes that are common in the food industry. A transition from a liquid-like to a solid-like macroscopic structure was observed upon the addition of different secondary liquid (water, glycerol and saturated sugar solution) and the hypothesis that a network of liquid bridges is being formed was supported by the visualization of water bridges between sugar and glass particles in oil by optical microscopy.

Rheological experiments and particle size measurements by laser diffraction showed that the sugar suspensions exhibit a different behaviour than the glass ones, although both of them have the same characteristic transition in macroscopic structure. This could be correlated with the fact that the sugar particles, in contrast to the inert glass ones, can dissolve in water and, therefore, there is a change in the properties of the bridge as schematized in Figure 4-21b. In addition, a significant increase in viscosity was observed in all samples, even with very small addition of binder liquid. Moreover, after the addition of a certain amount of binder liquid, there was no further increase in viscosity and a plateau was reached. In contrast to the particle size results, the viscosity measurements showed that the addition of water has an effect on glass suspensions (viscosity increase). In the particle size experiments, the highly concentrated suspensions had to be diluted in the continuous phase (HOSO) so that the laser beam could be refracted and particle sizes could be calculated (Figure 4-21 (a) & (b)). In the rheometer, the highly concentrated suspensions could be evaluated directly (Figure 4-21 (c) & (d)). Therefore, even if a bridge was ruptured due to shear stresses, it could form again due to the small distances between particles in the high concentrated suspensions even at a lower rate (hysteresis). Hence, rheology seems to be a better technique to evaluate agglomeration of suspensions such as the ones consisting of glass particles upon water addition.



Figure 4-21. Schematic drawing for the possible phenomena occurring during particle size (a & b) and viscosity (c & d) measurements. In PSD experiments, the dilution of the suspension results in a dispersion of the particles hindering the re-formation of liquid bridges once ruptured. For sugar suspensions, the dissolution of sugar into the added water results in a local increase in viscosity within the bridge and possible recrystallization would create very strong agglomerates. In viscosity experiments, the high concentration of suspensions is kept constant and if bridges are ruptured due to the application of shear, they can be formed again due to the very close proximity of particles.

Chapter 5

Effect of material parameters on the network formation

The analysis of the effect of each material parameter separately can provide essential information to understand the agglomeration mechanism on a macro-scale. In this chapter, the effect of particle size, shape, concentration, viscosity of the secondary liquid (or binder) and the presence of surfactant on the flow behaviour of oil-based suspensions is discussed.

5.1 Introduction

As mentioned in the literature review (Section 2.7), some authors have investigated the network formation in suspensions upon the addition of a secondary immiscible liquid by evaluating the sedimentation and flow behaviours.

The separate analysis of the effect of some material parameters has been done by McCulfor, Himes et al. (2011), Koos, Johannsmeier et al. (2012) and Hoffmann, Koos et al. (2014). They have shown that the viscosity and strength of the network is inversely proportional to the particle size and directly proportional to the interfacial tension, while independent of the viscosity of the secondary liquid (in capillary suspensions). They have also all reported decreases in viscosity and yield stress with the addition of surfactants, which was dependent of the type of surfactant used.

However, while McCulfor, Himes et al. (2011) has worked with suspensions of relatively low particle concentrations in mineral oil, Koos, Johannsmeier et al. (2012) and Hoffmann, Koos et al. (2014) have focused on what they have called "capillary suspensions", i.e. where the secondary liquid does not preferentially wet the particles. Therefore, the detailed analysis presented in this chapter has been identified as essential to fully understand the network formation in systems of concentrated suspensions containing immiscible liquids.

5.2 Materials & Methods

The oil-based suspensions were prepared as described in detail in Materials & Methods (Chapter 3) and consisted of sugar or glass particles dispersed in high oleic sunflower oil (HOSO). Unless otherwise stated the particle concentration was kept as 40% vol. The secondary liquid used in the experiments described in this chapter was by default anhydrous glycerol, unless specified otherwise. For each parameter analysed the materials used changed slightly, therefore, those are described in more detail separately.

5.2.1 Particle size distributions

In order to evaluate the effect of particle size distribution (PSD) of the solids on the flow behaviour of suspensions of hydrophilic particles in oil upon the addition of glycerol as a secondary immiscible liquid, glass and sugar particles were dry-sieved before suspensions were made. About 50 g of particles were sieved per batch using the vibratory sieve shaker (model AS 200, Retsch GmbH, Haan, Germany) at an amplitude of 1.5 mm for 15 minutes in order for the smaller mesh sieves not to "go blind" (i.e. when the mesh becomes blocked with material and smaller particles are retained in the larger fractions). After sieving, the PSDs obtained from the different fractions were measured using static laser diffraction (Mastersizer S, Malvern Instruments, United Kingdom; method described in Section 3.2.3). The percentile PSD parameters for the different fractions of sugar and glass particles are given in Table 5-1 and the distributions are shown in Figure 5-1. Two different size classes were chosen for the flow behaviour experiments: $25-45 \ \mu m$ and $75-100 \ \mu m$.

-	Icing sugar			Glass		
-	Sieve: 25-45 μm	Not sieved	Sieve: 75-100 μm	Sieve: 25-45 μm	Not sieved	Sieve: 75-100 μm
D _{10,3} [µm]	6.8 ± 0.2	8.1 ± 0.9	17.5 ± 0.9	22.6 ± 0.1	26.1 ± 0.5	55.7 ± 1.0
D _{50,3} [µm]	16.9 ± 1.1	28.9 ± 3.5	91.5 ± 5.7	35.0 ± 0.2	40.8 ± 0.2	78.1 ± 1.1
D _{90,3} [µm]	34.9 ± 4.2	95.5 ± 16.7	135.1 ± 3.1	51.9 ± 0.6	61.2 ± 1.0	103.1 ± 2.2

Table 5-1. Percentile PSD parameters for the different fractions/class sizes of sugar and glass particles used ($D_{10.3}$, $D_{50.3}$ and $D_{90.3}$ are given in μ m).



Figure 5-1. Particle size distributions for icing sugar and glass particles –effect of PSD - (a)&(c)Volume weighted logarithmic size frequency $(q_{3,lg})$ for glass and sugar suspensions in oil; (b)&(d) cumulative distributions

5.2.2 Particle shape and density

The effect of particle shape and density was evaluated by analysing the flow behaviour of suspensions with different glass particles.

The glass particles used were:

- Spherical solid glass particles (Soda-lime glass, Spheriglass[®], code 20035, Potters Industries LLC, United Kingdom)
- Spherical hollow glass particle (Borosilicate glass, Sphericell[®] 110 P8, Potters Industries-EGM Division, United Kingdom)
- Glass grains (Soda-lime glass, Potters Industries LLC, United Kingdom)

More information about the glass particles used is given in Table 5-2 and their particle size distributions are plotted in Figure 5-2.

Material	SEM micrograph	Density	D _{10,3}	D _{50,3}	D _{90,3}
Solid glass spheres		[g/cm] [*] 2.5	μm 26.1 ± 0.5	[μ m] 40.8 ± 0.2	[μ m] 61.2 ± 1.0
Hollow glass spheres	Stra	1.1	7.9 ± 0.1	16.6 ± 0.2	27.0 ± 0.4
Glass grains		2.4	15.7 ± 0.2	44.4 ± 5.3	141.1 ± 35.9

Table 5-2. Glass particles used for the evaluation of particle shape and density. SEM micrographs, densities and percentile PSD parameters ($D_{10.3}$, $D_{50.3}$ and $D_{90.3}$) are also given for each material.

* Density values were given by the supplier (Potters Industries LLC, UK) and were also measured using liquid pycnometry.



Figure 5-2. Particle size distributions for solid glass spheres, hollow glass spheres and glass grains. (a) Volume weighted logarithmic size frequency (q_{3,lg}) distribution (b) cumulative volume size distribution bution

5.2.3 Particle concentration

The effect of particle concentration on the flow behaviour of glass and sugar suspensions upon the addition of a secondary liquid (glycerol) was evaluated using the following volume concentrations: 30 %, 40 % and 50 %wt. Those volume concentrations correspond to the following weight concentrations for sugar and glass respectively: 54.20 % / 64.8 % / 77.1 % and 42.7 % / 53.7 % / 63.5 %wt.

5.2.4 Viscosity and wetting properties of the secondary liquid

In order to vary the viscosity of the secondary liquid (or binder) water/glycerol mixtures were used. Glycerol and water are readily miscible and their mixtures cover a wide range of viscosity values (Figure 5-3). In addition, glycerol is highly hygroscopic; thus water/glycerol mixtures can be created by changing the relative humidity, and through the glycerol sorption isotherm (Figure 5-3) one can calculate the volume fractions of the mixture and the correspondent viscosity. This feature will be especially interesting for the comparison of the results from a macroscopic level (which is shown in the present chapter) with the results from a microscale level (discussed later in Section 7.3.1).

In Table 5-3, the glycerol/water mixtures used along with their densities and apparent viscosity values at 25°C are listed. Water activity and apparent viscosity were measured using the Rotronic cells (HygroLab C1 with HC2 station probe, Rotronic AG, Bassersdorf, Switzerland) and the Kinexus rotational rheometer (Malvern Instruments, United Kingdom), respectively. The Rotronic cells measure the %RH in the headspace above the sample, and once this reaches equilibrium, the a_w for the sample at the given temperature is known. Viscosity measurements were carried out using the smooth cone-plate geometries CP 1°/50mm and the CP4°/40mm. All the water/glycerol mixtures showed a Newtonian behaviour. In addition, the values obtained for viscosity and water activity obtained experimentally were very close to the ones mentioned in literature (Cheng 2008).

Water activity a _w (or relative humidity)	Volume fraction of water	Mass fraction of water	Density [kg/m³]	Apparent viscosity (measured) [mPa·s]	Apparent viscosity (Cheng 2008)
0 (anhydrous glycerol)	0	0	1261	837.7 ± 6.9	905.7
0.30	0.131	0.106	1233	136.4 ± 3.6	143.1
0.60	0.325	0.275	1188	22.6 ± 0.5	22.2
0.90	0.726	0.677	1082	2.29 ± 0.03	2.31
1.00 (pure water)	1	1	997	0.94 ± 0.05	0.89

Table 5-3. Water-glycerol mixtures used and their respective water activity, volume and mass frac-tions of water, density and apparent viscosity at 25 °C



Figure 5-3. Diagram for water-glycerol mixtures showing the sorption isotherm (water activity vs. mass fraction of water in glycerol), viscosity and density dependence on the solution mass concentration at 25 °C [Data for the sorption isotherm of glycerol was provided by Nestlé Research Centre, Lausanne, Switzerland. The data for viscosity and density was adapted from Cheng (2008)].

Water/glycerol mixtures also have different wetting properties. As shown in Table 4-2 (Section 4.2), the values for the interfacial tension of water/oil and glycerol/oil are 26 and 17 mN/m, respectively; while the values for the contact angles formed by droplets of water and glycerol with a glass surface in oil are 39° and 64°, respectively. Therefore, the interfacial tension and contact angles for the water/glycerol mixtures will be between the extremes mentioned.

5.2.5 Surfactant addition

In order to evaluate the effect of the addition of a surfactant, sunflower lecithin (described in Section 3.1.3) was utilised. As mentioned earlier, lecithin is a surfactant composed of phospholipids (PL) which adsorb on the interface between the surface of the particles and the oil continuous phase. The lecithin was added to the oil phase prior to the suspensions preparation. It was dispersed into the oil by magnetic stirring at 600 rpm and 60 °C, as lecithin is very viscous at lower temperatures and difficult to disperse. Two concentrations of lecithin were used: 0.1 % and 0.5 % wt of the oil. Those concentrations of fluid lecithin resulted in a concentration of PL of 0.05 % wt and 0.25 % wt, respectively (based on Table 3-1). Since the PL are the surface-active molecules, the results will be expressed as a function of the concentration of PL.

The water-oil interfacial tension resulting of the lecithin addition can be seen in Table 5-4. A full description of the interfacial tension measurements and the effect of adding lecithin are shown in Appendix I. From Table 5-4 it is possible to notice that the addition of PL results in a strong decrease in interfacial tension at 0.05 %wt followed by an apparent plateau where the interfacial tension no longer decreases with further addition of emulsifier. This is most probably because the CMC (critical micellization concentration) is reached. Manjula, Kobayashi et al. (2011) reported values of CMC for phosphatidylcholine (PC) in high oleic sunflower oil and for mixed lecithin PL in soybean oil of 0.044 %wt and 0.085 %wt, respectively. They have attributed the difference in CMC values for those two systems to the degree of hydration of the PL. Lecithin is a mixture of different PL (including PC; Table 3-1) and PC has a relatively high degree of hydrations hence the higher CMC for PC in soybean oil.

Table 5-4. Interfacial/Surface tensions (mN/m) for different systems						
	Aim					
	$0 \$ wt PL	0.05~% wt~PL	$0.25~\%{ m wt~PL}$	AIľ		
Water	26.4 ± 0.1	11.3 ± 0.1^1	10.9 ± 1.0^1	72.0 ± 0.2		
Saturated sugar solution	25.1 ± 0.2	13.8 ± 0.1^1	13.0 ± 1.0^1	78.3 ± 0.9		
Glycerol	17.7 ± 0.5^2	11.0^{2}	11.0^{3}	64.7 ± 0.2		
Air	32.2 ± 0.3	32.2 ± 0.4				

¹taken as the average of the last five values for the interfacial tension before the rupture of the pendant drop

 2 values measured at the Nestlé Research Centre in Lausanne with Wilhelmy plate technique (Lazghab et al., 2005). The value for the interfacial tension between glycerol and HOSO with 0.05% wt PL is the value before the lamella rupture.

 3 since the interfacial tension values of the other two liquids (water & saturated sugar solution) with oil containing 0.5 %wt lecithin is practically the same as with the oil with 0.05 %wt PL, for practical reasons, the interfacial tension for glycerol/oil 0.25 %wt PL was considered to be 11 mN/m.

The effect of lecithin addition on the viscosity of the oil continuous phase was also measured using a rotational rheometer (Kinexus, Malvern Instruments, United Kingdom) and a cone-and-plate geometry (4°/40 mm) as shown in Figure 5-4. Purified oil has a Newtonian behaviour. The addition of 0.05 %wt PL has little effect on the viscosity at lower shear rate values. The apparent viscosity for the purified oil and the oil with 0.05 %wt PL can be approximated to 64.8 ± 0.6 mPa·s. A higher concentration of PL (0.25 %wt) gives a shear thinning characteristic to the viscosity curve at low shear rates and a Newtonian behaviour with a viscosity at high shear rates of 65 mPa·s; the latter being the same as in the oil without or with 0.05 %wt PL. The higher viscosity at low shear rates can be attributed to the CMC as aforementioned, and the decrease in viscosity with increase in shear rate is probably related to the breakup of such micelles and/or aggregates (Johansson 1995, Walstra and Vliet 2008).



Figure 5-4. Apparent viscosity curves for sunflower oil with different amount of lecithin PL

5.3 Results and Discussion

5.3.1 Effect of particle size

Figure 5-5 shows the viscosity curves for glass suspensions in oil prepared with glass particles of different size distributions. When no secondary liquid is present (Vr=0), the viscosity of the glass suspensions with both particle size fractions is very similar and deviates slightly from Newtonian behaviour. This indicates that the flow of glass suspensions when no liquid is present is dominated by the interaction of the particles with the oil continuous phase and that interparticle interactions are quite weak. This observation is consistent with the findings from Chen, Øye et al. (2005) who found that for glass particles of similar size range (mean of 40 to 90 µm) dispersed in mineral oil, the viscosity was independent of the particle size. In addition, it is interesting to point out that at higher shear rates, a slight shear thickening behaviour is observed. In concentrated suspensions, such as the ones presented here, the shear rheology is affected differently at low and high shear rates. When a shear flow is applied to the suspension at rest, an initial localized horizontal flow of groups of particles with fewer particle collisions result in a slight shear thinning behaviour. Once the shear rate is high enough, local transient self-organized clusters are formed which result in a shear thickening effect (Mewis and Wagner 2012).

When glycerol is added as the secondary immiscible liquid the characteristic increase in viscosity is observed for the suspensions with both particle size fractions (Figure 5-5).

However, a slightly more pronounced increase can be noticed for the smaller particle size fraction (25-45 μ m); showing that the network is stronger for smaller particles than larger ones. Smaller particles result in a larger surface area available for the formation of liquid bridges hence the stronger network. This is in agreement with the findings from McCulfor, Himes et al. (2011) and Koos, Johannsmeier et al. (2012).



Figure 5-5. Apparent viscosity curves for glass suspensions (40 %vol) of different size distributions (25-45 μ m/D_{50,3}= 35 μ m and 75-100 μ m/D_{50,3}= 78 μ m) in oil without and with added glycerol (Vr=0.02).

The behaviour for sugar suspensions prepared with particles of different size distributions is slightly more complicated than for glass, as shown in Figure 5-6. Firstly, if one compares the sugar suspensions with no added secondary liquid (glycerol), a shear thinning behaviour is observed for both size fractions while a higher viscosity is observed for the sugar suspensions made with the smaller particles (25-45 μ m). The sugar particles have a very irregular particle shape (Figure 4-1(b); Section 4.2). The irregular shape together with the fact that the suspensions are highly concentrated (40 %vol) gives rise to a shear thinning behaviour which is also dependent on the particle size (Macosko 1994). Similar behaviour of increasing viscosity for smaller particle sizes was observed in chocolate by Afoakwa, Paterson et al. (2008).

When glycerol is added, a viscosity increase is registered for both particle sizes at low shear rates (Figure 5-6). However, the relative viscosity increase is more pronounced for the larger particle size, nevertheless the viscosity of the suspension with smaller particle size is still higher. If one analyses the particle size distributions for the two size classes given in Figure 5-1, the distribution for the 25-45 μ m fraction is monomodal while the PSD for the 75-100 μ m class is bimodal, resulting in a considerable number of smaller particles. The presence of those smaller particles becomes especially important once the secondary liquid is added and interparticle forces due to the formation of liquid bridges dominate the flow behaviour.



Figure 5-6. Apparent viscosity curves for sugar suspensions (40 %vol) of different size distributions (25-45 μ m / $D_{50,3}$ = 17 μ m and 75-100 μ m / $D_{50,3}$ = 92 μ m) in oil without and with added glycerol (Vr=0.02).

5.3.2 Effect of particle shape and density

In Section 4.3.3, the rheological characterization of suspensions of hydrophilic particles in sunflower oil with the addition of three different secondary liquids was presented. A three-orders of magnitude increase in viscosity was observed for glass suspensions upon the addition of a secondary liquid (water, saturated sugar solution and glycerol; Figure 4-12, Figure 4-14 and Figure 4-16, respectively); while a two-orders of magnitude increase was observed for sugar suspensions (Figure 4-11, Figure 4-13 and Figure 4-15). The question was raised of whether the steeper increase for glass suspensions was observed due to sedimentation of heavy glass particles, resulting in an unrealistic low viscosity curve for the suspensions without secondary liquid. Therefore, suspensions with hollow glass particles were prepared. The effective density of the hollow glass particles is 1.1 g/cm³ while the effective (and true) density of the solid particles is 2.5 g/cm³ (Table 5-2). Since the densities of hollow particles and oil (density of oil 0.9 g/cm³) are much closer, sedimentation is significantly reduced. This can be supported by Stokes law, where the speed of sedimentation can be estimated based on the gravitational force (F_{grav}) and the drag force (F_{drag}) as given in Equation 5-1 and Equation 5-2, respectively (Coulson, Richardson et al. 1991):

$$F_{grav} = (\rho_p - \rho)gV_p$$
 Equation 5-1

$$F_{drag} = \frac{C_D A_p \rho v_{sed}^2}{2}$$
 Equation 5-2

Where ρ_p is the density of the particle; ρ is the density of the liquid continuous phase (in this case, HOSO); g is the gravitational acceleration (9.81 m/s²); V_p is the volume of the particle; C_D is the drag coefficient; A_p is the projected area of the particle and v_{sed} is the settling or sedimentation speed.

The speed of sedimentation can be determined once the drag force becomes equal to the net gravitational force, as shown in Equation 5-3.

$$v_{sed} = \sqrt{\frac{2(\rho_p - \rho)gV_p}{C_D A_p \rho}}$$
Equation 5-3

Considering the sedimentation is more significant for the suspension in a stationery state (or slow motion flows) since upon shearing, centrifugal forces may increase the particle velocity significantly, the simplification derived by Stokes for creeping flow can be used. With $C_D = \frac{24}{Re}$ where Re corresponds to the Reynolds' number ($Re = \frac{\rho D_p v_{sed}}{\eta}$), Equation 5-3 can be re-written as shown in Equation 5-4 (Coulson, Richardson et al. 1991).

$$v_{sed} = \frac{(\rho_p - \rho)g D_p^2}{18 \eta}$$
Equation 5-4

Where D_p is the diameter of the particle and η is the viscosity of the liquid continuous phase.

From Table 4-2 and Table 5-2, the sedimentation speed can be calculated for dense glass particles (ρ_p = 2500 kg/m³; $D_p \approx D_{50,3}$ = 41 µm) and also for the hollow glass particles (ρ_p = 1100 kg/m³; $D_p \approx D_{50,3}$ = 17 µm) in HOSO (ρ = 919 kg/m³ ; η = 65 × 10⁻³ Pa.s) and is equal to 22 µm/s and 0.4 µm/s. This difference in sedimentation speeds justify the use of hollow beads to decrease the effect of the settling of the particles. It is important to point out that this sedimentation speeds correspond to the free falling of a single particle in the liquid. In a concentrated suspension, such as the ones used in this project, frictional forces and interactions between particles alter the flow pattern significantly and hinder settling. The

increase in the concentration of particles results in a steadily decrease of their sedimentation velocity (Coulson, Richardson et al. 1991).

In Figure 5-7, the apparent viscosity curves of the oil-based suspensions are presented. The same three-orders of magnitude increase was observed for both suspensions of hollow glass particles and solid glass particles in oil upon the addition of glycerol. Therefore, it can be concluded that the sedimentation of particles is not the reason for the difference in viscosity between the sugar and glass suspensions, as previously hypothesized. It is important to note that the hollow glass particles were slightly smaller than the dense glass particles (Table 5-2; $D_{50,3,hollow glass} \approx 17 \ \mu m$; $D_{50,3,dense glass} \approx 41 \ \mu m$); which justifies the slightly higher viscosity values for the hollow particles, both with and without added glycerol.



Figure 5-7. Apparent viscosity curves for suspensions of glass particles (40 %vol) with different shapes and densities (Table 5-2) in oil without and with glycerol addition (Vr=0.02).

From Figure 5-7, one can also observe that the particle shape also has an effect on the flow of suspensions in oil. When no secondary liquid is present, the glass spheres (solid and hollow) show a flow pattern which deviates very slightly from Newtonian behaviour, as previously explained (Section 5.3.1). On the other hand, the suspension of glass grains has a clear shear thinning characteristic and also a higher viscosity. The irregular nature of the glass grain particles contributes to the shear thinning rheology because of the motion

and rotation of particles (to align with the flow) which are strongly influenced by the shape (Macosko 1994).

Once the secondary liquid (glycerol) is added, a very strong increase in viscosity (three orders of magnitude for low shear rates) and shear-thinning behaviour is observed for all samples. The viscosity for the glass grains is once again higher than the viscosity for the glass spheres. The irregular shape promotes the formation of more bridges and a more robust network. In addition, glass grains have a wider PSD and larger sizes than the hollow glass spheres (Figure 5-2). In spite of this, the glass grains still show the strongest increase in viscosity.

5.3.3 Effect of particle concentration

In suspension rheology, the volume fraction of particles is of utmost importance since it not only results in a simple increase in the magnitude of the viscosity but also can generate divergences from a Newtonian behaviour (Macosko 1994).

In Figure 5-8, the apparent viscosity curves for glass suspensions in oil with three different volume fractions are shown. When no secondary liquid (glycerol) is present, the three suspensions show a pseudo-Newtonian behaviour. The suspension with 30 %vol concentration shows the closest to a Newtonian pattern. When the volume fraction is increased, the resulting viscosity magnitude is higher and so are the deviations from the Newtonian behaviour. As previously discussed, the highly concentrated suspensions of spherical particles show a slight shear-thinning behaviour for low shear rates related with the particles starting to flow from an original static equilibrium state, and creating lines of flow. For higher shear stresses, the high packing of particles and formation of clusters result in a slight shear-thickening effect. When glycerol is added to the suspension, the characteristic increase in viscosity and strong shear-thinning pattern emerges for the suspensions at all particle concentrations. For 40 and 50 %vol glass suspensions, the relative increase in viscosity when glycerol is added is the same. Curiously, the suspension with 30 %vol glass particles showed the same increase in viscosity at low shear rates. However, the drop in viscosity at higher shear rates is much sharper. A hypothesis for this behaviour is that, at lower concentration, the distance between the particles is larger; thus, for the same secondary liquid amount, fewer bridges are formed. In addition, it could be that, due to the lower particle concentration, localized aggregation of particles instead of the formation of a continuous network throughout the entire sample could generate the flow behaviour observed for the 30 %vol suspensions - at very low shear rates, the localized aggregates would prevent the flow, giving rise to high viscosity values, but as soon as the

10000 30% (Vr=0) 40% (Vr=0) 1000 50% (Vr=0) 30% (Vr=0.02) Apparent viscosity [Pa.s] 40% (Vr=0.02) 50% (Vr=0.02) 100 10 1 0.1 0.01 0.01 0.1 1 10 100 1000 Shear rate [s⁻¹]

shear rate is slightly increased the movement of the localized aggregates past each other would result in the sudden break of the structure as well as a sharp decrease in viscosity.

Figure 5-8. Apparent viscosity curves for glass suspensions in oil at different volume particle concentrations (30%, 40%, 50%) without (Vr=0) and with glycerol addition (Vr=0.02). The non-sieved spherical solid glass particles were used ($D_{50,3}$ = 41 μ m).

In Figure 5-9, a similar evaluation of the effect of particle volume fraction in suspensions of sugar in oil with and without the addition of secondary liquid can be made. For the suspensions with no added glycerol, a shear-thinning profile can be observed at concentrations of 30 and 40 %vol. For the 50 %vol sugar suspension without glycerol, a shear thinning outline is observed for lower shear rates, followed by a shear thickening (around 10 s^{-1}) and then a drop in viscosity. At such high concentration, the sugar suspension had a solid-like behaviour (even without secondary liquid addition). This can be related with the packing of particle reaching a maximum value, and consequently ceasing the flow.

Once glycerol is added to the suspensions, an increase in viscosity is observed especially at lower shear rates. For the suspensions with 30 and 40 %vol particles, shear thinning followed by a shear thickening at higher shear rates is observed. This could be explained by relating these observations to the formation of the strong network of liquid bridges. At low shear rates the network, which was in an initial equilibrium, is disturbed and breakage of some liquid bridges results in the shear thinning behaviour. Once higher shear is applied, portions of the network or flocs that are strongly bound hinder the flow, generating a shear thickening effect. In addition, the 30 and 40 %vol sugar suspensions showed the same relative increase from Vr=0 to Vr=0.02. For the 50% sugar suspension with added glycerol, the suspension was so concentrated that it broke apart into pieces during the experiments and part of it was expelled from the area between the serrated plates. That is the reason a decrease in viscosity to values below than the suspensions with no added glycerol was observed.



Figure 5-9. Apparent viscosity curves for sugar suspensions in oil at different volume particle concentrations (30%, 40%, 50%) without (Vr=0) and with glycerol addition (Vr=0.02). The non-sieved icing sugar particles were used ($D_{50,3}$ = 29 µm).

5.3.4 Effect of the viscosity and wetting properties of the binder

Mixtures of water and glycerol were used as the secondary liquid in order to evaluate the effects of viscosity and also wetting properties on the flow behaviour on suspensions of glass (Figure 5-10) and sugar (Figure 5-11) in oil. The properties of the mixtures of water and glycerol used are given in Table 5-3 (Section 5.2.4).

From Figure 5-10 and Figure 5-11, the superposition of the curves for the different water/glycerol mixtures binders suggests that their impact is not extremely substantial. It is interesting to notice, however, that for both glass and sugar suspensions with added pure glycerol (or glycerol with very small amounts of water – 10.6% and 27.5%), the viscosity at low shear rates is lower than for the suspensions with added water (or glycerol with high amounts of water – 67.7%). These phenomena can be easily explained based on interparticle forces driven by the liquid bridges in the network. At low shear rates, the capillary forces due to interfacial tension and Laplace pressure are dominant. Water bridges have higher interfacial tension and also lower values of contact angles formed between the two liquids (secondary liquid/continuous phase) on the particle surfaces (Table 4-2). However, at higher shear rates, the stresses applied on the network and the resultant speeds of separation of particles connected by liquid bridges become considerable. Consequently, dynamic effects due to the high viscosity of glycerol bridges come into play and result in an increase in viscosity.



Figure 5-10. Effect of water/glycerol mixtures (Vr=0.02) on the apparent viscosity of glass in oil suspensions (40 %vol). The non-sieved spherical solid glass particles were used ($D_{50,3}$ = 41 µm). The correspondent relative humidity (or water activity) and viscosity for each water-glycerol mixtures is as given in Table 5-3.



Figure 5-11. Effect of water/glycerol mixtures (Vr=0.02) on the apparent viscosity of sugar in oil suspensions (40 %vol). The non-sieved icing sugar particles were used ($D_{50,3}$ = 29 µm). The correspondent relative humidity (or water activity) and viscosity for each water-glycerol mixtures is as given in Table 5-3.

The prevailing contribution of interfacial tension can also be detected by analysing the yield stress. The Herschel-Bulkley yield stress (σ_y^{HB}) can be extrapolated from the shear stress (or analogously, viscosity) curves by fitting in the model described in Section 2.5.1.2. The fitting of the curves from Figure 5-10 and Figure 5-11 with the Herschel-Bulkley model is given in Figure 5-12 and Figure 5-13, respectively. The fitting of the data for the glass-in-oil suspensions with the Herschel-Bulkley model is satisfactory. For the sugar suspensions, the fit of the data is adequate for the suspensions with 67.7 %wt water and pure water; however, some deviations are observed for the other samples. This is could be related with the breaking and reforming of liquid bridges. During the viscometry measurements, due to the fact that the particles are very close to each other, liquid bridges are constantly breaking and reforming. At low shear rates, the more viscous bridges break up (glycerol-rich binders) requires less stress than at higher shear rates, where dynamic effects are more significant.



Figure 5-12. Fitting of Herschel-Bulkley model toglass-in-oil suspensions with added water/glycerol mixtures (as data in Figure 5-10). The raw data is shown with the symbols while the model fit is given as the lines.



Figure 5-13. Fitting of Herschel-Bulkley model tosugar-in-oil suspensions with added water/glycerol mixtures (as data in Figure 5-11). The raw data is shown with the symbols while the model fit is given as the lines.

The yield stress of sugar and glass suspensions in oil containing secondary liquid (Vr=0.02) as a function of the amount of water in the secondary liquid is plotted in Figure 5-14. The yield stress is the minimum stress required to start to break the structure in the sample, or in other words, the stress at which the suspension begins to flow. At this point of minimum stress, the static part of the forces related to liquid bridges will be dominant. A significant increase in the yield stress as a function of the amount of water in the composition of the secondary liquid reflects this dominant effect from the static capillary forces due to the better wetting properties of water (if compared to glycerol). These results are in agreement with the findings from Hoffmann, Koos et al. (2014), who documented higher yield stresses in starch suspensions in oil with secondary liquids showing better wetting properties. Due to the shape of the viscosity curves for the sugar-in-oil suspensions with added secondary liquid (Figure 5-11), there were some deviations on fitting of the Herschel-Bulkley model (correlation factors \mathbb{R}^2 of about 0.80); however, the general trend in yield stress increase can still be considered.



Figure 5-14. Herschel-Bulkley yield stress (σ_y^{HB}) of sugar and glass suspensions in oil as a function of the amount of water in the secondary liquid. Particle volume fraction was ϕ = 0.4 and the amount of secondary liquid was Vr=0.02.

5.3.5 Effect of the addition of a surfactant

The addition of a surfactant, in this case, lecithin, to the oil continuous-phase reduces the interfacial tension between the oil and the hydrophilic secondary liquid (Table 5-4). The effect of this surfactant addition is investigated by evaluating the flow behaviour of sugar

and glass suspensions in oil containing different concentrations of lecithin phospholipids (0, 0.05 and 0.25 %wt PL) as shown in Figure 5-15 and Figure 5-16. The influence of the surfactant on the network of liquid bridges is also examined for glycerol as a secondary liquid at a concentration Vr=0.02.

Using the data from the particle size distributions, it was possible to calculate the specific surface area (SSA) for the glass and sugar particles using their respective densities. The calculations consider the particles as spheres (so does the particle size measurement method by laser diffraction in general). This assumption could result in an over- or underestimation of the SSA for the irregular sugar particles. The average SSA for glass and sugar are respectively 0.0577 and 0.2039 m²/g. Those values are much lower than the specific BET surface measured by nitrogen adsorption by Arnold, Schuldt et al. (2013), where values of 0.79 and 0.68 m²/g for glass particles and icing sugar (of smaller particle size) were reported.

The surface excess monolayer (Γ_m) for lecithin can be calculated according to:

$$\Gamma_{\rm m} = \frac{A_{\rm c} n_h N_{\rm A}}{M_{\rm w}}$$
Equation 5-5

Where A_c is the surface area per hydrocarbon chain which is assumed to be 35 Å², n is the number of hydrocarbon chains per molecule which is two for lecithin, N_A is the Avogadro's number (6.022 × 10²³ molecules/mol) and M_W is the molecular weight of lecithin which is assumed to be 760 g/mol (Johansson and Bergenståhl 1992, Ziegler, Garbolino et al. 2003). This calculation results in a Γ_m of 1.8 mg m⁻², which is consistent with the experimental work done by Johansson and Bergenståhl (1992), Hugelshofer, Windhab et al. (2000) and Ziegler, Garbolino et al. (2003).

If one uses the SSA for glass and sugar particles as given by the particle size distributions, the concentration of PL which would be correspondent to the monolayer (assuming all available PL are adsorbed at the monolayer) would be 0.04 and 0.02 %wt for sugar and glass, respectively. Those concentrations are smaller than the ones reported by Johansson and Bergenståhl (1992), Hugelshofer, Windhab et al. (2000) and Arnold, Schuldt et al. (2013) probably because the SSA calculation through the particle size distributions is being underestimated.

By analysing Figure 5-15, the addition of lecithin does not promote significant differences on the viscosity of the glass suspensions without added glycerol. However, for the suspensions with added glycerol, the presence of lecithin affects the viscosity significantly. When a secondary liquid is present, the surfactant can be adsorbed on the surface of the solid particles, present at the interface of the two liquids or available in the continuous phase as non-adsorbed molecules forming micelles (above CMC concentration). The reduction of the glycerol-oil interfacial tension results in a lower surface tension force of the liquid bridge (as per Equation 2-14 in Section 2.3.5.1 and discussion in more detail in Section 7.3.2). Also, the lecithin adsorption on the interface of the two liquids enables the creation of stable droplets of glycerol which would hinder the formation of liquid bridges. Those factors together would then result in a weaker network and lower viscosity.



Figure 5-15. Effect of the addition of lecithin (given in terms of phospholipids – PL – concentration) to the glass suspensions in oil (40 %vol) without (Vr=0) and with (Vr=0.02) the addition of glycerol. The non-sieved spherical solid glass particles were used ($D_{50.3}$ = 41 μ m).

The highest viscosity increase with glycerol addition is recorded for the suspension with no lecithin, followed by the 0.25 %wt PL, and with the 0.05 %wt PL showing the lowest viscosity for the samples with added glycerol. The greater viscosity decrease for 0.05 %wt PL containing suspensions followed by an increase with 0.25 %wt PL can be related with the critical micelle concentration (CMC) and with the fact that the concentration of the emulsifier is above the monolayer excess. Johansson and Bergenståhl (1992), Hugelshofer, Windhab et al. (2000) and Arnold, Schuldt et al. (2013) have determined the monolayer coverage to be at concentration values of 0.10%-0.15% lecithin PL for suspensions of particles in oil phase (without secondary liquid addition). In addition, the higher viscosity observed for the glass suspensions with 0.25% PL can be related with the higher viscosity of the continuous phase when non-adsorbed molecules of surfactant are present. The high concentration of PL (0.25 %wt) resulted in a shear thinning profile and an increase in the viscosity of the continuous phase, as can be seen in Figure 5-4. From Figure 5-16, one can observe that, contrary to the results from the glass suspension experiments, the viscosity of the sugar suspensions with added lecithin decrease with the increase in the concentration of PL for both the suspensions with and without added glycerol. The sugar particles not only have an irregular shape but also a wider particle size distribution with more fine particles than the glass particles. This results in a larger surface area for the PL molecules to adsorb as shown in the calculations above for the excess monolayer coverage for sugar particles. Consequently, this results in a reduction of the viscosity even for higher concentrations of PL.

In addition, by comparing Figure 5-15 and Figure 5-16, one can notice that the reduction in viscosity for the glass suspensions with added glycerol is much stronger than for the sugar suspensions with glycerol upon the addition of surfactant. This gives an indication that the addition of an emulsifier has a stronger impact in the network of liquid bridges formed by glass particles.



Figure 5-16. Effect of the addition of lecithin (given as the concentration of PL) to the apparent viscosity of sugar suspensions in oil (40 %vol) without (Vr=0) and with (Vr=0.02) glycerol addition. The non-sieved icing sugar particles were used ($D_{50,3}$ = 29 μ m).

5.4 Conclusions

In this chapter, the effect of material parameters on the network formation was evaluated by analysing the flow behaviour of sugar and glass suspensions with and without the addition of a secondary liquid. The influence of particle size, shape, density, concentration as well as secondary liquid viscosity and wetting properties were evaluated.

The network formed due to the presence of a secondary liquid (glycerol) is influenced by the size of the particles – smaller particles result in a larger surface area available for the formation of liquid bridges hence the stronger network. The density of the particles did not interfere in the rheological results as shown by the comparison in flow behaviour of hollow and solid glass particles suspensions. The particle shape also has an effect on the flow of suspensions and the network formation. The irregular glass grains have shown the strongest increase in viscosity despite having a larger particle size distribution. The irregular shape likely promotes the formation of more bridges (higher surface area-tovolume ratio than spherical particles) and a more robust network.

The particle volume fraction (or concentration) has a general impact on the flow behaviour of suspensions without and with secondary liquid – the higher the concentration of particles, the larger is the apparent viscosity. For glass suspensions of 40 and 50 % vol and sugar suspensions of 30 and 40 %vol the relative increase in viscosity from Vr=0 (no glycerol) to Vr=0.02 was the same, demonstrating that the particle concentration did not promote a further influence and that the relative increase was due to the formation of liquid bridges.

Water/glycerol mixtures were used as a secondary liquid in order to evaluate the influence of viscosity and wetting properties of the binder on the network formation. At low shear rates, suspensions with water-rich binder had a higher viscosity while, at high shear rates, the viscosity of suspensions with glycerol-rich binders showed an increase (to either the same value or very slightly higher than for suspensions with water-rich binders). This observation was explained in terms of the available forces due to the liquid bridges forming the network. At low shear rates, the contribution of the static capillary forces due to bridges formed by high interfacial tension liquids (water-rich binders) is dominant hence the higher viscosity. At higher shear rates, dynamic effects due to the high viscosity of glycerol bridges come into play and result in an increase in viscosity.

Finally, another way to change the wetting properties of the system was by adding a surfactant, in this case lecithin. Generally, the addition of lecithin resulted in a decrease in viscosity for sugar and glass suspensions. The reduction of the glycerol-oil interfacial tension results in a lower capillary force of the liquid bridge (as per Equation 2-14 in Section 2.3.5.1 and discussion in more detail in Section 7.3.2). In addition, lecithin can adsorb on

the interface of the two liquids, generating stable droplets of glycerol which could hinder the formation of liquid bridges. Those factors together would then result in a weaker network and lower viscosity. Finally, the increase in viscosity for the glass suspension with high concentration of lecithin (0.25 %wt PL) and added glycerol was discussed and related to the non-adsorbed molecules of surfactant forming micelles in the continuous phase, due to the fact that this concentration of lecithin was above the monolayer excess and CMC.
Chapter 6

Microscale study of particle agglomeration in oil-based suspensions

Information about the agglomeration process and consequent network formation in fatbased suspensions can be derived from the analysis of the individual strength of liquid bridges holding two particles or, analogously, a particle and a flat surface; hence the importance of directly measuring the interparticle forces. In this chapter, an atomic force microscope (AFM) is used to measure adhesion forces between a particle and a surface in a liquid hydrophobic continuous phase (oil; HOSO) and the formation of liquid bridges once a secondary immiscible liquid is added is discussed.

6.1 Introduction

The interaction forces between particles play an important role in determining the stability and flow behaviour in suspensions and other dispersed systems. For example, if attractive forces dominate in the system, aggregation of particles may occur, which could lead to sedimentation or localized phase separation (Walstra and Vliet 2008).

As mentioned in Section 2.6.1, one technique that has enabled the direct and experimental measurement of forces between micron-sized particles is atomic force microscopy (AFM) (Binnig, Quate et al. 1986). AFM has been used to measure normal capillary forces (Rabinovich, Esayanur et al. 2002, Rabinovich, Esayanur et al. 2005, Butt and Kappl 2009), and also the effect of relative humidity on them in air as a continuous phase (Jones, Pollock et al. 2002, Farshchi-Tabrizia, Kappl et al. 2008). It has also been employed to study forces in liquids (Weisenhorn, Maivald et al. 1992), forces between a particle and a bubble (Preuss and Butt 1999, Assemi, Nguyen et al. 2008, Padar 2009) and adhesion of particles to thin liquid films (Rao 2007, Padar 2009, Bowen, Cheneler et al. 2011). However, the direct and experimental measurement of forces due to the presence of liquid bridges by different immiscible binding liquids inside a viscous non-polar continuous phase such as vegetable oil has not been studied.

An AFM can be used as a force spectroscopy tool by measuring the deflection of the cantilever as it touches the surface, as described in Section 2.6.1. The adhesion force is readily measured when the tip retracts from the surface. An AFM integrated with an inverted optical microscope is an important requisite because it enables the identification of the small particles (order of micrometres), their attachment to the cantilevers, and also the precise definition of where the cantilever should repose.

The present chapter shows two methods to generate liquid bridges in a system of immiscible liquids and to measure them using an AFM. One approach is to create a water liquid bridge by increasing the relative humidity in the oil environment. The general effect of relative humidity increase in an oil environment is also discussed and compared to air as the continuous phase. The second approach consists of creating a dispersion of small droplets of secondary liquid into the continuous phase. Consequently, a liquid bridge could be created by approaching the colloidal probe particle on top of the droplet resting on the lower flat surface. A spherical particle-flat surface system is used as a model for interparticles interaction due to its controlled geometry, experimental advantage in the creation of liquid bridges and also because it can be easily generalized to interactions between two spherical particles (Jones, Pollock et al. 2002, Butt and Kappl 2009).

The effect of two binding liquids with different properties (viscosity, interfacial tension and wetting characteristics) on the adhesion between a particle and a flat surface was then examined using colloidal probe AFM and discussed in terms of the forces acting between them.

6.2 Theory

As explained in Section 2.3.5, when an immiscible liquid is added to an oil-continuous system, a liquid meniscus can form between hydrophilic particles (or hydrophilic particle and surface) when they approach one another and the secondary liquid preferentially wets the particles. If one considers a particle and a flat surface connected by a liquid bridge inside oil media, when these particles are separated, two forces contribute to the adhesion: a static capillary (or meniscus) force and a dynamic viscous force. The static capillary attractive force (F_{cap}) is a result of both the interfacial tension (γ) of the liquid around the contact line pulling the particle and surface together and the Laplace pressure (ΔP), as shown in Section 2.3.5.1.

By considering the 'boundary method', the capillary force can be calculated at the contact line as explained is Section 2.3.5.1 and given in :

$$F_{cap} = F_{cap,boundary} = \pi \gamma R \sin \beta \left[2\sin(\theta + \beta) + R \sin \beta \left(\frac{1}{r_1} - \frac{1}{r_2}\right) \right]$$
Equation 6-1

where the contact angles (θ) of water on the glass particle and glass surface are considered equivalent, β is the half-filling angle, R is the radius of the particle, r_1 and r_2 are the radii of the curvature of the bridge and D is the separation distance between the particle and surface (as shown in Figure 6-1).

In oil, the volume of the bridge (V_{bridge}) is constant and the radii of curvature are directly related to the volume, which leads to the simplification as shown in Equation 6-2 (Butt and Kappl 2010).

$$F_{cap} = 4 \pi \gamma R \cos \theta \left(1 - \frac{D}{\sqrt{D^2 + \frac{V_{bridge}}{\pi R}}} \right)$$
Equation 6-2

Figure 6-1. Schematic diagram of a liquid bridge between a spherical particle and a flat surface inside oil media and the toroidal approximation which considers the bridge as arcs of a circle (adapted from (Butt and Kappl 2009, Butt and Kappl 2010)).

If instead of considering a bridge with a constant volume, one considers a constant vapour pressure (as when the relative humidity is controlled), the capillary force can be simplified as shown in Equation 6-3 (Butt and Kappl 2010):

$$F_{cap,RH} = 2 \pi \gamma R \left(2 \cos \theta - \frac{D}{r_1} \right)$$
 Equation 6-3

Where r_1 , the curvature radius of the liquid bridge (toroidal approximation, Figure 6-1) can be given by Kelvin's equation (Equation 2-16; Section 2.3.5.1), as shown in Equation 6-4:



$$r_1 = \frac{\lambda_K}{\ln(P/P_0)}$$
 Equation 6-4

Where P is the actual vapour pressure of the curved bridge, P_0 is the saturation vapour pressure over a planar liquid surface and λ_K corresponds to the Kelvin length, which provides an indication of the length scale that the capillary condensation occurs and is given by Equation 6-5:

$$\lambda_K = \frac{Vm}{R_g T}$$
Equation 6-5

where R_g is the molar gas constant (8.314 J mol⁻¹ K⁻¹), γ is the interfacial tension and V_m is the molar volume of the liquid (forming the bridge).

In dynamic situations, a viscous component can contribute to the adhesion force of a liquid bridge. By integrating the Reynolds lubricating equation (Equation 2-19; Section 2.3.5.2), the pressure distribution in the gap between the sphere and surface and substituting in Equation 2-18, one obtains:

$$F_{vis} = 2 \pi \int_0^\infty \left(\frac{3 \eta R}{D^2} \frac{\partial D}{\partial t}\right) \mathbf{r} \, \mathrm{d}\mathbf{r}$$
 Equation 6-6

where η is the dynamic viscosity of the liquid and r is the radial coordinate in cylindrical coordinates and r is a function of D and R (Butt and Kappl 2010).

Considering the sphere moves with constant speed v_s (probe retraction speed), one can approximate Equation 6-6 with $\frac{\partial D}{\partial t} = v_s$:

$$F_{vis} = 6 \pi \eta \, v_s \, \frac{R^2}{D}$$
 Equation 6-7

Upon separation of surfaces connected by a liquid bridge, viscous forces act to prevent particle motion and are, therefore, attractive in nature. The equation for the viscous force (Equation 6-7) considers the confined liquid between sphere and flat surface as infinite. In the case of a liquid bridge with a finite volume, Matthewson (1988) defined a correction factor for Equation 6-7:

$$F_{vis} = 6 \pi \eta v_s \frac{R^2}{D} \left[1 - \frac{D}{H(r_w)} \right]^2$$
Equation 6-8

Where r_w is the wetted radius (Figure 6-1) and $H(r_w)$ is the separation of the surfaces at the edge of the bridge as given in Equation 6-9:

$$H(r_w) = D + \frac{r_w^2}{2R}$$
 Equation 6-9

For large bridges (i.e. very large r_w), Equation 6-8 becomes equivalent to Equation 6-7.

6.3 Materials & Methods

The general methodology for the direct measurement of force curves between a particle and a flat surface with the AFM is described in Section 3.2.6. The summary of the properties of the liquids used is given in Table 4-2 (Section 4.2).

For the current chapter, all the colloidal probes were prepared using spherical soda-lime glass particles (Spheriglass[®], product code 20035, Potters Industries LLC, United Kingdom). The continuous media used was the purified high oleic sunflower oil (HOSO; described in Section 3.1.3).

In order to measure the adhesion of a liquid bridge formed between a particle and a flat surface by a liquid which is immiscible with the continuous phase, two different methodologies were developed. When water is the secondary immiscible liquid, one approach to create liquid bridges was to control the relative humidity (see details in Section 6.3.1). When different secondary liquids are to be tested, the developed method consisted of creating a dispersion of droplets of the secondary liquid in the continuous phase (see details in Section 6.3.2).

6.3.1 Secondary immiscible liquid: water addition through relative humidity increase

One of the developed approaches to create water bridges between a particle and a flat surface in oil medium was to increase the relative humidity in the system high enough so that capillary condensation is promoted.

In addition, considering the numerous works regarding the effect of relative humidity on the adhesion of surfaces in air (Fuji, Machida et al. 1999, Jones, Pollock et al. 2002, Jones, Pollock et al. 2003, Farshchi-Tabrizia, Kappl et al. 2008, Men, Zhang et al. 2009), it is noteworthy to evaluate its effect in an oil medium and compare air and oil as continuous phases.

The measurements were carried out inside the AFM liquid cell (Biocell, JPK Instruments, Germany) where the glass colloidal probe and glass surface were immersed in sunflower oil. The amount of secondary liquid (water) was controlled by varying the relative humidity inside the Biocell. The relative humidity varied from 0 % to 100 %. It is important to point out that the controlled humidity generator Wetsys used for the experiments can nominally produce humid air up to 95% relative humidity. However, when condensation is observed at such extent in the liquid cell (and even some condensation in the tubing connecting the Wetsys unit to the liquid cell) one can assume that the relative humidity inside the cell is saturated, i.e. 100%. The measurements were performed at 25 °C. The

whole experimental setup was allowed to equilibrate for at least 2 hours (for experiments in air) or 15 hours (for experiments in oil) for each tested relative humidity.

The type of cantilever used for this set of experiments was the rectangular tipless cantilevers (NSC12, Mikromasch, Estonia). The glass particles attached to the cantilevers used had diameter values ranging from 18-22 μ m (Figure 6-2) and the measured spring constant ranged from 12 to 14 N/m. For this set of experiments the approach/retract speed used was 0.5 μ m/s and 10 μ m/s in oil and air, respectively. The delay time between approach and retract was 0 s and 30 s for oil and air media, respectively. A lower speed and longer delay time were used in oil media in order to minimize hydrodynamic effects due to the viscosity of the oil.



Figure 6-2. Colloidal probe - glass particle attached to a tipless cantilever (in this example, the particle diameter is approximately 18 μm).

6.3.2 Secondary immiscible liquid: Different binders dispersed in oil

In order to measure the adhesion forces between glass surfaces due to the formation of liquid bridges of different liquids inside oil, one has to first create small droplets of the secondary (bridging) liquid inside the continuous phase. The height of these droplets (or droplet caps) on the glass surface should be smaller than the particle on the colloidal probe (Figure 6-3) so that the cantilever would not sink in the secondary liquid. For this reason, a dispersion of secondary liquid droplets in oil was prepared. In order not to have an excessive number of droplets, a low concentration of secondary liquid was required. The liquid dispersions were prepared by thoroughly mixing the secondary liquid with purified high oleic sunflower oil at a concentration of 0.1 %wt with a homogenizer (L4R model, laboratory high-shear mixer, Silverson, UK) for 2 minutes at high speed (nominal speed of 2400 rpm).



Figure 6-3. Scanning electron micrograph (SEM) of an AFM colloidal probe: glass sphere (~28 μ m diameter) glued to the tip of a cantilever (a) and detail of the glass sphere (b). The image was taken after the probe was used and cleaned with hexane and ethanol to remove excess oil.

Figure 6-4 shows a schematic representation of how the AFM cycle measurements were conducted. After adding the liquid dispersion to the AFM liquid cell (BioCell, JPK Instruments, Germany), the system was left undisturbed for few minutes so that the droplets of the secondary liquid could settle on the lower glass surface. The colloidal probe (a glass sphere glued to a cantilever) was then positioned on top of one droplet and the force was measured on its approach, set point load force application and subsequent retraction from the surface. During this procedure, the vertical deflection of the cantilever was recorded versus the displacement in the vertical direction (normal to the surface). The force data could be obtained based on Hooke's law, i.e. by multiplying the deflection of the cantilever by its calibrated spring constant. The force curve was corrected according to the calibrated sensitivity of the cantilever. The approach and retracting speed was kept constant at 0.5 μ m/s and the delay between approach and retraction was 30 s for all experiments. Multiple force curves were performed for each set of experiments (at least 10) and the results are expressed as the average value and the error values represent a confidence interval of 95 %.



Figure 6-4. Schematic of a force measurement sequence with the AFM (drawings are not to scale).

Small amounts of colorant patent blue V (Sigma-Aldrich, UK) were added to the secondary liquids (concentration of 0.1 %wt) in order to facilitate their visualization with the inverted optical microscope. For the cases in which water was used as the secondary immiscible liquid, the oil phase and the environment in the AFM liquid cell had to be saturated with water vapour in order to reduce evaporation. For this reason, a purposetailored system was used to control temperature and relative humidity in the AFM liquid cell. Conditioned air generated by a Wetsys Humidity Generator (Setaram, France) was circulated through the AFM liquid cell. The air flow rate was set at 50 ml/min, at a temperature of 25 °C and relative humidity of 95 %.

The measured sensitivities of the cantilevers used for this set of experiments ranged from 13.9 to 15.7 nm/V and the spring constants were between 52.7 and 61 N/m. Both the glass particle and surface (soda-lime glass cover slip, 24 mm diameter, 0.20 mm thickness, Menzel-Glaser, Germany) were washed in absolute ethanol in an ultrasonic bath prior to use.

6.4 Results and Discussion

6.4.1 Forces in purified sunflower oil

A representative force curve performed inside purified high oleic sunflower oil (without the addition of a secondary liquid) is shown in Figure 6-5. The horizontal part of the curve (baseline) corresponds to the out-of-contact force line, i.e. where the cantilever is still far from the surface and no interaction forces are present. The red and blue curves represent the approach and the retraction of the cantilever towards and from the surface, respectively. Positive forces indicate repulsive interactions while negative forces represent attractive interactions such as adhesion. The maximum adhesion force is the highest negative force value observed in the retract part of the force-separation distance curve (minimum in the blue curve in Figure 6-5). The adhesion energy corresponds to the area below the baseline for the retract part of the force-separation distance curve.



Figure 6-5. Example force curves between a glass particle and a glass surface in purified high-oleic sunflower oil. Approach (red) and retraction (blue) curves are shown. The maximum adhesion force is given as the minimum on the retraction curve.

Measured attractive forces between a glass particle and a glass surface inside oil are considerably small. Maximum adhesion forces are of the order of 1-2 nN (1.61 \pm 0.68 nN) as seen in the inset in Figure 6-5. In apolar media such as sunflower oil, attractive van der Waals forces govern interparticle interactions (Liang, Hilal et al. 2007). For a spherical glass particle interacting with a flat glass surface (at room temperature ~25 °C), one can calculate the Hamaker constant to estimate the magnitude of the van der Waals forces using Equation 2-10 in Section 2.3.1.

Considering the dielectric constants (ϵ) and refractive indexes (n) from literature (CRC 1977, Johansson and Bergenståhl 1992): $\epsilon_{1(HOSO)}=2.5$, $\epsilon_{2(glass)}=6.9$, $n_{1(HOSO)}=1.47$, $n_{2(glass)}=1.53$, the Hamaker constant results in a value of 1.58×10^{-21} J. By deriving the interaction potential for a sphere and a surface (Equation 2-6; Section 2.3.1) over a distance (as in Equation 2-9), the van der Waals force can then be calculated using Equation 6-10:

$$F_{VdW} = \frac{A_H R}{6 D^2}$$
 Equation 6-10

where $A_{\rm H}$ is the Hamaker constant, R is the particle radius and D is the separation distance between the particle and surface.

Considering the separation distance of 1 nm where the maximum force in the example force curve in Figure 6-5 was measured, the van der Waals force is calculated to be 3.5 nN, which is of the same order of magnitude as the experimental results.

At very small separation distances, surface roughness can obstruct the exact approach of the glass particle and flat surface. The roughness of the glass surface used is given in Figure 6-6, and for an area of $5 \ \mu m^2$ the peak-to-valley roughness is calculated to be about 3 nm. At this separation distance, the van der Waals force is calculated to be 0.44 nN. Surface roughness, together with the fact that stiffer (less sensitive) cantilevers were used due to the viscous continuous medium (oil), can explain the noisy retraction part of the curves at small separation distances and the fact that the maximum force at 1 nm is slighter higher than the experimentally measured values.



Figure 6-6. AFM surface topography of the glass surface used and the calculated roughness for an area of $5 \ \mu m^2$. The average roughness is the arithmetic mean of the absolute height values while the root mean square (RMS) roughness consists of the mean squared absolute height values of the surface. The peak-to-valley roughness considers the maximum distance between the highest peak and the lowest valley within the area of the surface measured.

It is important to point out that hydrodynamic resistance due to the viscosity of the oil could affect the force curves measured (Butt, Cappella et al. 2005). In order to reduce their effect, a stiffer cantilever was chosen and a reduced cantilever approaching/retracting speed of $0.5 \,\mu$ m/s was used; these measures have shown to be effective as there was no hysteresis in the approach and retract baseline.

6.4.2 Effect of relative humidity on the adhesion of a spherical glass particle and flat glass surface

6.4.2.1 Continuous medium: oil

The dependence of the adhesion force on relative humidity for the contact of a spherical glass particle and a flat glass surface inside an oil medium is shown in Figure 6-7. As the relative humidity is increased in the AFM liquid cell, the magnitude of forces measured does not experience significant changes up to considerably high values (90-95 %). At approximately 100 % relative humidity, saturation occurs and condensation of water droplets on the surface of the glass surface was observed. This condensation can be seen in the optical micrographs in Figure 6-8. It was possible to observe that condensation happened only on the surface of the glass slide, i.e. once the focus of the image was moved up (away from the surface), droplets could not be visualized anymore.



Figure 6-7. Adhesion force between a spherical glass particle and a flat glass surface in oil normalized by particle radius as a function of the relative humidity in the AFM liquid cell.



(c) 100% RH (Condensed water droplet 2 = ~18 μm)

Figure 6-8. Optical micrographs of the glass colloidal probe in a liquid cell at (a) 75% relative humidity and at (b/c) saturation humidity (around 100%). The picture (b) shows the smaller drop used (condensed water droplet 1 of about 12 μm of diameter) and (c) shows the smaller drop (condensed water droplet 2 of around 18 μm). The dimension of the droplets is expressed in terms of its diameter, however, one has to take into consideration that since the contact angle of water on glass is quite low (40°) the actual height of the drop cap is very small.

(Condensed water

droplet 1 = $\sim 12 \,\mu m$)

When measuring force curves on top of the droplets indicated by arrows in the Figure 6-8, a strong adhesion was observed, as shown in Figure 6-9 (and previously in Figure 6-7). These attractive forces observed upon retraction of the particle from the water droplet resting on the glass surface indicate the formation of capillary bridges. In addition, the larger the volume of the droplet, the greater is the adhesion energy and the distance that the bridge ruptures. From Figure 6-9, one can see the rupture of the bridge at the point the retract curve (blue) jumps from negative values (attractive forces) to the baseline. For the smaller droplet a rupture of the bridge was observed around 1-2 µm away from the surface (Figure 6-9a) while for the larger droplet the rupture was observed around 3-4 µm (Figure 6-9b). In Figure 6-7, some extra points are shown for the 100% relative humidity which correspond to measurements with a different glass particle and flat glass surface in oil to evaluate the repeatability of the method. The slight difference between the data points for the 100% RH (in oil-curve) is because the difference in volume of the bridges (further discussed in Section 6.4.3.1); however, it is important to point out that despite the differences, the order of magnitude of the forces and of the increase when the oil system is saturated with water is similar.



Figure 6-9. Force-distance curves between a glass colloidal probe and a glass surface inside sunflower oil on: (a) condensed water droplet 1 (~12 μm diameter) and (b) condensed water droplet 2 (~18 μm diameter); with a load force of 500 nN. The spherical glass particle used for those curves had approximately 18 μm diameter. The red curve corresponds to the approach of the cantilever towards the surface and the blue curve its retraction away from the sample.

6.4.2.2 Forces between a glass particle and a glass surface – a comparison between air and oil as the continuous media

In order to evaluate the effect that the continuous medium has on this interaction between surfaces, forces have also been measured in air as a continuous medium.

The shape of the force-distance curves and the magnitude of adhesion forces in air are considerably different if measured in oil than in air (Figure 6-10). Adhesion forces in air are larger in air than in oil, which is a result of a number of factors, such as:

- larger interfacial tension ($\gamma_{water-air} = 72 \text{ mN/m} > \gamma_{water-oil} = 26 \text{ mN/m}$)
- drag effects in air are almost negligible (while they are not in oil)

In contrast, at very high humidity, adhesion forces in oil (Figure 6-10 (d)) have a longer range if compared with forces in air (Figure 6-10 (c)). This is because the interfacial tension between the two liquids (oil-water) is lower than the one with air (air-water), resulting in a shorter Kelvin length ($\lambda_{\rm K}$; Equation 6-5) and consequently a longer range capillary force (Butt and Kappl 2010). Although the relative humidity is not exactly the same in Figure 6-10 (c) and (d), the shape of the curves indicate the range difference – in air the bridge stretches up to few nanometres while in oil the bridge stretches to around 3-4 µm before rupturing.



Figure 6-10. Characteristic force-distance curves between a glass particle (≈ 20 µm diameter) and a glass surface in different environmental conditions and continuous media. Note that the scale of both axes for graphs (c) and (d) are different from graphs (a) and (b) due to the magnitude of the forces. The insets in graphs (c) and (d) show the detail of the force curves and the adhesion.

In Figure 6-11 and Figure 6-12 the adhesion force and adhesion energy, respectively, between a glass particle and a glass surface are plotted versus the relative humidity.

By analysing Figure 6-7 and Figure 6-11, one can see that the adhesion force normalized by particle radius show a monotonic increase with the increase in relative humidity above 30% for the measurements with air as the continuous phase while for the oil as medium a jump is observed when the oil is saturated with water. The same behaviour is observed for the normalized adhesion energy as shown in Figure 6-12. The increase seen in the ad-

hesion force upon separation of a glass particle and a glass surface in air with relative humidity is consistent with the findings from Jones, Pollock et al. (2002). They have shown a monotonic increase in the pull-off adhesion force between 20 μ m glass particles and flat glass surfaces above 40 %RH. The possible justification given is that glass surfaces are not perfectly smooth and therefore they are less perfectly wettable, resulting in a delay in capillary condensation.

Using Equation 6-3 with the values for interfacial tension and contact angle ($\gamma_{water-air} = 72 \text{ mN/m}$, $\gamma_{water-oil} = 26 \text{ mN/m}$, $\theta_{water-glass-air} = 20^{\circ}$ and $\theta_{water-glass-air} = 40^{\circ}$), for the point where the glass particle and flat surface are touching (D=0), the theoretical maximum capillary force one obtains is of the order of magnitude of 850 mN/m and 250 mN/m in air and oil media, respectively. The measured magnitude of the forces due to capillary condensation observed in both air and oil environments are below the predictions by the Laplace-Kelvin equation – the highest values measured are of the order of 220 mN/m in air and 3-8 mN/m in oil (as seen in Figure 6-11 and in Figure 6-7, respectively). In addition, if one analyses Equation 6-3, theoretically, the force between a sphere and a flat plate should be almost independent of the humidity (Farshchi-Tabrizia, Kappl et al. 2008). The fact that this has not been observed experimentally, together with the fact that the measured forces are lower than theoretical predictions, can be explained by the non-perfectly smooth characteristic of the glass surfaces (Figure 6-6 and further findings shown in Section 6.4.2.3).



Figure 6-11. Adhesion force between a glass colloidal probe and a flat glass surface as a function of the relative humidity in air as a continuous medium. The adhesion force is normalized in relation to the radius of the spherical glass particle.



Figure 6-12. Adhesion energy between a glass colloidal probe and a glass slide as a function of the relative humidity in two different continuous media: air and oil (HOSO). The adhesion energy is normalized in relation to the radius of the spherical glass particle.

6.4.2.3 Microscopic view of liquid bridge formation with increase in relative humidity

The capillary condensation between particles inside oil medium due to the increase of relative humidity was also investigated through optical microscopy. A single layer of spherical glass particles was suspended in purified high-oleic sunflower oil inside the AFM liquid cell (BioCell, JPK Instruments, Germany) were the temperature and relative humidity was controlled. The optical images recorded over time with the inverted optical microscope while the relative humidity was increased from 0% to 100% is shown in Figure 6-13.

In the first few images in Figure 6-13 (from 0 to 4 hours) not many changes can be observed. After 6 hours of equilibration at 100% relative humidity, some condensation can be observed on the surface of some glass spheres as indicated by the arrows in the corresponding image in Figure 6-13. This condensation continues and increases over time and, after 14 hours, it is clear the condensation of water droplets on the glass surface from the bottom of the liquid cell as well. The condensation is first visualized on the surface of the glass particles probably because they are rougher (or contain rougher patches) than the glass surface of the bottom of the liquid cell.

After 18 hours the environment becomes completely saturated with water and water bridges are formed when particles are close to one another (see Figure 6-13, after 18 hours

image). This optically visible result of liquid bridges being formed upon saturation of the oil continuous phase with water supports the increase in adhesion forces measured between glass surfaces with the AFM.

The nucleation points for condensation observed on the surface of the glass particles and also their distribution along the surfaces suggest the existence of microasperities and rough patches. This was also suggested by Jones, Pollock et al. (2002) and explains the magnitude of the adhesion forces in air being much smaller than the predicted using the Laplace-Kelvin equation for the capillary force.



Figure 6-13. Agglomeration of glass particles suspended in sunflower oil upon increase in relative humidity from 0% to 100% over time. A 50 μ m scale bar is shown in the first image (0 min, bottom right corner).

In Figure 6-14, some extra images of the experiment described above, after 20 hours of equilibration time (and at different locations inside the cell) are shown. Liquid bridges (see arrows in Figure 6-14) and extensive condensation on the surface of the glass spheres can be seen in Figure 6-14 (a) and (b). In Figure 6-14 (c), it is possible to see a large droplet of water that has probably fallen from the top of the liquid cell after condensation on the upper glass cover. This droplet of water encapsulates the glass particles that are close to it due to surface tension forces.



Figure 6-14. Agglomeration and/or water distribution in different areas of the liquid cell containing glass particles suspended in sunflower oil at 100% relative humidity. A 50 μ m scale bar is shown at the bottom right corner in (a).

6.4.3 Effect of different secondary binding liquids on the adhesion of spherical glass particle and flat glass surface

6.4.3.1 Addition of a secondary liquid: water

Once water is added to the system as droplets (Figure 6-15), the force curves have a very characteristic shape: a strong long-ranged adhesion is observed due to the formation of a liquid bridge. A characteristic force curve is shown in Figure 6-16 and the maximum adhesion force and energy for two differently sized water droplets are given in Table 6-1.





(a) Water droplet 1 (diameter ~ 11 μm)



Figure 6-15. AFM cantilever immersed in a dispersion of water droplets in sunflower oil. The droplets indicated by the arrows correspond to the ones that were used for the force-distance measurements (shown in Figure 6-16).

In Figure 6-16a, the stages during the force curve measurement cycle as described in Figure 6-4 are shown (I to VI). When the cantilever is far from the surface, there are no forces acting upon it and, therefore, an out-of-contact force line is observed (I). At a certain point, approximately 2 μ m from the surface, a jump of the cantilever towards the surface (II) is seen. This jump-in occurs due to van der Waals attractive forces followed by capillary forces as soon as the contact of the glass particle with the water droplet occurs. The glass particle is hydrophilic as the contact angle is 39°, as shown in Table 4-2. Therefore, the meniscus formed between the particle and the droplet results in an attractive force. The cantilever continues to approach until it touches the surface and reaches the set point load force (in this case, 1.5 μ N). Before contact with the surface, the particle has to drain part of the liquid in the water droplet – this can be seen by the shape and slope of the curve (III) before reaching the hard glass surface (IV). Once the cantilever retracts from the surface, a strong and long-ranged adhesion is observed (V) followed by an abrupt rupture of the bridge approximately 4 μ m from the surface (VI). In Figure 6-16b, where force curves were measured on a larger water droplet, the force curve has the same shape. However, the jump-in occurs earlier (3 μ m from the surface) and the rupture happens later at approximately 5 μ m from the surface. The jump-in and rupture positions in the force-distance curves do not coincide with one another, showing the hysteretic nature of the rupture and reformation of liquid bridges (Pitois, Moucheront et al. 2001).



Figure 6-16. Characteristic force curve between a spherical glass particle ($\approx 28 \ \mu m$) and a flat glass surface inside sunflower oil in the presence of water. Approach (red) and retraction (blue) curves are shown. The maximum adhesion force is given as the minimum on the retraction curve, and the adhesion energy corresponds to the grey area below the baseline.

The droplet height (Table 6-1) can be determined from the jump-to-contact position measured with the AFM as shown in Figure 6-16a. The glass particle jumps towards the surface when strong attractive forces arise. In oil media, van der Waals forces have a much lower magnitude when compared to the capillary force; therefore one can assume the jump-in is due to capillary attraction to the secondary liquid. The cantilever continues to move in the direction of the surface until it reaches the glass slide and the established set point load force is applied. The height of the droplet is given by the difference between the jump-in position and the point that the glass surface touches the glass surface (Ally, Vittorias et al. 2010, Bowen, Cheneler et al. 2011). From the droplet height, it becomes possible to calculate the volume of droplet by assuming its geometry as a spherical cap as schematized in Figure 6-17. From geometrical considerations, the volume of the droplet (V_{drop}) is given by Equation 6-11:

$$V_{drop} = \frac{\pi h_{drop}}{6} \left(3 R_{drop}^2 + h_{drop}^2 \right)$$
 Equation 6-11

Where h_{drop} is the droplet height and R_{drop} is the radius of the drop. The results for the calculated V_{drop} are given in Table 6-1.

By comparing the results for the bridges formed with the differently sized droplets (Figure 6-16 a & b; Table 6-1), one can see that the larger the drop (or similarly, the larger the volume of the bridge), the higher the maximum adhesion and rupture distances, which is in agreement with Equation 6-2.

and culculated contact angle for the afferent water aropiets measured with AFM.						
Water droplet	Maximum adhesion force (µN)	Adhesion Energy (pJ)	Droplet height (µm)	Rupture distance (µm)	Calculated droplet volume (µm ³ ; Equation 6-11)	Calculated θ (°; Equa- tion 6-12)
Droplet 1 (Figure 6-15a)	0.40 ± 0.02	1.13±0.07	1.99 ± 0.09	3.87±0.30	98.7±4.9	39.8±1.7
Droplet 2 (Figure 6-15b)	0.61±0.03	2.11±0.09	3.08 ± 0.11	5.40 ± 0.08	407.2±15.7	37.8±1.3

 Table 6-1. Maximum adhesion force, adhesion energy, droplet height and volume, rupture distance

 and calculated contact angle for the different water droplets measured with AFM.

By comparing the rupture distances and the calculated volume of the bridges for the two different water droplets, it is observed that the rupture distance equals 1.2 and 1.4 times the cube root of the volume. Lian et al. (1993) have suggested a straightforward relationship between the rupture distance and the bridge volume for a liquid bridge between two rigid spheres. They found that, for small contact angles, the rupture distance results in the cube root of the bridge volume.

In addition, from the geometrical considerations shown in Figure 6-17, one can also calculate the contact angle θ from the droplet dimensions using Equation 6-12:

$$\theta = \sin^{-1} \left(\frac{2 h_{drop} R_{drop}}{R_{drop}^2 + h_{drop}^2} \right)$$

Equation 6-12



Figure 6-17. Schematic for the approximation of the secondary liquid droplet as a spherical cap and dimensions used for the calculation of the volume (for $\theta < 90^{\circ}$).

The calculated contact angles for the water droplet on the glass surface inside an oil medium are shown in Table 6-1. The values calculated using Equation 6-12 are very similar for the different sized droplets and also close to the measured contact angle using the sessile drop method (39°; Table 4-2).

Another feature worth mentioning is the discontinuities of the retract portion of force curves in Figure 6-16 as opposed to a smooth profile one would expect. The curves in Figure 6-16 are characteristic examples; however, every curve measured showed the same pattern. Those irregularities are interpreted as arising due to the movement of the contact line along the glass particle. One possible explanation for this phenomenon is the dewetting over surface asperities. The glass surface is relatively smooth (Figure 6-6). However, as one can see on Figure 6-3, even after cleaning of the colloidal probe, some impurities still remain on the glass particle, which could alter the receding of the contact line and also cause slippage.

6.4.3.2 Addition of a secondary liquid: glycerol

Micrographs of the AFM cantilever immersed in the dispersion of glycerol droplets in oil are presented in Figure 6-18. The images are focused on the bottom glass surface, i.e. on the glycerol droplets. However, the visualization of the droplets is challenging because the refractive indices of glycerol and oil are very similar ($n_{HOSO}=1.473$; $n_{glycerol}=1.474$ (CRC 1977)).





Force curves were performed on top of the glycerol droplets as shown in Figure 6-18 following the sequence and system given in the schematic in Figure 6-4. The average results extracted from these measurements (maximum adhesion force, adhesion energy, droplet height and volume, rupture distance and contact angle) are given in Table 6-2. Strong maximum adhesion forces of similar magnitude were observed for both the smaller glycerol droplet (Figure 6-19a) and the larger glycerol droplet (Figure 6-19b), as stated in Table 6-2. In contrast, the adhesion energy for the larger droplet is almost twice as large for the small droplet. This shows that the range of the interactions is larger with the increase in volume of the bridge, and also a rupture of the bridge is observed at larger distances between glass surfaces. For the smaller glycerol droplet, the rupture distance equals the cube root of the calculate bridge volume and for the larger droplet the rupture distance scales to 1.4 times the cube root of the calculated volume.



Figure 6-19. Characteristic force-distance curve between a spherical glass particle (≈ 28 µm) and a flat glass surface inside sunflower oil in presence of glycerol (Glycerol droplet 1 - Figure 6-18a; Glycerol droplet 2 - Figure 6-18b). Approach (red) and retraction (blue) curves are shown. The maximum adhesion force is given as the minimum on the retraction curve, and the adhesion energy corresponds to the grey area below the baseline. Slopes of the curves are also indicated.

When the glass particle is in contact with a hard surface such as glass and the force curve has been corrected for the cantilever deflection, the contact part of the curve appears as a vertical line (high slope of 30-45 N/m as shown in Figure 6-19a). This is not observed for the larger glycerol droplet where a slope of 0.2 N/m for the approach part of the curve and a slope of 0.4 N/m for the retract part were measured (see Figure 6-19b). This is because the height of the droplet was close to the maximum range that the piezo translator of the AFM can reach (15 μ m). Therefore, one can interpret that for the larger glycerol droplet the glass particle does not actually contact the bottom glass surface.

Similar to the calculations done for the water droplet, the contact angle between the glycerol droplet and the glass surface in oil was calculated using Eq. 8. For the smaller droplet the calculated θ (60.2 ± 2.1°) is close to the 64° measured with the sessile drop method (Table 4-2; Section 4.2). However, for the larger glycerol droplet a smaller θ was obtained. This is because the height of the larger droplet has been underestimated due to the fact that the glass particle does not actually contact the lower glass surface as aforementioned.

Glycerol droplet	Maximum adhesion force (µN)	Adhesion Energy (pJ)	Height of the droplet (µm)	Rupture distance (µm)	Calculated droplet volume (μm ³ ; Equa- tion 6-11)	Calculated θ (degrees; Equation 6-12)
Droplet 1 (Figure 6-18a)	1.21±0.16	5.30 ± 0.15	4.06±0.17	6.81±0.24	347.5±17.7	60.2 ± 2.1
Droplet 2 (Figure 6-18b)	1.09 ± 0.11	9.63 ± 0.43	8.33±0.13	13.38±0.15	6926.8±117.8	40.6±0.6

 Table 6-2. Maximum adhesion force, adhesion energy, droplet height and volume, rupture distance

 and calculated contact angle for the different glycerol droplets.

6.4.3.3 Comparison between different binding liquids

In order to establish an initial comparison between the different binding liquids, one can calculate the half-filling angle β for one example of each system. The half-filling angle gives information about the location of the contact line along the particle. It can be calculated from the volume of the meniscus at the jump-in position and also at the maximum adhesion force point, provided that all other parameters are known. The volume of the meniscus can be determined from geometry (Figure 6-1), considering the bridge as a cylinder and discounting the spherical cap of the particle immersed in the bridge (Equation 6-13).

$$V_{bridge} = \pi h R^2 \sin^2 \beta - \frac{\pi}{6} R (1 - \cos \beta) [3 R^2 \sin^2 \beta + R^2 (1 - \cos \beta)^2]$$
 Equation 6-13

In Equation 6-13, the volume of the lateral rims of the bridge due to its curvature are neglected as $\mathbb{R} \ll r_1$. Considering β small, Equation 6-13 can be further simplied to considering $h = R(1 - \cos\beta) + D$ and $1 - \cos\beta = \frac{\sin^2\beta}{2}$ as shown in Equation 6-14 (Butt and Kappl 2010).

$$V_{bridge} = \frac{\pi}{2} R^2 \sin^2 \beta \left(2 D + \frac{R}{2} \sin^2 \beta \right)$$
 Equation 6-14

For this comparison, droplets with similar volumes were chosen: the water droplet 2 $(407.2 \ \mu\text{m}^3)$ and the glycerol droplet 1 $(347.5 \ \mu\text{m}^3)$. The separation distance at the jump-in and maximum adhesion force points were extracted from each force curve. This resulted in values of β for the jump-in position of 25.0° and 21.1° for the water and glycerol droplets, respectively. And for the maximum adhesion position, β values of 33.2° and 26.7° were obtained for the water and glycerol droplets, respectively. At the jump-in position, the meniscus is formed. When the particle contacts the surface, β reaches a maximum value followed by its reduction upon retraction until the bridge ruptures. This explains the lower values of β at the maximum adhesion if compared to the jump-in position. It is also important to point out that the calculated value of β is taking into consideration only the capillary contribution for comparison reasons. This simplification results in an underestimation of β if viscous forces are considered as contributing to the adhesion, especially for the case of glycerol.

For water, the surface tension is higher and contact angle lower, while the viscosity is lower than for glycerol. This results in a stronger capillary force due to surface tension force and Laplace pressure as shown in the Theory Section (Equation 6-2). In addition, for a liquid bridge formed with a large droplet (on the order of micrometres) (Ally, Kappl et al. 2010), the curvature of the meniscus becomes prominent resulting in a larger contribution of the pressure deficiency across the oil-water interface. This explains the dependency of the maximum adhesion force on the volume of the bridge (Equation 6-2).

On the other hand, for the glycerol bridge, the viscosity value dominates (approximately 3 orders of magnitude higher than water, and more than 10 times higher than oil; Table 4-2). From Equation 6-7 and Equation 6-8, one can see that the viscous contribution to the maximum adhesion force for a glycerol bridge is significantly higher than for a water bridge. Also, the viscous contribution is less dependent of the volume of the bridge and, therefore, the forces of similar magnitudes for the two glycerol bridges of different size. As mentioned earlier, a low probe retraction speed (0.5 μ m/s) was used for the experiments in order to reduce hydrodynamic resistance due to the oil media. The viscosity of glycerol is much higher than the oil (Table 4-2); hence the viscous effects due to the glycerol bridge could still be measured.

6.4.4 Saturated sugar solution as the secondary liquid

In a similar way to the experiments performed for water and glycerol as secondary immiscible liquids, a dispersion of saturated sugar solution droplets in oil was added to the AFM liquid cell according to the method described in Section 6.3.2. Firstly, force curves were performed on top of several different small sugar droplets (10-20 μ m) as shown in Figure 6-20.



Figure 6-20. AFM colloidal probe (glass particle diameter ~24 μ m) immersed in the oil continuous phase containing dispersed droplets of saturated sugar solution (blue spheres).

The hypothesis was that a bridge of saturated sugar solution would be formed between the spherical glass particle and the lower flat glass surface, similarly to what has been observed for droplets of water and glycerol (Section 6.4.3). However, low short-ranged adhesion forces, relatively similar to adhesion forces in pure oil, were measured (Figure 6-21 (a)). Forces in pure oil were very low (order of magnitude of 1-2 nN) and shown in Section 6.4.1.

Hereafter force curves were carried out on top of larger sugar droplets (approximately $30 \ \mu$ m). In this case larger adhesion (order of magnitude of 6-8 μ N) was observed, as shown in Figure 6-21b. The dispersion of saturated sugar solution droplets in oil was left overnight in the AFM liquid cell, and experiments were performed on the following day. Force curves were measured on top of small and larger sugar "droplets" and very low adhesion ($\approx 95 \ n$ N) was observed (Figure 6-21c). By approaching the cantilever on a point with no droplets and then moving it sideways until it reached a droplet, it was possible to observe the movement of the whole "droplet". This is a strong indication that the apparent sugar droplet was in fact a sugar particle. The highly concentrated sugar solution had already a low water content, and due to the formation of very small droplets (around 10 μ m), the remaining water rapidly diffused to the drier oil, hardening the particles. Due to the size of the larger sugar particle, the water diffusion takes longer. This explains the large adhesion measured (Figure 6-21b) on the first day and the consequent very low adhesion on the following day, when the particle was drier.



(a) Day 1

F/D curve on small saturated sugar solution droplet (~13 μ m) Adhesion: ~ 154 nN Hysteresis of 71 nm between retract and approach curves

(b) Day 1 F/D curve on large saturated sugar solution droplet (~31 $\mu m)$ Adhesion: ~ 6.8 μN

(c) Day 2

F/D curve on large saturated sugar solution droplet (~30 μm) Adhesion: ~ 95 nN Reduced hysteresis between retract and approach curves on the contact regime (14 nm)

Figure 6-21. Characteristic F/D curves between a glass particle ($\approx 24 \ \mu m$) and a glass surface with different saturated sugar solution droplets between them, inside an oil continuous media at ambient conditions (25 °C and 40-60% RH). The approach of the glass colloidal probe towards the surface (red curve) and its retraction from the surface (blue curve) are shown. The adhesion force is given as the minimum on the retraction.

Therefore, in order to ensure the saturated sugar solution would remain in the liquid state and also evaluate the effect that relative humidity would have on the adhesion forces, the environment in the AFM liquid cell was controlled. A high humidity was kept (95% at 25 °C), so that the solution would not dry out in the oil. The shape of the F/D curves on droplets of saturated sugar solution in this controlled environment changed drastically (as observed in Figure 6-22). A larger adhesion force of 426 ± 10 nN and a strong adhesion energy of 2.36 ± 0.08 pJ were measured. The range of the adhesion when a viscous sugar bridge was formed was much higher and the rupture distance, i.e. the point where the retraction curve (blue curve, Figure 6-22) goes to the zero force line, was quite high relative to the size of the glass particle ($10.27 \pm 0.06 \mu m$).



Figure 6-22. Typical F/D curve between a glass particle ($\approx 24 \ \mu m$) and a glass surface with a saturated sugar solution droplet between them, inside an oil continuous media at 95% RH, 25°C.

6.5 Conclusions

In this chapter, the forces between a glass particle and a glass flat surface in oil were measured. It was shown that when a secondary hydrophilic liquid is present, the adhesion forces become stronger (larger magnitude) and long-ranged if compared to adhesion forces in pure oil, indicating the formation of liquid bridges.

The effect of relative humidity on the adhesion between a glass particle and a glass surface in oil was studied. The increase in relative humidity does not promote any changes in adhesion up to very high values (90-95 %RH). At the saturation point (100 %RH), however, an increase in adhesion forces indicates the formation of water bridges in this system of immiscible liquids. Such observations are particularly interesting for the industry, where the control of relative humidity could be used to create strong interparticle forces and consequently, tailored structures could be created by promoting the agglomeration of particles.

The effect of the properties of the binding liquid on the adhesion and forces between a particle and a surface inside oil was also investigated. In addition, it was shown that forces between hydrophilic glass surfaces inside oil are dominated by capillary attraction when liquids of high interfacial tension and low viscosity such as water form a liquid bridge. When a highly viscous liquid forms the bridge, a dynamic viscous interaction contributes to the adhesion leading to higher maximum adhesion forces, which is less dependent on the volume of the bridge.

Finally, forces in the glass-saturated sugar solution-oil system are stronger at an elevated relative humidity (95 %RH) compared to ambient conditions (40-60 %RH). The relative humidity influences the state in which the saturated sugar solution is present in the system (solid or liquid); showing that the environmental conditions can play an important role in the agglomeration process.

Chapter 7

Effect of material parameters on the surface forces

In a similar way to the analysis presented in Chapter 5 for the macroscopic behaviour of sugar and glass suspensions in oil, the effect of material parameters on the interparticle forces is shown in this chapter. The influence of the viscosity of the liquid bridge and the presence of a surfactant on the interaction of a particle and a surface in oil are measured using colloidal probe AFM. In addition, the use of a sugar colloidal probe and also the formation of liquid bridges between a glass colloidal probe and a sugar surface are discussed.

7.1 Introduction

As stated in the literature review (Section 2.7) and also reinforced in the previous chapter (Chapter 6), the study of forces between a particle and a surface due to the formation of liquid bridges in an oil-continuous phase has not been thoroughly investigated in the past. Claesson and co-workers (1996, 1997, 1998) have used the surface force apparatus (SFA) to measure such forces and have also analysed the effect of the addition of surfactants to them. However, they were limited to the use of mica as model particles since the SFA needs a transparent, smooth and malleable surface.

Recently, Arnold et al. (2013, 2013) have measured the effect of the addition of surfactants (lecithin and individual phospholipids) on the interactions of glass and sugar particles with glass and sugar flat surfaces, respectively, in soybean oil. Their systems were simpler and did not include a secondary liquid and formation of liquid bridges. However, they have identified that, in pure oil, the addition of lecithin results in a reduction of the adhesion force of sugar surfaces while no apparent reduction was observed for glass surfaces.

Studies have also evaluated the effect of the viscosity of the liquid bridge on the adhesion force; however, such studies have been carried out in air as the continuous media (Ally, Kappl et al. 2010, Ally, Vittorias et al. 2010, Bowen, Cheneler et al. 2011).

Therefore, in this chapter, the effect of material parameters in the interaction forces between particle and surface in oil media mediated by liquid bridges is investigated. More specifically, the effect of viscosity and wetting properties of the binding liquids as well as the addition of a surfactant (lecithin) is explored. Additionally, the influence of the separation speed and time that the surfaces remain in contact on the adhesion force is discussed. Finally, forces in more industrially relevant systems, such as sugar surfaces, are detailed.

7.2 Materials & Methods

In this chapter, forces between spherical colloidal probes and flat surfaces inside oil are measured. The overall methodology for the measurement of such force curves with the AFM is described in Section 3.2.6.

In Sections 7.3.1, 7.3.2 and 7.3.4, colloidal probes were prepared using spherical soda-lime glass particles (Spheriglass[®], code 20035, Potters Industries LLC, United Kingdom). The size of glass particles used varied from 18 to 28 μ m. The cantilevers used for those sections were the ACT-TL (AppNano, tipless, described in Section 3.2.6) and the measured sensitivities and spring constants varied from 16.3 to 20.8 nm/V and 24.7 and 37.7 N/m, respectively. Examples of the cantilevers used are shown in Figure 7-1. In the colloidal probe shown in Figure 7-1 (a), it is possible to observe some excess of glue on the surface of the cantilever; however, since this layer is thin, the glass particle is still prominent, and the measurements were not affected.



Figure 7-1. Scanning electron micrograph (SEM) of AFM glass colloidal probes: (a) glass sphere with ~19 µm diameter; (b) glass sphere with ~18 µm diameter. The images were taken after the probes were used for AFM experiments and cleaned with hexane and ethanol to remove excess oil.

The continuous media used was the purified high oleic sunflower oil (described in Section 3.1.3). In Section 7.3.2, the effect of surfactant added to the continuous phase is evaluated. The surfactant used and concentrations are the same as in Section 5.2.5. The properties of the liquids once surfactant is added is also presented in Section 5.2.5 (Table 5-4).

The lower flat surface used was generally a glass slide (soda-lime glass cover slip, 24 mm diameter, 0.20 mm thickness, Menzel-Glaser, Germany). Both the glass particles and glass surfaces were washed in absolute ethanol in an ultrasonic bath prior to use.

In Section 7.3.3, a sugar colloidal probe was used. The sugar particle was produced similarly to the method proposed by Haider, Althaus et al. (2012). Drops of saturated sugar solution (67.47 %wt pure sucrose) were dispersed into high oleic sunflower oil (HOSO) and further broken into smaller droplets (micron size range) by thorough mixing with a magnetic stirrer. The saturated sugar solution was dyed blue (Patent Blue V, Sigma-Aldrich) in order to facilitate the visualization of the droplets. This dispersion of saturated sugar solution droplets was dried in an oven at 40 °C for about 4 hours so that the excess water could be evaporated and droplets could solidify. The small spherical sugar particles were then washed multiple times with hexane so that the gluing of the particle to the AFM cantilever with epoxy-glue would be possible. The cantilever used in this set of experiments was the NSC 12 (Mikromasch, tipless, described in Section 3.2.6). The sugar particle size was approximately 28 μ m, and the measured sensitivity and spring constant of the cantilever were 12.33 nm/V and 20.95 N/m, respectively.

In Section 7.3.4, forces between a glass colloidal probe and a sugar surface were measured. The sugar surface was produced by crystallizing a saturated sugar solution (67.47 %wt pure sucrose) in a depression created with a rubber seal onto a cover glass slip (Menzel-Glaser, diameter 24 mm, 1.5 mm thickness) as shown in the scheme in Figure 7-2. Few drops of the sugar saturated solution were applied onto the depression, the excess of solution was gently scraped with a glass slide and the whole setup was left at room conditions (25 °C and 40-60% RH) for at least 2 days to allow crystallization.



Figure 7-2. Schematic drawing of the depression created on a glass cover slip with a rubber seal in order to create a thin sugar surface.

The apparent contact angle of the different secondary liquid on the produced flat sugar surface were measured using the sessile drop method and are listed in Table 7-1. The values for the contact angles of the different secondary liquids in oil on glass are also given as a comparison.

	Table 7-1. Apparent contact angles (°) for three-phase systems							
		Continuous media						
			HOSO					
	Droplet	Water	Saturated sugar solution	Glycerol				
Flat	Glass	39	40	64				
surface	Sucrose	10	12	33				

In order to measure forces curves between a spherical particle and a glass surface in oil upon the addition of a secondary liquid, the method described in Section 6.3.2 was used. The secondary liquid used for all the experiments present in this chapter was glycerol (Sigma-Aldrich, United Kingdom). Droplets of the secondary liquid were dispersed in the oil and force curves were measured on top of such small droplets.

Force curves were measured at least 20 times on each point. Several points/droplets were measured on each surface and also different set of colloidal probe/surface/medium were used for each experimental conditions. The error bars shown in the plots in the results section correspond to a confidence interval of 95 %.

The environmental conditions (relative humidity and temperature) were controlled using the setup described in Section 3.2.6 – AFM liquid cell (Biocell, JPK Instruments, Germany) connected to a relative humidity generator Wetsys (Setaram, France).

7.3 **Results and Discussion**

Effect of viscosity and wetting properties on the bridge – glycerol and 7.3.1 relative humidity

In order to experimentally investigate the effect of secondary binding liquid viscosity on the liquid bridge forces between particles in oil media with an AFM, mixtures of glycerol and water were used in a similar way as in Section 5.3.4 for rheological experiments. Glycerol has a viscosity three orders of magnitude higher than water. Mixtures of glycerol and water cover a wide range of viscosity values as explained in Section 5.2.4 and shown in Figure 5-3 and Table 5-3. In order to control the concentration of water in the waterglycerol mixture one can control the relative humidity. Glycerol is very hygroscopic and readily absorbs water upon increase in relative humidity. Consequently, by using the sorption isotherm of glycerol (Figure 5-3, Section 5.2.4) one can determine the composition of the mixture water-glycerol and, in turn, its viscosity.

It is known that the interfacial tension and contact angle of such mixtures will also slightly change according to the respective concentrations of water and glycerol. However, the change in viscosity is expected to superimpose the other parameters as shown in Section 6.4.3.

Initial trials were performed in order to evaluate the uptake of water by glycerol dispersed in oil media (sunflower oil) as shown in Figure 7-3. At 0% relative humidity, anhydrous glycerol has a refractive index very close to that of the continuous oil phase so glycerol droplets optically appear almost completely transparent (Figure 7-3 (a)). Upon relative humidity increase, one can observe that the contour of the glycerol droplets not only become more distinguishable but also the droplets increase slightly in size.



Figure 7-3. Glycerol droplets in oil upon increasing humidity imaged with an inverted optical microscope.

The effect of different binders (water and glycerol) was analysed in the previous chapter (Section 6.4.3) and it was shown that viscous bridges (glycerol) have a dynamic contribution to the force of the bridge and are less dependent on the volume of the bridge. Therefore, in this chapter the effect of parameters such as speed of retraction, delay between approach and retraction and set-point load force will be evaluated separately.

7.3.1.1 Effect of speed and viscosity

Force curves were measured between a glass colloidal probe and a glass surface immersed in oil mediated by a glycerol droplet as shown in Figure 7-4.

By controlling the relative humidity, as explained in Section 5.2.4, mixtures of glycerol and water are formed within the droplets of secondary liquid. At 0% relative humidity it is considered that the bridge is formed of anhydrous glycerol, which has a viscosity of 824 mPa·s. At 60% and 90% relative humidity values, the bridge is formed by a mixture of



Figure 7-4. Glass colloidal probes immersed in dispersions of glycerol droplets in oil at 60% relative humidity. The droplets indicated with the arrows correspond to the ones used for force curves measurements.

In Figure 7-5, representative AFM force curves between a glass spherical particle and a glass flat surface mediated by bridges of glycerol at different relative humidity values (glycerol-water mixtures) are plotted for different probe speeds.

From Figure 7-5, one can observe that the increase in the probe speed influences the jump-in and bridge rupture distances. At $2 \mu m/s$, a jump-in is observed for all the different liquid bridges (0%, 60% and 90% RH). This jump-in is related to van der Waals attractive forces and subsequently by capillary forces when the glass particle comes into contact with the secondary liquid droplet, as shown in Figure 6-4 and explained in Section 6.4.2. It is also observed that the jump-in for the anhydrous glycerol bridge occurs at approximately 6 μ m away from the glass surface while for a bridge at 90% RH (i.e. containing more water) the jump-in occurs at about 8 µm. This difference in jump-in gives an important indication that the water uptake by the glycerol droplet results in a larger volume bridge. If one calculates the volume of the bridge using Equation 6-11 (Section 6.4.3.1) considering the radius of the droplet constant and equal to 11 µm (Figure 7-4), one obtains a volume of 1253 µm³ (1.25 pL) and 1789 µm³ (1.79 pL) for the anhydrous glycerol bridge and the water-glycerol bridge at 90% RH, respectively. The volume for the anhydrous glycerol bridge is probably overestimated by considering the radius of the droplet as in Figure 7-4 constant throughout all the relative humidity values. It is not only hard to detect small differences in the droplet radius through an optical image but also, considering the refractive index of pure glycerol and oil is very similar, it is not possible to properly visualize the droplet optically. When the speed is increased to 10 μ m/s, it is possible to observe a repulsive force on the approach for all the three force curves in Figure 7-5. This repulsion is supposed to be caused by the hydrodynamic resistance due to the squeezing-out of the oil-continuous phase. On approach, the layer of oil between the glass spherical particle and the secondary liquid droplet opposes their approach. This resistance is a dynamic process, hence a repulsive force is observed with speed increase (Aston and Berg 2001, Vinogradova and Yakubov 2003, Streator 2005, Bowen, Cheneler et al. 2011). This repulsive force is overcome when the thin layer of oil is drained and the contact with the secondary liquid results in a jump-in at about 2.5 μ m for anhydrous glycerol bridge and at approximately 3.5 μ m for the glycerol-water bridges at 60% and 90% RH. This jump-in at a

shorter distance from the glass surface, if compared to the speed of 2 μ m/s, can be explained by the deformation of the soft interface of the secondary liquid droplet due to the strong repulsive forces generated by the hydrodynamic resistance of the oil phase. Finally, at 100 μ m/s the hydrodynamic resistance due to the lubrication effects becomes so large that no jump-in is observed for any of the force curves.

The increase in the probe retraction speed results in a slight increase in the rupture distance for all the force curves shown in Figure 7-5. As discussed by Mazzone, Tardos et al. (1987), dynamic bridges result in a longer and narrower neck and also significantly larger rupture distances. This finding is also in agreement with Pitois, Moucheront et al. (2001). They found that when viscous effects are existent, the bridge rupture does not take place straightaway and also the rupture of the bridge can be related to the capillary number, hence the increase in the rupture distance with the increase in viscosity.


Figure 7-5. Characteristic force curves between a glass sphere and a glass flat surface on top of a droplet of glycerol in oil at different relative humidity values. The curves for different probe retraction speeds (2, 10 and 100 μm/s) are plotted. Settings used were 10 s delay and 500 nN set point load force. The approach of the cantilever towards the surface is shown in red and the retraction is shown in blue.

In Figure 7-6, the adhesion force (normalized by the glass particle radius) is plotted as a function of the speed of retraction of the glass colloidal probe from the surface for the different glycerol-water bridges.



Figure 7-6. Effect of relative humidity and consequently viscosity of the liquid bridge (glycerolwater mixtures) in the adhesion force of a glass spherical particle and a flat glass surface in oil as a function the speed of retraction – drop of approximately 22 μ m indicated in Figure 7-4 (a) (delay time between approach and retraction of 10s).

From Figure 7-6, one can observe that, similarly to the results presented in the previous chapter (Section 6.4.3), the adhesion forces are slightly higher for the bridges formed by more viscous liquids. It is also observed that for speeds up to 2 μ m/s the magnitude of the forces remains relatively constant. Above 2 μ m/s the adhesion force increases for all the samples. This observation gives evidence that a dynamic contribution is adding to the adhesion, as discussed in Section 6.4.3 and predicted by Equation 6-7 (Section 6.2). Since the anhydrous glycerol (0% RH) has a much higher viscosity than the bridges at 60% and 90% RH, the adhesion force becomes even greater for the anhydrous glycerol bridge at elevated speeds and its increase is steeper, as shown by the higher slope of the curve in Figure 7-6.

An increase in the adhesion force is also observed for the liquid bridges with lower viscosity (60% and 90% relative humidity; Figure 7-6). This can be related to the contribution of the viscous effects due to the oil-continuous phase. The oil has a viscosity of 65 mPa·s and, upon separation of particle and surface at elevated speed values, it can cause a hydrodynamic resistance which opposes the separation of the particle and surface. Therefore, this hydrodynamic resistance due to the oil phase would contribute attractively to the adhesion force (as explained in Section 2.3.5.3).

7.3.1.2 Delay time

It was noted, during the AFM experiments, that the delay time between approach and retract – i.e. the amount of time that the particle was left in contact with the surface at a defined constant a set-point load force – influenced the force curves and magnitude of the adhesion forces.

In Figure 7-7, the effect of 10 s delay (compared to no delay) to the adhesion force between a glass spherical particle and a glass flat surface in different media is shown. For air and pure oil experiments, the trials were performed at room conditions ($25 \degree C / 40-60 \% RH$). For the glycerol-in-oil media at different relative humidity values, the force curves were measured on drops of glycerol as explained in the earlier chapters (Section 6.3.2).



Figure 7-7. Effect of the delay between approach and retraction of the glass sphere from the flat glass surface on the adhesion force in different environments (approach/retraction speed of 2 μ m/s).

From Figure 7-7, one observes that the magnitude of the adhesion forces when a delay time was applied is larger for all the media. In air and pure oil as continuous phase (no secondary liquid added as a droplet), the increase in adhesion could be explained by capillary condensation. In air (at room conditions), when the glass particle contacts the glass flat surface, capillary condensation can occur as per Kelvin's equation as discussed by Rabinovich, Esayanur et al. (2005), Butt (2008) and Butt and Kappl (2009). Capillary

condensation has been reported to occur in nanoscale pores in time scales ranging from milliseconds to seconds (Kohonen, Maeda et al. 1999). Due to the roughness of the glass surfaces (Figure 6-6; Section 6.4.1), capillary condensation occurs on the micro asperities, and it is believed that if an extended contact time is allowed, multiple bridges can be formed, increasing the adhesion force, as suggested by Butt (2008) and De Souza, Brinkmann et al. (2008).

In pure oil, a stronger adhesion, higher than the magnitude of van der Waals forces alone (Section 6.4.1), is also observed with increased delay time. It is hypothesized that during the set-up of the experiment at room conditions, traces of water could enter the system, mainly through the adsorption on the hydrophilic surfaces. Consequently, a longer contact time would enable the drainage of the oil layer existing between particle and surface, and consequently allow the contact of thin water films adsorbed on the surfaces, leading to a higher adhesion, which is in agreement with the findings from Banerjee, Mulder et al. (2012). This hypothesis that a thin water film is adsorbed on the glass surfaces at room conditions is consistent with the results shown in Figure 6-10b (Section 6.4.2), where a characteristic force curve in purified oil at controlled 0% RH shows very low adhesion forces. At low relative humidity any traces of water incorporated during experimental setup dry out and higher adhesion forces even with longer delay times are not observed.

The time-dependent behaviour was also observed for the glycerol bridges formed between the glass surfaces in oil at different relative humidity values. A similar feature of timedependent behaviour of force curves was observed by Banerjee, Mulder et al. (2012). They observed that the adhesion of a silica spherical particle to a cellulose layer in hexane increased with longer delay times of 10s to 200s and also that the force was even stronger in hexane saturated with water. They related this time-dependent behaviour to the fact that cellulose surfaces are softer (Young's modulus of 7 MPa in water and 7 GPa in hexane) and also rough. Glass surfaces are relatively rigid (Young's modulus of 69 GPa as given by the supplier), therefore, the measured dependency of the force curves on the delay time can be related to the roughness of the samples and to the consequent time it takes for the oil layer to drain and enable the wetting of a larger area of the particle and also the formation of multiple liquid bridges between the different micro-asperities of the glass surfaces.

One interesting aspect to be noted is that the delay was important to enable the formation of the bridge. However, other experiments with higher delay times showed that the increase in the delay has no effect of the force and energy of adhesion, suggesting that an equilibrium state is reached (*data not shown*).

7.3.1.3 Set-point load force

The set-point load force is the force applied on the approach and contact of the particle with the surface. The AFM was operated in constant force mode, meaning that once particle and surface were in contact, the set-point load force was steadily applied for the set delay time. The effect of set-point load force on the adhesion force and energy between a glass particle and a glass flat surface in oil was also evaluated. The range tested varied from 500 nN to 2000 nN and for the glass colloidal probe in oil with a glycerol bridge no significant difference was observed as shown in Figure 7-8.

This independence of the adhesion forces and energies from the set-point load force applied can be explained by the type of surface used. As already mentioned, glass is a rigid material (Young's modulus of 69 GPa as given by the supplier), therefore, no deformation of the surface occurs with the application of the set-point load forces used in this study (or feasible with the range of the AFM/cantilever used).



Figure 7-8. Effect of the set-point load force on the adhesion force (red) and adhesion energy (blue) between a glass spherical particle and a glass flat surface in oil mediated by a glycerol bridge at 60 %RH (drop 2 in Figure 7-4 (b)) with a speed of 100 μ m/s and 10 s delay time between approach and retract. Both adhesion force and energies are normalized with the glass particle radius.

7.3.2 Effect of the addition of a surfactant on surface forces in oil

In order to evaluate the effect of the addition of a surfactant and consequently the effect of interfacial tension (IT) on surface forces in oil media, lecithin, a common food surfactant (or emulsifier), was added to the oil phase. The concentration of lecithin in oil was 0.1 %wt and 0.5 %wt, in a similar way to the rheology experiments (Section 5.2.5). These concentrations of fluid lecithin result in a concentration of phospholipids (PL) corresponding to 0.05 %wt and 0.25 %wt, respectively. The resulting interfacial tension with different secondary liquids was given in Table 5-4.

AFM force curves were measured between a glass colloidal probe and a flat glass surface inside the oil media containing different concentrations of lecithin. The force curves were measured with and without a delay time between approach and retract, when the glass surfaces were in contact, as shown in Figure 7-9.

When the surfaces were disconnected immediately after approach (no delay), there is no significant difference between adhesion forces in pure oil or oil with 0.05 %wt PL, which is in agreement with the observations from Arnold, Schuldt et al. (2013). However, a higher concentration of lecithin (0.25 %wt PL) seems to result in a slight increase of the adhesion force. This could be related to the surfactant being present in excess, as discussed in Section 5.2.5 and observed through an increase in apparent viscosity (in relation to 0.05 %wt PL). The formation of lecithin micelles in the oil phase or bilayers around the glass surfaces (Johansson and Bergenståhl 1992, Beckett 2009) could influence the interaction forces between the glass surfaces in oil.

When the glass particle and surface are left in contact for a period of time (delay of 10 s; Figure 7-9), the addition of lecithin to the oil resulted in a reduction of the adhesion force between glass surfaces, as seen in Figure 7-9. Lecithin can adsorb to the interface between glass and oil as shown in Figure 3-6 (Section 3.1.3), with the polar head of the surfactant preferentially adsorbing to the glass hydrophilic surfaces and the aliphatic tail to the oil phase. Such adsorption creates a steric repulsive force which would inhibit particle surface aggregation and consequently result in a decrease in the interaction attractive forces (Johansson and Bergenståhl 1992, Babin, Dickinson et al. 2005). The high adhesion force observed in purified oil when the surfaces are left in contact for a longer period of time was explained earlier (Section 7.3.1.2), and it is suggested that traces of water in the system and the drainage of the oil layer between the surfaces would result in capillary condensation. It is interesting to note that in the systems where surfactant is added, such phenomena are not observed to the same extent – although the increase in delay time results in an increase of the adhesion force, this increase is small and much less significant than the one in purified oil.



Figure 7-9. Adhesion force between a glass colloidal probe and a flat glass surface in oil containing different concentrations of lecithin phospholipids and the effect of delay between approach and retract (Force curve parameters: set-point load force of 500 nN, speed 10 μ m/s).

The effect of the addition of a surfactant on the formation of glycerol bridges between a glass particle and a glass surface in oil was also investigated by measuring force curves on top of glycerol droplets dispersed in oil. This effect is shown, in general terms, in Figure 7-10. Although the addition of a surfactant seems to result in an increase of the adhesion force, a strong opposing effect is seen for the adhesion energy, which decreases significantly with the addition of lecithin. This opposing behaviour gives an indication that it is important to evaluate the general shape of the force curves (Figure 7-11).



Figure 7-10. Effect of the addition of a surfactant (lecithin) on the adhesion force (red) and adhesion energy (blue) between a glass spherical particle and a glass flat surface in oil mediated by a glycerol bridge. Both adhesion force and energies are normalized with the glass spherical particle radius. (Force curve parameters: set-point load force of 500 nN, speed 10 μ m/s and delay time of 10s between approach and retract).

The addition of lecithin resulted in a very different shape of the force curves between a glass particle and a glass surface. The long range adhesion, large rupture distance and jump-in on approach characteristic of force curves mediated by glycerol bridges in oil was not observed for the systems with added surfactant (Figure 7-11). In contrast, force curves in oil media containing lecithin showed a certain level of repulsion on approach of the surfaces and a very steep short-ranged adhesion. This suggests that the addition of lecithin did not enable the formation of a large or multiple liquid bridges. It was also observed during the experiments that the glycerol droplets were quite stable and could be squeezed between the colloidal probe and lower surface without collapsing. The phospholipid molecules can adsorb very strongly to the glycerol droplets and to the glass surfaces. This can create glycerol droplets which are very stable and would not readily coalesce and form liquid bridges between the particle and lower surface. The sharp adhesion forces observed for the systems containing lecithin could be related with the formation of tiny liquid bridges in patches that the surface is not covered by the surfactant caused by micro-asperities, for example.



Figure 7-11. Characteristic force curves between a glass sphere and a glass flat surface on top of a droplet at glycerol in oil with different concentrations of lecithin (none – purified oil; 0.1 %wt and 0.5 %wt). The approach of the cantilever towards the surface is shown in red and the retraction is shown in blue. (Force curve parameters: set-point load force of 500 nN, speed 10 μ m/s and delay time of 10s between approach and retract).

It is important to point out that the magnitude of the force curves should not be overanalysed because the volume of the glycerol droplets was not the same for the different conditions due to experimental limitations.

Finally, this difference in interparticle interactions and lower adhesion energies in systems containing surfactant are in agreement with the results of rheological behaviour shown in Section 5.3.5; where it was shown that the addition of a surfactant result in lower apparent viscosities in suspensions of hydrophilic particles (sugar and glass) in oil with added glycerol.

7.3.3 Sugar colloidal probe

So far, the interactions between glass surfaces (a glass particle and a glass slide) inside oilcontinuous media have been discussed and surface forces have been experimentally determined with an AFM. These model systems are interesting due to their inert character; however, in the food industry, particles are virtually never inert.

Therefore, a sugar colloidal probe (i.e. sucrose particle glued to a cantilever) was produced. The sugar particle production is described in the Materials & Methods part (Section 7.2). The effect of relative humidity (RH) on the sugar particle (Figure 7-12) and on its adhesion with a flat glass surface was evaluated.



(g) 02h:50min

(h) 04h:30min

(i) 26h:15 min

Figure 7-12. Sugar colloidal probe in oil at increasing and decreasing relative humidity (from 0% to 70% RH followed by 70% to 0% RH). At 0h:00min (a) the humidity was changed to 70%. The equipment takes few minutes to stabilize at the set relative humidity. Pictures (b) to (h) show the changes in the particle shape upon this increase in RH. After 16h (picture not shown) the relative humidity was changed back to 0% and the final image (i) is taken when assumed equilibrium was achieved (no further visual changes were observed).

One can observe in Figure 7-12 (a) that the sugar particle at 0 %RH is spherical and, therefore, it is in the amorphous state since sucrose cannot exist as a single crystal in the spherical shape as it crystallizes in a monoclinic structure (Vaccari and Mantovani (1995), Figure 3-2, Section 3.1.2). This can also be observed in the SEM image of a similar sugar colloidal probe in Figure 7-13. The surface of the spherical sugar particle was very smooth and no crystal nucleation points can be observed, indicating that the observed spherical particle is not an aggregate of smaller crystals. The crack on the sugar particle is an artefact of the SEM imaging, and due to the sensitive nature of the sugar surface, it got "burned" by the high power of the electrons beam of the SEM.



Figure 7-13. SEM image of a sugar colloidal probe. The crack on the surface was caused by the high power (20 kV) of the electrons beam of the SEM – the surface of the sugar particle was very smooth.

By creating very small saturated sugar solution droplets (micrometre size range) inside dry oil (HOSO), a fast diffusion of water from the initial droplets to the oil occurred and, resulted in a very high concentration of sugar inside these droplets. At very high concentration, the viscosity increases dramatically, retarding mass transfer and consequently sucrose crystallization rates were reduced (Shastry and Hartel 1996).

Once the relative humidity was increased and, in turn, the water activity, the ad/absorption of water into the amorphous structure resulted in a decrease of the viscosity, which provided greater mobility to the sugar molecules enabling their reorganization and, depending on the glass transition temperature relative to the environmental temperature (Palzer 2011), consequent crystallization could occur (Mathlouthi 1995). This can be seen in the sequence of pictures shown in Figure 7-12. As the humidity was increased from 0% to 70%, a time-dependent process happened, resulting in a visual change in the shape of the sugar particle, indicating that crystallization was probably occurring. The humidity was not increased further because the deliquescence point of crystalline sucrose is at around 80%RH; i.e. capillary condensation of water occurs on the surface, dissolving the material on the surface (Yao, Yu et al. 2011, Dupas-Langlet, Benali et al. 2013).

Forces between the sugar colloidal probe and the glass surface inside oil were measured at these two different values for relative humidity (0% and 70%). The colloidal probe inside the oil phase was left at the specific relative humidity overnight (at least 10 hours) prior to the measurements to guarantee that the system was at equilibrium. The effect of relative humidity and also load force on the adhesion forces between a sugar colloidal probe and a flat glass surface is shown in Figure 7-14. The adhesion force is the maximum force observed upon disconnection of colloidal probe and glass surface inside the oil continuous media and the set-point load force is the force applied prior to disconnection. The results at 0% RH in Figure 7-14 were taken when the particle was still spherical (Figure 7-12 (a)).

At 0% RH (spherical sugar particle) the adhesion increases with the load force, suggesting that the amorphous sugar particle exhibits a viscoelastic behaviour. At the highest load force (700 nN) the possible deformation of the particle and formation of a larger contact area resulted in a larger adhesion force. The harder crystalline structure formed at 70 %RH results in adhesion forces that are independent of the load force, similarly to the results observed for glass surfaces (Section 7.3.1.3).



Figure 7-14. Effect offset-point load force on the adhesion force between a sugar colloidal probe and a flat glass surface in oil at different environmental conditions: 0 %RH and 70 %RH (probe speed was 0.5 μ m/s and the delay time 30s). The adhesion force is normalized in respect to the sugar spherical particle radius (~ 12.5 μ m).

7.3.4 Sugar surface

Due to the fact that sucrose deliquesces at around 80 %RH, , it was attempted to use binder liquids in which sucrose is poorly soluble (e.g. glycerol) in order to evaluate the formation of liquid bridges between a sugar particle and a sugar surface. For this, the method described in Section 6.3.2 where a dispersion of micron-sized droplets of glycerol in HOSO was used. However, due to the micrometre size of the sugar particle together with the fact that such oil dispersions are saturated with glycerol, resulted in the dissolution of the particle in the colloidal probe. Therefore, an alternative way to investigate the adhesion features of sugar was to measure force curves between a glass colloidal probe and a sugar surface. Flat sugar surfaces were produced according to the method described in Materials & Methods (Section 7.2) on the depression schematized in Figure 7-2. The general topography of the sugar surfaces is shown in the SEM images in Figure 7-15. The SEM images were taken after the surfaces were used for AFM measurements and cleaned with pure hexane. Surfaces are relatively rough and some cracks can be observed.



Figure 7-15. SEM micrographs of the used sugar surfaces. The surfaces were cleaned with pure hexane after the AFM measurements.

7.3.4.1 Forces between a glass colloidal probe and a sugar surface in pure oil

Adhesion forces between a glass spherical particle and a flat sugar surface in pure oil were taken at several different points on the surface (at least 5 per surface), and also the whole set-up was repeated for three different sugar surfaces at room conditions. Two characteristic force curves are shown in Figure 7-16.

When there was no delay between the approach and retract of the glass probe, the adhesion forces were generally low as shown in Figure 7-16. The fact that a small spike is observed for the adhesion force and that the baseline is not completely flat is attributed to the rough characteristic of the surface. When 10 s delay between approach and retract of the glass probe was utilized, very high magnitude but short ranged adhesion forces were obtained. The magnitude of the adhesion force varied depending on the point at the surface (from 200 nN to 1 μ N), but since the curves looked very similar they are not all shown. This behaviour is analogous to the observations for glass surfaces discussed in Section 7.3.1.2. It can be attributed to the roughness of the surface (shown in Figure 7-15). These irregularities, upon set-point load force application, would facilitate the drainage of the thin lubricating film of oil around the surfaces and capillary condensation due to traces of water could occur between the micro-asperities causing such strong adhesion as suggested by Banerjee, Mulder et al. (2012).



Figure 7-16. Characteristic force curves between a glass sphere and a sugar surface in purified oil.
(a) and (b) show force curves with different delay times between approach and retract of the spherical glass particle from the sugar surface. The relative set-point load force and speed were kept constant for all experiments and equal to 500 nN and 2 μm/s, respectively. The approach (extend) of the cantilever towards the surface is shown in red and the retraction is shown in blue.

7.3.4.2 Sugar surfaces in oil with glycerol droplets

In order to measure liquid bridge forces between a spherical glass probe and flat sugar surface, the method consisting of adding a dispersion of small glycerol droplets in oil to the AFM liquid cell was used (described in Section 6.3.2). Glycerol was used because sucrose has a limited dissolution in it (5.7 %wt). Due to the pattern of crystallization of the sugar surfaces and cracks on the surface, the visualisation of the glycerol droplets with the inverted microscope was hindered.

Since it was not possible to directly visualize the glycerol droplets, force curves were taken at several points on the sugar surface containing the dispersion of glycerol droplets and the shape of the curve was analysed. However, it is worth mentioning that, in some experiments, it was possible to focus the inverted microscope on an area of the sugar surface which was seemingly smoother, i.e. the image was less distorted and the surface was translucent. Once the dispersion of glycerol droplets in oil was added to the AFM cell and the glycerol droplets sedimented on sugar surface, it was noticed that the surface became rougher as seen through the optical microscope. This suggested that glycerol and sugar surface were interacting and possibly a limited dissolution of the surface into the glycerol droplet occurred.

7.3.4.2.1 Effect of delay time

Representative force curves between a glass colloidal probe and a sugar surface in oil containing glycerol droplets is shown in Figure 7-17. The shape of the curves were found to be very similar to the force curves between a glass colloidal probe and a flat glass surface in oil mediated by glycerol bridge as shown in previous chapters (see force curves in Sections 6.4.3.2 and 7.3.1). This similarity in the shape of the curves and strong long-ranged adhesion suggest the formation of a liquid glycerol bridge between the spherical glass particle and the sugar surface.

The effect of the delay time between approach and retract of the glass colloidal probe is also shown in Figure 7-17. Similarly to the results for glycerol bridges formed between glass surfaces (particle and flat slide; Section 7.3.1.2) the adhesion force and energies between a glass particle and a sugar surface have also shown a hysteretic nature and the dependence of the delay time. A delay time of 10 s (Figure 7-17b), if compared to no delay, resulted in larger adhesion forces. From Figure 7-17, the adhesion force with 10 s delay was about 20% higher than with no delay ($F_{adh} \approx 825$ nN for no delay and $F_{adh} \approx 975$ nN for 10 s delay).



Figure 7-17. Effect of delay on the adhesion on a spherical glass probe and a flat sugar surface (setpoint load force of 500 nN and speed of 2 μ m/s).

7.3.4.2.2 Effect of speed

The effect of the probe approach/retraction speed was also analysed. In Figure 7-18, characteristic force curves for a glass probe and a sugar surface in oil mediated by a glycerol droplet at different probe speeds are shown.

Similarly to the results obtained for glass surfaces (Section 7.3.1.1), the increase in speed resulted in larger adhesion forces indicating the input of a viscous dynamic contribution related to the high viscosity of the glycerol bridge to the total adhesion force. In addition, the same pattern on the effect of speed on the jump-in of the probe towards the surface and rupture distances was observed. At 2 μ m/s, a clear jump-in is observed at about 4 μ m from the sugar surface. At 10 μ m/s a repulsive force is observed prior to a jump-in at a closer distance to the surface (about 2 μ m); which is related to the repulsive force due to the hydrodynamic resistance of the oil phase and consequent deformation of the soft glycerol droplet interface. Finally, at 100 μ m/s, no jump-in was observed. Rupture distances also increased slightly with increases in speed, supporting the findings for glass surfaces that dynamic bridges have a longer neck and consequently longer rupture distances.



Figure 7-18. Characteristic force curves between a glass sphere and a sugar flat surface on top of a droplet at glycerol in oil at different speeds: (a) $2 \mu m/s$; (b) $10 \mu m/s$; (c) $100 \mu m/s$. The approach (extend) of the cantilever towards the surface is shown in red and the retraction is shown in blue.

7.3.4.2.3 Effect of volume

The effect of the volume of the glycerol bridge formed between a spherical glass particle and a sugar surface was analysed.

Since it was not possible to visualize the droplets with the inverted microscope, the equation for the volume of the drop (V_{drop}) considering it as spherical cap (Equation 6-11; Section 6.4.3.1) was modified to be given in terms of the contact angle (θ) formed by the glyc-

erol droplet on the sugar surface inside oil media using Equation 6-12 and geometrical relationships (Figure 6-17), as shown in Equation 7-1:

$$V_{drop} = \frac{\pi h_{drop}^3}{3} \left(\frac{2 + \cos \theta}{1 - \cos \theta} \right)$$
 Equation 7-1

Where h_{drop} is the height of the drop/spherical cap and, as described in Section 6.4.3.1, can be extracted from the AFM force curves as the jump-in distance, and the contact angle (θ) of glycerol on a sugar surface in oil is 33° as given in Table 7-1.

Force curves were taken at several different points on three distinct sugar surfaces where a glycerol liquid bridge between the glass colloidal probe and sugar surface was formed. The formation of the glycerol bridge was identified by the shape of the force curve (as in Figure 7-17 and Figure 7-18). The force curve experimental parameters were kept constant and equal to: set-point load force of 500 nN; speed of 2 μ m/s and delay time of 10s. The measurements were done in a controlled environment and the relative humidity was kept constant at 0%. The jump-in position was determined for at least 5 curves in each point on the surface and the volume of the drop was calculated according to Equation 7-1. In Figure 7-19 the adhesion force and adhesion energy (normalized by the glass particle size) are plotted as a function of the calculated volumes.



Figure 7-19. Effect of the volume of the bridge between a glass spherical particle and a flat sugar surface in oil on the adhesion force (red) and on the adhesion energy (blue). Both adhesion force and energy are normalized with the glass spherical particle radius. Error bars are given for both vertical and horizontal axis and represent a confidence interval of 95%.

From Figure 7-19 one can observe that the adhesion force seems not to be so dependent on the volume of the glycerol bridge, while the energy of adhesion increases with the volume. Such an observation is consistent with the results found for bridges formed by high viscosity liquid such as glycerol between a glass particle and a glass surface, as shown in Section 6.4.3.2. The high viscosity of the glycerol liquid bridge results in the viscous forces playing a dominant role in the total adhesion force, and, as shown in Equation 6-7 and Equation 6-8, the viscous contribution is less dependent of the volume of the bridge. The energy of adhesion, however, corresponds to the integration of the adhesion force over the separation distance between glass colloidal probe and sugar surface, i.e. the area below the baseline for the retraction part of the force curves. The larger the volume of the bridge, the larger the rupture distance will be. In addition, as previously discussed, viscous bridges form longer necks and display larger rupture distances, hence the dependence and increase of the adhesion energy with the volume of the bridge.

7.4 Conclusions

In this chapter, the effect of material parameters on the interaction forces between hydrophilic particle and surface was discussed.

The effect of the viscosity of the bridge formed between a glass particle and a glass surface in oil was analysed by varying the relative humidity in the liquid cell which in turn resulted in a change on the amount of water in the glycerol bridge and, consequently, different viscosities. It was shown that an increase in the probe retraction speed caused an increase in the adhesion force which was even higher and steeper for the anhydrous glycerol bridge (higher viscosity). In addition, the probe retraction speed strongly influenced the jump-in of the glass particle towards the surface and rupture distance of the bridge. These observations support the idea of a strong dynamic contribution due to the viscosity of the liquid bridge formed. Furthermore, it was shown that longer contact times between the particle and surface (delay time) have a significant impact on the adhesion forces which can be explained by the probable formation of a larger or multiple liquid bridges.

The effect of the addition of a surfactant, lecithin, was shown to decrease the magnitude of the forces in pure oil when a delay was applied. When forces were measured on top of glycerol droplets dispersed in oil containing lecithin, a very different shape for the force curves was noticed. The decrease in energy of adhesion provided evidence that the droplets of glycerol became stabilized with the surfactant and the formation of liquid bridges as in oil free from lecithin was not observed to the same extent.

The challenges involved in producing sugar colloidal probes were described and force curves were measured between a sugar colloidal probe and a flat glass surface in oil upon increase in relative humidity up to 70 %RH.

Finally, forces between a glass colloidal probe and a sugar flat surface in oil containing glycerol droplets dispersed in oil were evaluated. The shape of those force curves was very

similar to the ones between glass surfaces as well as the effect of delay time and speed on those. The adhesion force due to the glycerol liquid bridge formed was shown to be less dependent of the volume of bridge (as discussed in Section 6.4.3.2); while the energy of adhesion reflected the large rupture distances observed for viscous bridges.

Chapter 8

Conclusions & Future Work

In this work, the agglomeration of hydrophilic particles in oil-based systems was studied using model suspensions of sucrose and glass particles in vegetable oil upon the addition of an immiscible liquid (water, saturated sugar solution and glycerol). Such systems are especially appealing because they can be used as a model to investigate processes that are common in the food industry. In addition, since suspensions and pastes are common in many industries such as pharmaceutical, cosmetic and chemical to cite a few, the knowledge and conclusions from this work could easily be conveyed to other areas. A transition from a liquid-like to a solid-like macroscopic structure in suspension is observed upon the addition of an immiscible secondary liquid; which is related to the aggregation of particles through liquid bridges. Such systems were evaluated on both macro- and micro scales. This unique approach enabled a better understanding of the mechanisms driving particle agglomeration in model oil-based suspensions and also the effect of material parameters on them.

8.1 Macroscopic behaviour: Particle size and rheology

The transition of sugar and glass suspensions in oil upon the addition of water, glycerol and saturated sugar solutions from liquid-like to solid-like structure was observed macroscopically and the formation of liquid bridges was confirmed through optical microscopy.

Two methodologies were employed for the analysis of the network formed by the addition of a secondary immiscible liquid: particle size (laser diffraction) and viscosity (rotational rheometry) determination. An increase in viscosity upon the addition of the three different secondary liquids examined (water, glycerol and saturated sugar solution) was recorded for all the suspensions. Additionally, it was identified that above a certain amount of secondary liquid (Vr) the viscosity does not increase any further (a plateau was reached), and extra secondary liquid could also result in phase separation.

A difference in the behaviour between sugar and glass suspensions in oil upon the addition of water was discovered based on apparently contradicting experimental results. Sugar suspensions with added water showed the formation of agglomerates through particle size measurements and an increase in viscosity; while the agglomeration was not observed for glass suspensions. The hypothesis raised was that the dissolution of sugar within the bridge would result in a higher localized viscosity and possible recrystallization that in turn would yield stronger agglomerates which would resist dilution followed by mixing during the particle size measurements. The formation of some agglomerates in glass suspensions with added glycerol tested this hypothesis and gave an indication that very high viscosity binders create stronger bridges in highly dynamic situations.

Moreover, the effect of material parameters on the network formation was evaluated by analysing the flow behaviour of sugar and glass suspensions with and without the addition of a secondary liquid. The influence of particle size, shape, density, concentration as well as secondary liquid viscosity and wetting properties were evaluated and conclusions can be summarized as follows:

- Particle size: Suspensions with smaller particles resulted in a more pronounced viscosity increase. The larger total surface area of smaller particles enable the formation of more liquid bridges, hence the stronger network.
- Density: Up to the values tested, the density of the particles did not interfere with the network formation and stability during rheological experiments.
- Particle shape: Irregularly shaped particles promote a general increase in viscosity and, upon the addition of a secondary liquid, the formation of more bridges and a more robust network.
- Particle concentration: The flow behaviour of suspensions with and without added secondary liquid is influenced by the particle volume fraction with higher concentrations leading to larger apparent viscosity. However, the relative increase in viscosity upon addition of secondary liquid showed to be independent of particle concentration and can be attributed solely to the formation of liquid bridges.
- Viscosity and wetting properties of the secondary liquid: Glycerol/water mixtures were used as the secondary liquid in order to evaluate the influence of viscosity and wetting properties of the binder on the network formation. At low shear rates, suspensions with water-rich binders had a higher viscosity and, at high shear rates, the viscosity of suspensions with glycerol-rich binders showed an increase (to either the same or slightly higher value than for suspensions with water-rich binders). This phenomenon was explained in terms of the forces by the liquid bridges forming the network. At low shear rates, the contribution of the static capillary forces due to bridges formed by high interfacial tension liquids (water-rich binders) is dominant hence the higher viscosity. At higher shear rates, dynamic effects due to the high viscosity of glycerol bridges come into play and result in an increase in viscosity.

Presence of surfactants (lecithin): The addition of lecithin resulted in a decrease in viscosity for sugar-and-glass suspensions related to the lower capillary force of the bridges due to the reduction of the glycerol-oil interfacial tension by lecithin. In addition, the formation of stable droplets of secondary liquid in the oil due to the adsorption of lecithin on the interface of the two liquids could hinder the formation of liquid bridges. Those factors together would then result in a weaker network and lower viscosity. Finally, the increase in viscosity for the glass suspension with added glycerol in a medium containing a high concentration of lecithin (0.2 %wt PL) was related to the non-adsorbed molecules of surfactant forming micelles in the continuous phase, since this concentration of lecithin was above the critical micelle concentration (CMC).

8.2 Microscopic behaviour: AFM

The interaction forces between a particle and a flat surface mediated by an immiscible secondary liquid in an oil medium were measured using the colloidal probe AFM technique. In order to enable the formation of liquid bridges between particle and flat surface two new methods were developed. One approach entailed the generation a water liquid bridge by increasing the relative humidity in the oil environment to the point water drop-lets condensed on the lower surface. The second approach consisted of creating a dispersion of small droplets of secondary liquid into the continuous phase. Consequently, a liquid bridge could be created by approaching the colloidal probe particle on top of such small droplet.

It was shown that when a secondary hydrophilic liquid was present, the adhesion forces between a glass particle and a glass flat surface in oil became stronger (larger magnitude) and longer-ranged if compared to adhesion forces in pure oil, indicating the formation of liquid bridges. The effect of relative humidity on the adhesion between a glass particle and a glass surface in oil was also studied. Up to very high values of relative humidity (90-95 %RH), no changes in adhesion were registered. However, above the saturation point (100 %RH), an increase in adhesion forces indicated the formation of water bridges in the studied ternary systems.

The effect of the properties of the binding liquid on the adhesion forces between a particle and a surface inside oil was also investigated. It was demonstrated that forces between hydrophilic glass surfaces inside oil are dominated by capillary attraction when liquids of high interfacial tension and low viscosity such as water form a liquid bridge. When a highly viscous liquid forms the bridge, a dynamic viscous interaction contributes to the adhesion leading to higher maximum adhesion forces, which is less dependent on the volume of the bridge. The challenges involved in producing sugar colloidal probes were described and force curves were measured between a sugar colloidal probe and a flat glass surface in oil upon increase in relative humidity up to 70 %RH so that the sugar particle would not reach the deliquescence point. A sugar flat surface was used in order to produce systems which are more relevant to food materials. The shape of force curves between a glass particle and a sugar surface inside oil mediated by a glycerol bridge was very similar to the ones between glass surfaces. The adhesion force due to the glycerol liquid bridge formed was shown to be less dependent on the volume of the bridge; while the energy of adhesion reflected the large rupture distances observed for viscous bridges.

Furthermore, the effect of material parameters on the interaction forces between hydrophilic particle and surface in oil upon the addition of a secondary liquid was discussed and can be summarized as follows:

- Viscosity and wetting properties of the secondary liquid: by controlling the relative humidity of the system, the amount of water in the glycerol droplets dispersed in oil could be controlled, and used to create liquid bridges of different properties between a glass particle and surface. It was shown that an increase in the probe retraction speed caused an increase in the adhesion force which was even higher and steeper for the bridges formed by highly viscous liquids (anhydrous glycerol). In addition, the probe retraction speed strongly influenced the jump-in of the glass particle towards the surface and rupture distance of the bridge. These observations support the strong dynamic contribution due to the viscosity of the liquid bridge formed. Furthermore, it was shown that longer contact times between the particle and surface (delay time) have a significant impact on the adhesion forces which can be explained by the probable formation of a larger or multiple liquid bridges.
- Presence of surfactants (lecithin): The magnitude of the forces between a glass particle and a surface in pure oil decreased when lecithin was present. Additionally, very different shape of force curves were obtained when interactions were measured on top of glycerol droplets dispersed in oil containing lecithin. The significant decrease in energy of adhesion gives evidence that the droplets became stabilized by the surfactant and the formation of liquid bridges to the same extent as in lecithin-free oil was not observed.

8.3 Parallels between macroscopic and microscopic behaviour

By evaluating the network formation on a macroscale and also the interaction surface forces on a microscale, a better understanding of the phenomena involved could be built.

In Chapters 4 and 6, the effect of the addition of different secondary liquid (water, glycerol and saturated sugar solution) on the interactions of glass particles/surfaces in oil media was explained on a macro and a microscale, respectively. The strong and long-ranged adhesion forces measured by AFM when the contact of a particle and a surface in oil was mediated by water or glycerol droplets explain the macroscopic behaviour of increase in viscosity and agglomerate formation in analogous suspensions. Moreover, the behaviour where a shift from liquid to solid is observed in saturated sugar solution droplets in oil upon change of environmental conditions on a microscale (AFM) is likewise noticed on the formation of aggregates in sugar suspensions in oil with added water.

In Chapters 5 and 7, a similar study was made in a macro and microscopic approach by evaluating the effect of material parameters. The effect of the viscosity, the wettability of the secondary liquid and the addition of lecithin were analysed using exactly the same materials as for the evaluation of flow behaviour (macro) and the determination of the force curves using the AFM (micro). The observed dynamic contribution to the adhesion force when highly viscous secondary liquid (glycerol-rich binders) at high separation speeds were used can also be related to the increase in viscosity for suspensions with similar binders at elevated shear rates; when dynamic contributions start to become relevant. Finally, the addition of lecithin showed very comparable results both on macro and micro scales. The stabilization of secondary liquid droplets by the surfactant leading to decreased adhesion energies explain the lower viscosities in suspensions of particles with added glycerol containing surfactant.

8.4 Future Work

In the light of the results obtained and the conclusions drawn in the present thesis, suggestions for future work and research can be proposed.

The force curves between particles and surfaces measured with the AFM were thoroughly discussed based on the theory existent for forces due to liquid bridges, and a parallel was built with the macroscopic behaviour. The theoretical force curves could be modelled based on the existent theory and validated with the experimental results. Calculations considering capillary and viscous forces due to the liquid bridge between flat surfaces were initiated (Appendix III), however, the incorporation of the effect of the hydrody-namic resistance due to the oil continuous phase and slip of the contact line of the bridge should be incorporated, as well as the consideration of particle-surface geometry and roughness. In addition, in order to build a direct link of microscopic (interparticle forces) and macroscopic (flow properties and agglomerate formation) behaviours, a model based on the work of Washino (2011) using computational fluid dynamics (CFD) and discrete element modelling (DEM) could be built. The results of such model could be validated based on the results obtained experimentally in the present work.

The method described in this work which enabled the measurement of forces due to liquid bridges of different binging liquids could be used with a variety of colloidal probes and surfaces. In Section 7.3.3, it was identified that food particles such as sugar can exhibit different behaviours depending on the state of the material. Viscoelasticity and deformation of particles and the modelling of the kinetics of the dissolution of the particle material into the bridge are topics which could be further investigated by using the experimental approaches developed in this thesis.

In addition, since food materials are usually complex systems containing different components, it would be interesting to study the interactions mediated by liquids bridges for other materials (e.g. with different wetting properties, different solubility levels, etc.) as well as for oil-based systems composed of more food particles such as lactose, maltodextrin, cocoa to name a few.

The work from Babin (2005) has pointed that there are differences in the behaviour of food model suspensions made with different fat materials (different triacylglycerol composition). Due to the large number of variables analysed in the present work, the continuous phase used was fixed as sunflower oil. Therefore, the investigation of forces due to the formation of liquid bridges with the AFM in different fat continuous media could be an interesting study.

During the mixing of the different secondary liquids into the glass and sugar suspensions it was noticed that the transition from liquid to solid-like behaviour was a dynamic process and the time for the transition was dependent on the secondary liquid used. The complete investigation of these dynamics could be an appealing area for further research. In addition, once the network of agglomerated particles is formed, migration or movement of the secondary liquid through different mechanisms such as diffusion or capillary transport could occur.

In the present work it was also shown that the addition of lecithin has a very strong effect on the interactions in the studied systems which are also highly dependent on the concentration of the surfactant. Using the methods developed in this work, the effect of the addition of different concentrations of lecithin as well as the use of different surfactants could be analysed. In the food industry, surfactants such as PGPR, monoolein, individual phospholipids, among others are also used. Their very different chemical composition and adsorption pattern could result in different effects on the network formation and interparticle forces. In addition, in parallel with such evaluation, it would be interesting to measure the adsorption of the surfactants at the different particles interface in order to identify and calculate if an incomplete layer, monolayer or double layer of surfactant adsorbs at the interface using the methods described in Johansson and Bergenståhl (1992).

Notation

a	Activity [-]
A_c	Surface area per hydrocarbon chain [m ²]
$A_{\rm H}$	Hamaker constant [J]
A_P	Projected area of the particle $[m^2]$
\mathbf{a}_{W}	Water activity [-]
$c^0_{\ B}$	Saturation concentration [mol/m ³]
$c_{\rm B}$	Concentration of molecules of liquid B in the A-rich phase [mol/m ³]
Ca	Capillary number [-]
CD	Drag coefficient [-]
d	Half distance between plates (liquid bridges) [m]
D	Separation distance between particle and surface and between plates [m]
D*	Separation between tip and sample (AFM) [m]
D _{10,3}	Percentile PSD parameter (volume-based size which 10% of the PSD lies below) [m]
D _{50,3}	Median; Percentile PSD parameter (volume-based size which 50% of the PSD lies below) [m]
$D_{90,3}$	Percentile PSD parameter (volume-based size which 90% of the PSD lies below) [m]
D_P	Particle diameter [m]
F	Force [N]
$\mathbf{F}_{\mathrm{adhesion}}$	Adhesion force [N]
$\mathbf{F}_{\mathrm{bridge}}$	Total liquid bridge force [N]
$\mathbf{F}_{\mathrm{cap}}$	Capillary (or meniscus) force [N]
$\mathbf{F}_{\mathrm{cap,gorge}}$	Capillary (or meniscus) force calculated as per the 'gorge method' [N]
$\mathbf{F}_{\mathrm{cap,boundary}}$	Capillary (or meniscus) force calculated as per the 'boundary method' [N]
$\mathbf{F}_{\mathrm{drag}}$	Drag force [N]
$\mathbf{F}_{\mathrm{grav}}$	Gravitational force [N]
$\mathbf{F}_{\mathbf{hydyn}}$	Hydrodynamic force [N]
$\mathbf{F}_{\mathrm{elet}}$	Electrical double layer forces [N]
$\mathbf{F}_{\mathrm{VdW}}$	van der Waals force [N]
$\mathbf{F}_{\mathbf{vis}}$	Viscous force [N]
\mathbf{F}_{γ}	Surface tension force [N]
$F_{\Delta P}$	Laplace pressure force [N]
g	Gravitational acceleration [9.81 m/s2]
G*	Complex shear modulus [Pa]
G'	Elastic or storage modulus [Pa]
G"	Viscous or loss modulus [Pa]

h'	Planck constant $[6.62607 \text{x} 10^{-34} \text{ J s}]$
$\mathbf{h}_{\mathrm{drop}}$	Droplet height [m]
Н	Plate thickness [m]
$H(r_w)$	Separation of the surfaces at the edge of the bridge [m]
\mathbf{k}_{B}	Boltzmann constant [$1.38065x10-23 \text{ J K}^{-1}$]
\mathbf{k}_{c}	Cantilever spring constant [N/m]
\mathbf{M}_{w}	Molecular weight [kg/mol]
n	Refractive index of a specific media [-]
$n_{\rm h}$	Number of hydrocarbon chains per molecule [-]
\mathbf{N}_{A}	Avogadro's number $[6.022 \times 10^{23} \text{ mol}^{-1}]$
Р	Actual vapour pressure of the curved bridge [Pa]
\mathbf{P}_{0}	Saturation vapour pressure over a planar liquid surface [Pa]
$q_{3,lg}$	Logarithmic volume weighted particle size frequencies [-]
Q_3	Cumulative volume size frequency [-]
$r_{1,}r_{2}$	Curvature radii of liquid bridge (Laplace equation) [m]
$\mathbf{r}_1, \mathbf{r}_2$	Curvature radii of liquid bridge (toroidal approximation) [m]
\mathbf{r}_{w}	Wetted radius of the particle/surface by the liquid bridge [m]
R	Particle radius [m]
$\mathbf{R}_{\mathrm{drop}}$	Droplet radius [m]
$\mathbf{R}_{\mathrm{eff}}$	Effective radius [m]
\mathbf{R}_{g}	Molar gas constant [8.314 J mol-1 K-1]
Re	Reynolds' number [-]
t	Time [s]
$\mathbf{t_s}$	Separation time [s]
Т	Temperature [K]
v _s	Separation speed / Probe separation or retraction speed [m/s]
$\mathbf{v}_{\mathrm{sed}}$	Sedimentation/ settling speed [m/s]
$\mathbf{V}_{\mathrm{bridge}}$	Volume of the liquid bridge [m ³]
V_{drop}	Droplet volume [m ³]
V_{m}	Molar volume of the liquid [m ³ /mol]
V_{p}	Particle volume [m ³]
Vr	Amount of secondary liquid added to the suspension (Vr = $V_{\rm secondary liquid}$ / $V_{\rm particles}$) [-]
V_{vdW}	van der Waals interaction energy [J]
W_{adh}	Work of adhesion [N/m]
$\mathbf{Z}_{\mathbf{e}}$	Deflection of the cantilever [m]
$\mathbf{Z}_{\mathbf{p}}$	Position of the piezo translator [m]

Greek characters

β	Half-filling angle [°]
γ	$Interfacial/surface\ tension\ [N/m]$

$\gamma_{\rm LL}$	Interfacial tension between the liquid phases [N/m]
γ_{so}	Interfacial tension between the solid surface and oil (liquid 1) [N/m]
$\gamma_{\rm SW}$	Interfacial tension between the solid surface and water (liquid 2) $[\rm N/m]$
γwo	Interfacial tension between the water (liquid 2) and oil (liquid 1) $[N/m]$
γ_{st}	Strain (relative deformation) [-]
Ϋ́	Shear rate [s ⁻¹]
$\Gamma_{\rm m}$	Surface excess monolayer [kg/m ²]
δ	Phase shift [°]
ΔP	Laplace pressure [Pa]
3	Dielectric constant for a specific material [-][relative to ϵ_{vacuum} =1]
η	Viscosity [Pa.s]
$\eta_{\mathbf{s}}$	Viscosity of the liquid continuous phase [Pa.s]
θ	Contact angle [°]
$\lambda_{\rm K}$	Kelvin length [m]
ν_{e}	Adsorption or resonance frequency [Hz]
ρ	Density [kg/m ³]
$\rho_{\rm P}$	Particle density [kg/m ³]
σ	Shear stress [Pa]
σ_y	Yield stress [Pa]

•	
φ	Volume fraction [-]

ሰ	Myimum	nacking	volume	fraction	[_]
φ_{max}	MAIIIIUIII	packing	volume	maculon	[-]

Abbreviations

AFM	Atomic Force Microscope
CMC	Critical Micelle Concentration (for surfactants)
HOSO	High-oleic sunflower oil
PGPR	Polyglycerol polyricinoleate (type of emulsifier)
$_{\rm PL}$	Phospholipids
PSD	Particle size distribution
MASIF	Measurement and analysis of surface interactions forces
MFB	Micro-balance balance
\mathbf{RH}	Relative Humidity
SEM	Scanning Electron Microscope
SFA	Surface Force Apparatus
SSA	Specific Surface Area
TAG	Triacylglycerols

List of Figures

Figure 2-1. Contact angle between a three-phase (liquid-liquid-solid) system. Interfacial
tensions between phases are indicated7
Figure 2-2. Contact angle on different surfaces; (a) ideally smooth surface (given by
Young's equation); (b) actual contact $angle(\theta_{ac})$ and (c) apparent contact $angle(\theta_{ap})$
(adapted from Charles-Williams (2007))
Figure 2-3. Proposed layering of anhydrous triolein molecules between hydrophilic mica
surfaces: (a) separation of 60-50 Å and (b) 30-20 Å. The calculated length of the triolein
molecule was approximately 27 Å (Claesson, Dedinaite et al. 1997)12
Figure 2-4. Scheme of the dimensions of a liquid bridge formed between two flat plates
(Cai 2008)
Figure 2-5. The effect of roughness on the formation of capillary bridges at different water
activities (or vapour pressure of condensing liquid) (adapted from Butt and Kappl (2009)).
Figure 2-6. Liquid states depending on the saturation of liquid binder (adapted from
Hapgood and Rhodes (2008))16
Figure 2-7. Tensile strength as a function of liquid saturation. $S_{\rm p}$ and $S_{\rm c}$ correspond to the
liquid saturation points where the states are changed from pendular to funicular and
from funicular to capillary, respectively (adapted from Schubert (1975) and Hapgood and
Rhodes (2008))17
Figure 2-8. Schematic of the contact between a sphere and a flat surface (a) rigid surfaces;
(b) elastically deformable surfaces under external compressive load F in the absence
(Hertz model) or presence (JKR model) of surface forces; (c) elstic adhering sphere upon
tensile load (-F) before disconnection from surface (Israelachvili 1985). In this figure, R
corresponds to the radius of the particle, K is the elastic moduli, a is the contact radius, δ
is the central displacement or indentation, γ is the surface energy
Figure 2-9. Velocity or deformation profile (shear flow) between an upper rotating plate
and a lower fixed plate separated by a defined gap. The upper plate moves with a speed v
in the x direction (adapted from Barnes, Hutton et al. (1989))
Figure 2-10. Flow curves (shear stress as a function of shear rate) for different systems
(adapted from Tadros (2010))

Figure 2-11. Typical hysteresis loop observed for materials with time-dependent flow behaviour - thixotropic and rheopectic samples (adapted from Barnes (2000) Barnes, Figure 2-12. Schematic of the surface force apparatus (SFA): (a) The measuring chamber with the detail of the arrangement of the silvered mica sheets; (b) Optical interferometry the white light passes through the mica sheets and the interference fringes (FECO) are analysed in a spectrometer, resulting in the distance H between the sheets; (c) The crossed-cylinder arrangement of the mica sheets (Claesson, Ederth et al. 1996, Dedinaite, Figure 2-13. Scheme of an AFM setup (adapted from Butt, Cappella et al. (2005))......29 Figure 2-14. Scheme of an AFM force measurement adapted from Butt and Kappl (2010). 30 Figure 2-15. Morphological map and ternary composition diagram (in volume fraction) for the system glass particles/ mineral oil/water. In the schematic drawing, the glass particles are represented by glass circles while the mineral oil is given in pink and the molecule conformation (α-D-glucopyranosyl-(1,2)-Figure 3-1. Sucrose β -Dfructofuranoside) (Asadi 2007)40 Figure 3-2. Sucrose crystal showing its eight most important faces (Vaccari and Mantovani 1995)......40 Figure 3-3. Phase equilibrium diagram sucrose-water (Bubník and Kadlec 1995)40 Figure 3-4. Viscosity of sugar solutions – dependence on solids concentration at 25 °C Figure 3-5. Example of the chemical structure of a triacylglycerol molecule, formed by three fatty acids attached to a glycerol molecule (McClements 1999)......42 Figure 3-6. Schematic examples of the structure of phospholipids as amphiphilic molecules and some of their possible configurations once associated into micelles, reversed micelles or bilayers (Adapted from Walstra and Vliet (2008) and McClements Figure 3-7. Serrated plates geometry used showing the detail of the serration......46 Figure 3-10. Purpose-built AFM setup consisting of a relative humidity and temperature Figure 4-1. SEM micrographs of the hydrophilic particles used: (a) solid glass spheres (b) icing sugar......54 Figure 4-2. Effect of water addition on fat-based suspensions - transition from a fluid-like to a solid-like behaviour is visible (weight percentages of water added are specified above

Figure 4-3. Effect of glycerol addition on fat-based suspensions
Figure 4-4. Glass suspensions in oil with different amounts of added glycerol after 1 day
storage at room conditions. The amount of added glycerol is stated below each picture
and it corresponds to Vr (as stated in Equation 3-1)
Figure 4-5. Glass and sugar suspensions in sunflower oil (HOSO) with and without added
water. Water was coloured with erythrosine and was added to the suspensions at Vr=0.02.
Figure 4-6. Volume weighted logarithmic size frequency $(q_{3,lg})$ for glass and sugar
suspensions in oil, with and without water addition (ratio of water is given as Vr)
Figure 4-7. Effect of water addition on the particle size distribution of sugar in oil
suspensions
Figure 4-8. Effect of glycerol addition on the particle size distribution of sugar-in-oil
suspensions
Figure 4-9. Comparative effect of water vs. glycerol addition in glass-in-oil suspensions60
Figure 4-10. Effect of prolonged impeller mixing on the particle size distribution of glass
be ad suspensions in oil with Vr= 0.1 glycerol added. The different runs correspond to the
approximate time the sample has been mixed (run 1 \approx 1 min; run 2 \approx 2.5 min; run 3 \approx 4
min)60
Figure 4-11. Steady state apparent viscosity curves for 40 %vol sugar in oil suspensions
with different amounts of added water (given as Vr). At Vr=0.1, large phase separation was
observed, therefore, the viscosity curve is not shown. Slip is observed for Vr=0.05 at high
shear rate values64
Figure 4-12. Steady state apparent viscosity curves for 40%vol glass in oil suspensions
with different amounts of added water (given as Vr)64
Figure 4-13. Steady state apparent viscosity curves for 40%vol sugar in oil suspensions
with different amounts of added saturated sugar solution (given as Vr). Slip is observed
for samples with Vr $\!\geq\! 0.05$ at higher shear rate values
Figure 4-14. Steady state apparent viscosity curves for 40%vol glass in oil suspensions
with different amounts of added saturated sugar solution (given as Vr)65
Figure 4-15. Steady state apparent viscosity curves for 40%vol sugar in oil suspensions
with different amounts of added glycerol (given as Vr)
Figure 4-16. Steady state apparent viscosity curves for 40%vol glass in oil suspensions
with different amounts of added glycerol (given as Vr)
Figure 4-17. Apparent viscosity curves for glass and sugar suspensions in oil at different
shear rates (0.1 s ⁻¹ , 1 s ⁻¹ and 10 s ⁻¹), as a function of the amount of secondary liquid (water,
saturated sugar solution and glycerol) added to the suspension

Figure 4-18. Apparent steady-state viscosity curves for glass suspensions plotted for different secondary liquids (water and glycerol) added to the suspension at two different Figure 4-19. Viscosity curves for 40 %vol glass-in-oil suspensions with added water Figure 4-20. Apparent viscosity for sugar and glass suspensions in oil with added glycerol (Vr=0.02) for increasing and decreasing shear rate ramps - hysteretic nature of the samples.....72 Figure 4-21. Schematic drawing for the possible phenomena occurring during particle size (a & b) and viscosity (c & d) measurements. In PSD experiments, the dilution of the suspension results in a dispersion of the particles hindering the re-formation of liquid bridges once ruptured. For sugar suspensions, the dissolution of sugar into the added water results in a local increase in viscosity within the bridge and possible recrystallization would create very strong agglomerates. In viscosity experiments, the high concentration of suspensions is kept constant and if bridges are ruptured due to the application of shear, they can be formed again due to the very close proximity of particles......73 Figure 5-1. Particle size distributions for icing sugar and glass particles –effect of PSD – (a)&(c) Volume weighted logarithmic size frequency $(q_{3,lg})$ for glass and sugar suspensions in oil; (b)&(d) cumulative distributions76 Figure 5-2. Particle size distributions for solid glass spheres, hollow glass spheres and glass grains. (a) Volume weighted logarithmic size frequency $(q_{3,lg})$ distribution (b) cumulative volume size distribution.....77 Figure 5-3. Diagram for water-glycerol mixtures showing the sorption isotherm (water activity vs. mass fraction of water in glycerol), viscosity and density dependence on the solution mass concentration at 25 °C [Data for the sorption isotherm of glycerol was provided by Nestlé Research Centre, Lausanne, Switzerland. The data for viscosity and Figure 5-4. Apparent viscosity curves for sunflower oil with different amount of lecithin Figure 5-5. Apparent viscosity curves for glass suspensions (40 %vol) of different size distributions (25-45 μ m/D_{50.3}= 35 μ m and 75-100 μ m/D_{50.3}= 78 μ m) in oil without and with Figure 5-6. Apparent viscosity curves for sugar suspensions (40 %vol) of different size distributions (25-45 μ m / D_{50.3}= 17 μ m and 75-100 μ m / D_{50.3}= 92 μ m) in oil without and with

Figure 5-8. Apparent viscosity curves for glass suspensions in oil at different volume particle concentrations (30%, 40%, 50%) without (Vr=0) and with glycerol addition Figure 5-9. Apparent viscosity curves for sugar suspensions in oil at different volume particle concentrations (30%, 40%, 50%) without (Vr=0) and with glycerol addition Figure 5-10. Effect of water/glycerol mixtures (Vr=0.02) on the apparent viscosity of glass in oil suspensions (40 %vol). The non-sieved spherical solid glass particles were used $(D_{50,3}$ = 41 µm). The correspondent relative humidity (or water activity) and viscosity for Figure 5-11. Effect of water/glycerol mixtures (Vr=0.02) on the apparent viscosity of sugar in oil suspensions (40 %vol). The non-sieved icing sugar particles were used ($D_{50.3}$ = 29 μ m). The correspondent relative humidity (or water activity) and viscosity for each waterglycerol mixtures is as given in Table 5-3.90 Figure 5-12. Fitting of Herschel-Bulkley model toglass-in-oil suspensions with added water/glycerol mixtures (as data in Figure 5-10). The raw data is shown with the symbols Figure 5-13. Fitting of Herschel-Bulkley model tosugar-in-oil suspensions with added water/glycerol mixtures (as data in Figure 5-11). The raw data is shown with the symbols Figure 5-14. Herschel-Bulkley yield stress (σyHB) of sugar and glass suspensions in oil as a function of the amount of water in the secondary liquid. Particle volume fraction was ϕ = 0.4 and the amount of secondary liquid was Vr=0.02......92 Figure 5-15. Effect of the addition of lecithin (given in terms of phospholipids – PL – concentration) to the glass suspensions in oil (40 %vol) without (Vr=0) and with (Vr=0.02) the addition of glycerol. The non-sieved spherical solid glass particles were used ($D_{50.3}$ = 41 Figure 5-16. Effect of the addition of lecithin (given as the concentration of PL) to the apparent viscosity of sugar suspensions in oil (40 %vol) without (Vr=0) and with (Vr=0.02) Figure 6-1. Schematic diagram of a liquid bridge between a spherical particle and a flat surface inside oil media and the toroidal approximation which considers the bridge as arcs of a circle (adapted from (Butt and Kappl 2009, Butt and Kappl 2010)).....100 Figure 6-2. Colloidal probe - glass particle attached to a tipless cantilever (in this example, the particle diameter is approximately 18 µm).103

Figure 6-3. Scanning electron micrograph (SEM) of an AFM colloidal probe: glass sphere (~28 µm diameter) glued to the tip of a cantilever (a) and detail of the glass sphere (b). The image was taken after the probe was used and cleaned with hexane and ethanol to remove excess oil......104 Figure 6-4. Schematic of a force measurement sequence with the AFM (drawings are not to Figure 6-5. Example force curves between a glass particle and a glass surface in purified high-oleic sunflower oil. Approach (red) and retraction (blue) curves are shown. The maximum adhesion force is given as the minimum on the retraction curve.106 Figure 6-6. AFM surface topography of the glass surface used and the calculated roughness for an area of 5 μ m². The average roughness is the arithmetic mean of the absolute height values while the root mean square (RMS) roughness consists of the mean squared absolute height values of the surface. The peak-to-valley roughness considers the maximum distance between the highest peak and the lowest valley within the area of the Figure 6-7. Adhesion force between a spherical glass particle and a flat glass surface in oil normalized by particle radius as a function of the relative humidity in the AFM liquid Figure 6-8. Optical micrographs of the glass colloidal probe in a liquid cell at (a) 75% relative humidity and at (b/c) saturation humidity (around 100%). The picture (b) shows the smaller drop used (condensed water droplet 1 of about 12 µm of diameter) and (c) shows the smaller drop (condensed water droplet 2 of around 18 µm). The dimension of the droplets is expressed in terms of its diameter, however, one has to take into consideration that since the contact angle of water on glass is quite low (40°) the actual height of the drop cap is very small......109 Figure 6-9. Force-distance curves between a glass colloidal probe and a glass surface inside sunflower oil on: (a) condensed water droplet 1 (~12 µm diameter) and (b) condensed water droplet 2 (~18 µm diameter); with a load force of 500 nN. The spherical glass particle used for those curves had approximately 18 µm diameter. The red curve corresponds to the approach of the cantilever towards the surface and the blue curve its retraction away from the sample.....110 Figure 6-10. Characteristic force-distance curves between a glass particle (≈ 20 µm diameter) and a glass surface in different environmental conditions and continuous media. Note that the scale of both axes for graphs (c) and (d) are different from graphs (a) and (b) due to the magnitude of the forces. The insets in graphs (c) and (d) show the detail of the force curves and the adhesion. 111
Figure 6-11. Adhesion force between a glass colloidal probe and a flat glass surface as a function of the relative humidity in air as a continuous medium. The adhesion force is normalized in relation to the radius of the spherical glass particle......112 Figure 6-12. Adhesion energy between a glass colloidal probe and a glass slide as a function of the relative humidity in two different continuous media: air and oil (HOSO). The adhesion energy is normalized in relation to the radius of the spherical glass particle. Figure 6-13. Agglomeration of glass particles suspended in sunflower oil upon increase in relative humidity from 0% to 100% over time. A 50 μm scale bar is shown in the first image (0 min, bottom right corner).....115 Figure 6-14. Agglomeration and/or water distribution in different areas of the liquid cell containing glass particles suspended in sunflower oil at 100% relative humidity. A 50 µm scale bar is shown at the bottom right corner in (a).....116 Figure 6-15. AFM cantilever immersed in a dispersion of water droplets in sunflower oil. The droplets indicated by the arrows correspond to the ones that were used for the forcedistance measurements (shown in Figure 6-16).116 Figure 6-16. Characteristic force curve between a spherical glass particle ($\approx 28 \ \mu m$) and a flat glass surface inside sunflower oil in the presence of water. Approach (red) and retraction (blue) curves are shown. The maximum adhesion force is given as the minimum on the retraction curve, and the adhesion energy corresponds to the grey area below the baseline......117 Figure 6-17. Schematic for the approximation of the secondary liquid droplet as a spherical cap and dimensions used for the calculation of the volume (for $\theta < 90^{\circ}$)......119 Figure 6-18. AFM cantilever immersed in a dispersion of glycerol droplets in sunflower oil. The droplets indicated by the arrows correspond to the ones that were used for the force-Figure 6-19. Characteristic force-distance curve between a spherical glass particle (~ 28 μm) and a flat glass surface inside sunflower oil in presence of glycerol (Glycerol droplet 1 - Figure 6-18a; Glycerol droplet 2 - Figure 6-18b). Approach (red) and retraction (blue) curves are shown. The maximum adhesion force is given as the minimum on the retraction curve, and the adhesion energy corresponds to the grey area below the baseline. Slopes of the curves are also indicated.....120 Figure 6-20. AFM colloidal probe (glass particle diameter ~24 µm) immersed in the oil continuous phase containing dispersed droplets of saturated sugar solution (blue Figure 6-21. Characteristic F/D curves between a glass particle ($\approx 24 \ \mu m$) and a glass surface with different saturated sugar solution droplets between them, inside an oil

continuous media at ambient conditions (25 °C and 40-60% RH). The approach of the glass

colloidal probe towards the surface (red curve) and its retraction from the surface (blue curve) are shown. The adhesion force is given as the minimum on the retraction......124 Figure 6-22. Typical F/D curve between a glass particle ($\approx 24 \,\mu m$) and a glass surface with a saturated sugar solution droplet between them, inside an oil continuous media at 95% Figure 7-1. Scanning electron micrograph (SEM) of AFM glass colloidal probes: (a) glass sphere with $\sim 19 \mu m$ diameter; (b) glass sphere with $\sim 18 \mu m$ diameter. The images were taken after the probes were used for AFM experiments and cleaned with hexane and Figure 7-2. Schematic drawing of the depression created on a glass cover slip with a rubber seal in order to create a thin sugar surface......129 Figure 7-3. Glycerol droplets in oil upon increasing humidity imaged with an inverted optical microscope......131 Figure 7-4. Glass colloidal probes immersed in dispersions of glycerol droplets in oil at 60% relative humidity. The droplets indicated with the arrows correspond to the ones Figure 7-5. Characteristic force curves between a glass sphere and a glass flat surface on top of a droplet of glycerol in oil at different relative humidity values. The curves for different probe retraction speeds (2, 10 and 100 μ m/s) are plotted. Settings used were 10 s delay and 500 nN set point load force. The approach of the cantilever towards the surface is shown in red and the retraction is shown in blue......134 Figure 7-6. Effect of relative humidity and consequently viscosity of the liquid bridge (glycerol-water mixtures) in the adhesion force of a glass spherical particle and a flat glass surface in oil as a function the speed of retraction – drop of approximately 22 µm Figure 7-7. Effect of the delay between approach and retraction of the glass sphere from different environments the flat glass surface on the adhesion force in Figure 7-8. Effect of the set-point load force on the adhesion force (red) and adhesion energy (blue) between a glass spherical particle and a glass flat surface in oil mediated by a glycerol bridge at 60 %RH (drop 2 in Figure 7-4 (b)) with a speed of 100 μ m/s and 10 s delay time between approach and retract. Both adhesion force and energies are normalized with the glass particle radius......138 Figure 7-9. Adhesion force between a glass colloidal probe and a flat glass surface in oil containing different concentrations of lecithin phospholipids and the effect of delay between approach and retract (Force curve parameters: set-point load force of 500 nN,

Figure 7-10. Effect of the addition of a surfactant (lecithin) on the adhesion force (red) and adhesion energy (blue) between a glass spherical particle and a glass flat surface in oil mediated by a glycerol bridge. Both adhesion force and energies are normalized with the glass spherical particle radius. (Force curve parameters: set-point load force of 500 nN, speed 10 µm/s and delay time of 10s between approach and retract).141 Figure 7-11. Characteristic force curves between a glass sphere and a glass flat surface on top of a droplet at glycerol in oil with different concentrations of lecithin (none - purified oil; 0.1 %wt and 0.5 %wt). The approach of the cantilever towards the surface is shown in red and the retraction is shown in blue. (Force curve parameters: set-point load force of 500 nN, speed 10 µm/s and delay time of 10s between approach and retract)......142 Figure 7-12. Sugar colloidal probe in oil at increasing and decreasing relative humidity (from 0% to 70% RH followed by 70% to 0% RH). At 0h:00min (a) the humidity was changed to 70%. The equipment takes few minutes to stabilize at the set relative humidity. Pictures (b) to (h) show the changes in the particle shape upon this increase in RH. After 16h (picture not shown) the relative humidity was changed back to 0% and the final image (i) is taken when assumed equilibrium was achieved (no further visual changes were observed)......143 Figure 7-13. SEM image of a sugar colloidal probe. The crack on the surface was caused by the high power (20 kV) of the electrons beam of the SEM – the surface of the sugar particle Figure 7-14. Effect offset-point load force on the adhesion force between a sugar colloidal probe and a flat glass surface in oil at different environmental conditions: 0 %RH and 70 %RH (probe speed was 0.5 μ m/s and the delay time 30s). The adhesion force is normalized Figure 7-15. SEM micrographs of the used sugar surfaces. The surfaces were cleaned with pure hexane after the AFM measurements......146 Figure 7-16. Characteristic force curves between a glass sphere and a sugar surface in purified oil. (a) and (b) show force curves with different delay times between approach and retract of the spherical glass particle from the sugar surface. The relative set-point load force and speed were kept constant for all experiments and equal to 500 nN and 2 μ m/s, respectively. The approach (extend) of the cantilever towards the surface is shown in red and the retraction is shown in blue.....147 Figure 7-17. Effect of delay on the adhesion on a spherical glass probe and a flat sugar surface (set-point load force of 500 nN and speed of 2 µm/s).149 Figure 7-18. Characteristic force curves between a glass sphere and a sugar flat surface on top of a droplet at glycerol in oil at different speeds: (a) $2 \mu m/s$; (b) $10 \mu m/s$; (c) $100 \mu m/s$. The approach (extend) of the cantilever towards the surface is shown in red and the

retraction is shown in blue......150

List of Tables

Table 2-1. van der Waals interactions free energies between bodies of different geometries
(Israelachvili 1985, Butt and Kappl 2010)10
Table 3-1. Specification of the lecithin used (Topcithin® SF) provided by the supplier
(Cargill, Netherlands)44
Table 4-1. Summary of materials used for experiments in this chapter
Table 4-2. Liquid properties (25 $^\circ\mathrm{C}$)
Table 4-3. Percentile PSD parameters for sugar and glass suspensions in HOSO with and
without water addition (D $_{10,3}$, D $_{50,3}$ and D $_{90,3}$ are given in μ m)
Table 5-1. Percentile PSD parameters for the different fractions/class sizes of sugar and
glass particles used (D $_{10,3},$ D $_{50,3}$ and D $_{90,3}$ are given in μm)
Table 5-2. Glass particles used for the evaluation of particle shape and density. SEM
micrographs, densities and percentile PSD parameters ($D_{10,3}$, $D_{50,3}$ and $D_{90,3}$) are also given
for each material77
Table 5-3. Water-glycerol mixtures used and their respective water activity, volume and
mass fractions of water, density and apparent viscosity at 25 $^\circ\mathrm{C}$
Table 5-4. Interfacial/Surface tensions (mN/m) for different systems
Table 6-1. Maximum adhesion force, adhesion energy, droplet height and volume, rupture
distance and calculated contact angle for the different water droplets measured with
AFM118
Table 6-2. Maximum adhesion force, adhesion energy, droplet height and volume, rupture
distance and calculated contact angle for the different glycerol droplets121
Table 7-1. Apparent contact angles (°) for three-phase systems 130

References

Adams, M. J., S. A. Johnson, J. P. K. Seville and C. D. Willett (2002). "Mapping the influence of gravity on pendular liquid bridges between rigid spheres." Langmuir **18**(16): 6180-6184.

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Appendix I.

Interfacial properties measurement

I.1. Introduction

As mentioned in the literature review (Section 2.2) and throughout this thesis, in the ternary systems studied, the interactions between the different phases are key to understand the macroscopic behaviour hence the importance of studying the interface phenomena.

Therefore, in this appendix the measurement of the interfacial properties (interfacial tensions and contact angles) of the systems studied are detailed.

I.2. Materials

The materials used are the same as described in Chapter 3.

For contact angle measurements of different secondary liquids on sugar in oil, two different sugar surfaces were used: (1) candy sugar (Südzucker AG, Mannheim, Germany; Figure I-1) and (2) the sugar surfaces produced by crystallization on a glass slide (method described in Section 7.2). Those large single sucrose crystals (candy sugar or lump sugar) are produced via cooling crystallization of sucrose solutions (Asadi 2007).



Figure I-1. Large single sugar crystals - candy (or lump) sugar

I.3. Methods

The methods for the measurement of interfacial tension and contact angle are described in Sections 3.2.4 and 3.2.5.

I.4. Detailed Results

I.4.1. Interfacial tension

The determination of interfacial tensions of the systems studied is of importance because, as shown in Section 2.3.5.1, they play a major role in the formation of liquid bridges. Therefore, the interfacial tensions of water-HOSO and glycerol-HOSO were determined.

Figure I- 2 shows the interfacial tension measured with the pendant drop method for water and HOSO. A relatively low interfacial tension for the commercially available HOSO was observed, and also a considerable reduction of the interfacial tension with time. This is because commercially available oils may naturally contain considerable amounts of minor components such as free fatty acids and phospholipids which may act as surfactants and considerably reduce the interfacial tension when adsorbed on the surface (O'Brien 2004). As one can observe from Figure I- 2, the purification of the oil had a significant impact on the interfacial tension of HOSO with water.



Figure I-2. Interfacial tension between water and HOSO - commercial and purified samples

If one considers the formation of a water liquid bridge between two sugar particles, it is expected that some dissolution of sugar can occur. One can assume that the sugar would dissolve until saturation is reached within the bridge. The interfacial tension is directly related to the strength of the liquid bridge. Taking this into account, the interfacial tension between the saturated sugar solution and high oleic sunflower oil (HOSO) was measured and compared with the interfacial tension between water and HOSO. In addition, the effect of surfactant addition was evaluated (Figure I- 3).



Figure I-3. Interfacial tension between purified HOSO and water/saturated sugar solution, with and without lecithin addition.

Saturated sugar solution has a lower interfacial tension than water with purified HOSO (about 7%) (Figure I- 3). The addition of surfactant, even in small quantities (0.17 %wt), resulted in a substantial reduction of the interfacial tension to the point that the pendant droplets of both saturated sugar solution and water detached from the needle. Therefore, the addition of surfactant can be used in the later stages of this project to evaluate the effect of interfacial tension on bridge and network formation.

The summarized results for interfacial/surface tensions for the different systems studied was presented in Table 5-4 (Section 5.2.5) and is repeated below for ease of referencing (Table I- 1):

		HOSO		Aim			
	$0 \$ wt PL	$0.05~\%{ m wt~PL}$	PL 0.25 %wt PL				
Water	26.4 ± 0.1	11.3 ± 0.1^1	10.94 ± 1.0^1	72.0 ± 0.2			
Saturated sugar solution	25.1 ± 0.2	13.8 ± 0.1^1	14.0 ± 0.8^{1}	78.3 ± 0.9			
Glycerol	17.7 ± 0.5^2	11.0^{2}	11.0^{3}	64.7 ± 0.2			
Air	32.2 ± 0.3	32.2 ± 0.4					

Table I-1. Interfacial/Surface tensions (mN/m) for different systems

¹ taken as the average of the last five values for the interfacial tension before the rupture of the pendant drop

 2 values measured at the Nestlé Research Centre in Lausanne with Wilhelmy plate technique (Lazghab et al., 2005). The value for the interfacial tension between glycerol and HOSO with 1% lecithin is the value before the lamella rupture.

 3 Since the interfacial tension values of the other two liquids (water & saturated sugar solution) with oil containing 0.5 %wt lecithin is practically the same as with the oil with 0.1 %wt lecithin, for practical reasons, the interfacial tension for glycerol/oil 0.5 %wt lecithin was be considered to be 11 mN/m.

I.4.2. Contact angle

Contact angles of droplets of water and glycerol on sugar and glass surfaces inside oil (HOSO) were measured. A typical curve for the contact angle of water on sugar in oil versus time is shown in Figure I-4.



Figure I- 4. Contact angle of a water droplet on top of a large sugar crystal inside purified HOSO over time

It was observed that the droplet of water would repose on top of the surface (glass or sugar) and once the thin film of oil between the sessile drop and surface was drained, the secondary hydrophilic liquid would wet the surface. The spreading of the droplet was observed and, for the case of glass surfaces a clear equilibrium contact angle was observed (data not shown). For the case of sugar, however, some dissolution of the surface into the secondary liquid or some possible penetration of the secondary liquid in cracks on the surface resulted in a slight decrease of contact angle over time, as seen in Figure I- 4. The contact angle value was considered to be close to equilibrium, which, in the case shown in Figure I- 4, corresponded to the last 40s of the measurement.

The results obtained for the contact angles of the different ternary systems used are summarized in Table I-2.

	1 able 1-2. Contact angles () for three-phase systems							
		Continuous media						
		HOSO Air						
			Saturated					
	Droplet	Water	sugar solution	Glycerol	Water			
	Glass	39	40	64	20			
Flat	Sucrose surface (on glass slide)	10	12	33	5			
surface	Large sugar crystal	16		49				

It is interesting to notice that the contact angles measured for the two types of sugar surfaces differ slightly – the contact angles for water and glycerol on the large sugar surface were marginally higher than for the thin sugar surface produced by crystallization on a depression on a glass slide. This can be related with the different roughness of the surfaces.

Although contact angle measurements might seem quite simple, it is in fact a rather complicated technique depending on the system studied. It is well documented that surface roughness has a vast impact on the contact angles and also several models have been developed to account for the effect of surface roughness (Adamson and Gast 1997). Therefore, several attempts were made in order to produce smooth sugar crystalline surfaces. Detailed information is given in Appendix II. In short, the production of thin sucrose films and the treatment of commercially available sucrose large single crystals were evaluated.

Appendix II.

Investigation to obtain smooth sugar surfaces

Since the roughness of the surface can strongly influence the contact angle, the production of thin crystalline sucrose films has been investigated. Some works from different authors on the production of thin films were evaluated (Shastry and Hartel 1996, Ben-Yoseph, Hartel et al. 2000, Howell and Hartel 2001, Howell, Ben-Yoseph et al. 2001, Vigh, Sheehan et al. 2008), however, there is a lack of studies concerning the production of smooth crystalline films. Sucrose solutions of different concentrations (20%, 70%, 80% wt) were dispensed into the depression of approximately 90 μ m on a microscope slide in order to control the thickness of the film. The films were then dried in a convection oven at different temperatures (40 °C and 100 °C) and the crystallization and apparent smoothness of the films were evaluated with an optical microscope. Polarized light was used to identify crystalline parts as shown in Figure II-1.



(a) (b) (c) Figure II-1. Optical microscope images for sugar thin films of initial concentrations of (a) 20 %wt (b) 70 %wt and (c) 80%wt, dried at 40 °C

Films produced at different concentrations were crystalline. At 20 %wt initial concentration, the films produced were not evenly distributed over the surface, with the formation of some "spots" of film on the surface. At 70 %wt initial concentration (close to saturation point of sucrose at 40 $^{\circ}$ C), crystallization took place with several nucleation points, as one can see on Figure II- 1(b). This is not desirable because "cracks" on the surface could alter the contact angle. Finally, an 80 %wt initial concentration produced a rough surface with several very small crystals. Elevated temperatures (100 $^{\circ}$ C) produced even rougher surfaces.

Instead of convective drying, conductive drying (hot plate at 40 °C) was tested in order to evaluate if surfaces would be smoother. Sucrose films were produced by conductive drying of saturated sucrose solutions, however, they were even rougher than the ones dried by convection (see Figure II-2).



Figure II-2. Micrographs of sucrose films produced by conductive drying of saturated sucrose solutions at 40 °C.

Large sugar single crystals can be found commercially ("candy sugar"; see Section 3.1.2). However, the commercially available crystals are considerably rough and, therefore, different treatments in order to smoothen the surface were evaluated. In Figure II- 3, one can observe the difference in roughness before and after treatment with methanol solutions (90 %wt). Sucrose is poorly soluble in anhydrous methanol (0.66 %wt at 25 °C) and slightly more soluble in methanol solutions (2.22 %wt for 90 %wt methanol solutions at 25 °C); therefore a controlled dissolution on the sugar crystal surfaces can be obtained.

Figure II- 3 shows the changes on the sugar surface caused by the treatment. One can observe that before the treatment (Figure II- 3 (a) & (c)) the surface is extremely rough; also representing a problem for atomic force microscopy (AFM) measurements. The AFM has a maximum limit in topography roughness of around 10 μ m (difference between peaks and valleys). In Figure II- 3 (c) the long and high peak of about 8 μ m is probably a very high roughness that caused the cantilever tip to break at that point, giving no realistic results of the topography. The treatment with methanol solution resulted in a smoother surface however, it still contains some roughness of micrometre range. This is already one step

towards smoother surfaces for contact angles measurements. However, it might be interesting to try methanol solutions with higher fractions of water so that a more extensive dissolution of sucrose on the surface can be obtained.





(c) (d) Figure II- 3. Optical and AFM images of sugar crystals before (a,c) and after (b,d) treatment with methanol solutions.

Appendix III.

Calculation of forces due to liquid bridges between flat surfaces

The adhesion force of a liquid bridge formed between particles, as illustrated in Figure III-1 and the theory described in Section 2.3.5, has two contributions upon the particle separation: a static meniscus force and a dynamic viscous force.



Figure III-1. Schematic of liquid bridge between two flat surfaces

Due to the monoclinic structure of the sucrose crystal, the geometry chosen to represent the particles is composed of two flat plates, instead of the common approach of assuming particles to be spherical. The particles are also assumed to be rigid, the liquid incompressible and the evaporation of liquid negligible. The particles are considered to be small and, consequently, gravitational and buoyancy effects are taken as negligible.

Capillary force

As mentioned earlier, the meniscus force arises from a pressure deficiency inside the bridge (Laplace pressure) and from the liquid surface tension acting on the solidliquid boundary.

The Laplace pressure term in the capillary force was calculated using the toroidal approximation where the curvatures of the liquid bridge are approximated by an arc of a circle $(1/r_1 \text{ and } 1/r_2)$. Taking this approximation into account, geometrical relationships can be drawn (Figure III- 1):

$$r_1 = \frac{h}{\sin \alpha} \qquad [Eq. 1]$$

$$\theta + \alpha = \pi/2$$
 [Eq. 2]

Where α is the angle formed between r_1 at the edge of the bridge and the line passing the neck of the bridge.

The volume of the bridge is assumed to be constant and, based on the toroidal approximation it can be obtained by rotating a circular arc of radius r_1 about the Y axis (Tselishchev and Val'tsifer 2003). Since the geometry of the particles consists of 2 plates the volume of the particles does not need to be subtracted. Then, the volume of the bridge V_{bridge} is given by:

$$V_{\text{bridge}} = 2 \int_0^h \pi \left(r_1 + r_2 - \sqrt{r_1^2 - x^2} \right)^2 dx \qquad [Eq. 3]$$

The solution of this integral is given in Appendix IV, and the capillary force is as given in Section 2.3.5:

$$F_{cap} = 2\pi\gamma_{LL}r_2 + \pi r_2\gamma_{LL}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$
[Eq. 4]

♦ Viscous force

The viscous force is the dynamic part of the liquid bridge force. By integrating the Reynolds lubrication equation (Equation 2-19, Section 2.3.5.2), the viscous force can be calculated as (Cai and Bhushan 2007):

$$F_{\text{vis}} = \int_0^{r_2} 2\pi \left(\frac{3\eta}{2(2h)^3} r_2^2 \frac{\partial h}{\partial t}\right) r \, dr \qquad [Eq. 5]$$

Considering the upper plate moves with constant velocity v_s , one can approximate the above equation with $\frac{\partial h}{\partial t} = v_s$:

$$F_{\rm vis} = \frac{3\pi\eta r_2^4 v_{\rm s}}{16h^3} \qquad [Eq. 6]$$

At this stage only the viscous contribution of the bridge was taken into account. It is known, however, that for high particle separation speeds, hydrodynamic resistance related with the continuous phase (oil) will also become significant and contribute to the total force and adhesion force. Upon approach of the particles, this hydrodynamic force will be repulsive, and it will be attractive upon separation of the particles. Therefore, it is expected that the hydrodynamic effects due to the oil continuous media will increase the adhesion force.

The rupture distance was assumed as the point when the Laplace pressure becomes zero, i.e. the pressure inside and outside the bridge are the same. This assumption is true when $r_1=r_2$ (Washino 2011).

The interfacial tensions and contact angles used in the calculations were the measured values presented in previous Sections (I.4.1 and I.4.2). Viscosity data for sugar solutions are given in Section 3.1.2 and the remaining values for the viscosity were taken from literature (CRC 1977).

In addition, since a dimensional study is being performed at this point in order to compare the meniscus and viscous forces, some assumptions have to be made:

Volume of liquid bridge: $7.2 \cdot 10^{-16} \text{ m}^3$ Initial distance between plates: $2 \cdot 10^{-6} \text{ m}$ Velocity of plate: $2 \cdot 10^{-3} \text{ m/s}$

These assumptions are made taking into consideration that the particle size is approximately 30 μ m, which is based on the median size of sugar particles used in the suspensions. Therefore the volume of the liquid cannot be higher than the wetted diameter d (in Figure III-1). For short distances, the wetted radius (d/2) is very close to r_2 , but to be more precise, from geometrical relations one can state:

$$d = 2(r_1 + r_2 - r_1 \cos \alpha)$$
 [Eq. 7]

In addition, the volume of the liquid bridge was calculated based on the macroscopic experiments with suspensions (Section 4.3.1), where water addition at a ratio Vr=0.02 resulted in a transition in texture. Hence, using once more the assumption that the particles are 30 μ m and cubical, the volume of the liquid bridge was determined as 7.2·10⁻¹⁶ m³.

As an initial crude assumption, the velocity of the plates was considered to be as the maximum linear velocity of the rheometer at a shear rate of 1 s⁻¹ (ω = 0.096 rad/s \rightarrow v = 2·10⁻³ m/s with radius of vane as 25 mm).

The assumption that the particles are flat plates has the consequence that particles cannot be located at a distance zero between them. Obviously, this condition would imply that there is no liquid bridge. Therefore, for very small distances the capillary and viscous force would result in unrealistic large values (tending to infinite). Consequently, an initial distance between particles of 2 μ m was defined. In addition, from [Eq. 6] one can observe that the force diverges to infinity when the distance between the plates tends to zero. The viscous force is predicted from a continuum theory, thus, at molecular dimensions it fails. Therefore the assumption of (non-zero) initial distance is needed.

The model was built in Wolfram Mathematica 8.0 (Wolfram Research, USA) and the code is presented in Appendix IV.

III.1. Bridge behaviour for different liquids

In Figure III- 2 the contribution of the capillary and viscous forces for different liquid bridges can be observed. These results are calculated considering bridges between two sugar particles. For the case of water bridges one can notice that the capillary forces are dominant over the viscous forces, which are about 3 orders of magnitude smaller, independent of particle separations.

When one considers a water bridge between two sucrose particles, it is expected that the dissolution of sucrose will change the characteristics of the bridge over time. Assuming the sucrose dissolution into the bridge would reach equilibrium upon saturation of the bridge and that recrystallization is not occurring, it is possible to determine this effect. The interfacial tension of a saturated sugar solution and HOSO is similar to water. In order to draw comparisons, the contact angle for saturated sugar solution on a sugar surface in oil is assumed to be the same as the one for water. Therefore, the viscosity of the saturated sugar solution bridge is the parameter which significantly changes (two orders of magnitude higher than water). This increase in viscosity results in stronger viscous forces, which contribute to the total liquid bridge force for small separations.

One can observe that for a glycerol bridge, the viscous contribution becomes dominant when the plates are close to each other, and the meniscus force becomes more important at larger separations. This example supports how the dynamic component can play an important role in the total and adhesion forces of liquid bridges.



 $(\gamma=0.0177 \text{ N/m}, \theta=49.3^{\circ}, \eta=1.420 \text{ Pa.s}, \text{Ca}=8.0 \cdot 10^{-2})$

Figure III- 2. Capillary (continuous grey line) and viscous (dashed line) forces for different liquid bridges

In Figure III- 3 the curves for the total force versus the distance are presented. The total force is given as the sum of the capillary and viscous forces. It is noticeable that the water and saturated sugar solution bridges have an earlier rupture. The rupture distance is a function of the initial distance between the particles, the particle speed, the volume of the bridge and the contact angle (assumption: $\Delta P \rightarrow 0$; $r_1=r_2$). From this, one can conclude that the contact angle is the parameter which determines the larger rupture distance for the glycerol bridge.



Figure III- 3. Comparison of total force for different liquid bridges: water (continuous line), saturated sugar solution (dashed line) and glycerol (dotted line)

When considering bridges of different liquids, several parameters are changed. In order to analyse the effect that each parameter has on the liquid bridge (volume, viscosity, contact angle and interfacial tension), they should be examined separately. For the analysis of the effect of each parameter, a water bridge between sugar particles was considered, and only the specific parameter was changed, unless otherwise stated.

III.2. Volume of the bridge

In Figure III- 4, the effect of the volume of the bridge on the total force is evaluated. The volumes considered here are built in parallel with the experiments (Section 4.1) and the weight percentages of water addition were converted to relative volume of water to the volume of solid particles.

The volume of the bridge has a significant influence on the liquid bridge forces, and a similar tendency to the one observed for the interfacial tension effect. The more liquid between the plates, the stronger the bridges, and also for a longer period of time. This can be explained in terms of the Laplace pressure (Figure III- 4).



Figure III- 4. Total liquid bridge force versus particle separation distance - effect of bridge volume

Because the contact angle is maintained constant, the curvature radius r_1 is the same for the different amounts of liquid in the bridge in the case of bridge between the flat plates configuration. The curvature radius r_2 , however, becomes considerably higher when the volume of the bridge is increased, resulting in a larger Laplace pressure. Small volumes of the liquid bridge also show a rapid and steep decrease in the Laplace pressure, resulting in fast bridge ruptures (Figure III- 5).



Figure III- 5. Laplace pressure contribution to the capillary force versus particle separation distance - effect of volume (legend is the same as in Figure III- 4)

It is important to point out that the wetted radius for the higher volumes is not in agreement with the $30 \ \mu m$ particle size assumption. This is because the calculations con-

sider infinite plates. For Vr=0.05 and Vr=0.1, the wetted diameter corresponds to 30.9 and $49.2 \mu m$, respectively.

III.3. Effect of viscosity

The viscous force is proportional to the viscosity ([Eq. 6]). Therefore, an increase in viscosity results in a proportional increase of the viscous forces as seen in Figure III- 6 (b). However, when considering the total force of the liquid bridge, one can see curves with a similar tendency as the one observed for changes in interfacial tension with a rapid decrease in the total force with the increase in separation distance (Figure III- 6 (a)). For small separation distances the viscosity shows a significant contribution to the total force, with considerably higher values for the total force for higher viscosities. The viscosity acts towards preventing particles from separating, hence the stronger forces for smaller separations. Once the particles start to move, the viscous effects become less important than the capillary effects. This explains why, at large separation distances, the total force is less sensitive to the viscosity.



Figure III- 6. Total liquid bridge force (a) and viscous force (b) versus particle separation distance effect of viscosity (viscosity units: Pa.s).

As mentioned earlier, the unique aspect of water bridges between sugar particles is that they change due to dissolution of sugar into the bridge. Also previously mentioned, the viscosity is the parameter that shows greater changes upon sugar dissolution. If one interprets the adhesion force as the maximum force to separate the particles, it can be considered as the force at t = 0 s (or the force at the initial distance). Thus, Figure III- 7 plots the adhesion force with respect to the concentration of sugar in the bridge (which directly affects the viscosity of the bridge; see Figure 3-4).

The increase in adhesion force from a water bridge (no sucrose) to a fully saturated bridge (66.72 %wt sucrose) is about 30 %. This shows the large impact that the dissolution of sucrose and consequent viscous effects have on the bridge.



Figure III-7. Adhesion force for liquid bridges with different sucrose concentrations

III.4. Effect of contact angle

The effect of contact angle is shown in Figure III- 8. The contact angles determine the wettability of the particles, and they are closely related to the curvature of the liquid bridge and, therefore, have an impact in the capillary force strength. At short separation distances, larger forces are observed for smaller contact angles. Lower contact angles at small separations result in smaller radii of curvature, which in turn, result in a larger value of the Laplace pressure. However, for larger separation distances the opposite effect is observed. This is because the Laplace pressure degenerates faster for smaller contact angles, resulting in faster bridge ruptures as well. However, the effect of the contact angle alone is not very significant in the total force (Figure III- 8), especially if compared with the effect the other parameters such as the volume and viscosity of the bridge.



Figure III-8. Total liquid bridge force versus particle separation distance - effect of contact angle

III.5. Effect of interfacial tension

The effect of the interfacial tension on the total liquid bridge force can be seen in Figure III- 9. Illustrative values of interfacial tensions from 0.01 N/m to 0.05 N/m were taken in order to build a comparison. When the separation distance is short, the total force is highly sensitive to the interfacial tension, with larger forces for higher values of interfacial tension. However, when the separation distances are larger, the force is less sensitive to the changes in interfacial tension.



Figure III- 9. Total liquid bridge force versus particle separation distance - effect of interfacial tension

Appendix IV.

Liquid bridges Mathematica[®] code
Modelling of liquid bridges between particles in a fat-continuous phase

SetDirectory[NotebookDirectory[]];

```
Needs["PlotLegends`"]
```

Bridge Dimensions

From geometry (Figure in Appendix III):

h[{h0_, vplate_, t_}] := h0 + vplate t

dis[{h0_, vplate_, t_}] := 2 * h[{h0, vplate, t}]

 $r1[{h0_, vplate_, t_, \theta_}] := h[{h0, vplate, t}] / Sin[0.5 Pi - \theta]$

Using the toroidal approximation, the bridge meniscus is described by a circular arc. See "Solving-toroidal-volume" for details. Solving the volume of the bridge integral for r2:

$$r2[\{h0_{, vplate_{, t_{, \theta_{, vol_{}}}}] := With \left[\{ht = h[\{h0, vplate, t\}]\}, \frac{1}{6 ht \pi} \left(-6 ht \pi (ht / Sin[0.5 Pi - \theta]) + 3 ht \pi \sqrt{-ht^{2} + (ht / Sin[0.5 Pi - \theta])^{2}} + 3 \pi (ht / Sin[0.5 Pi - \theta])^{2} \theta + \sqrt{3 \pi} \sqrt{\left(4 ht^{4} \pi - 12 ht^{2} \pi (ht / Sin[0.5 Pi - \theta])^{2} + 3 ht^{2} \pi (-ht^{2} + (ht / Sin[0.5 Pi - \theta])^{2}) + 6 ht vol + 6 ht \pi (ht / Sin[0.5 Pi - \theta])^{2}} \sqrt{-ht^{2} + (ht / Sin[0.5 Pi - \theta])^{2}} \theta + 3 \pi (ht / Sin[0.5 Pi - \theta])^{4} \theta^{2}} \right) \right]$$

This calculates the rupture distance, i.e. r1=r2

```
tr[{h0_, vplate_, θ_, vol_}] := Module[{tsols, tvals, tposv},
  tsols = Solve[r1[{h0, vplate, t, θ}] == r2[{h0, vplate, t, θ, vol}], t];
  tvals = If[Length[tsols] > 0, t /. tsols, {}];
  tposv = Select[tvals, Positive];
  Min[tposv]]
trprint[{h0_, vplate_, θ_, vol_}] := Module[{tsols, tvals, tposv},
  tsols = Solve[r1[{h0, vplate, t, θ}] == r2[{h0, vplate, t, θ, vol}], t];
  Print["tsols = ", tsols];
  tvals = If[Length[tsols] > 0, t /. tsols, {}];
  Print["tvals = ", tvals];
  tposv = Select[tvals, Positive];
  Print["tposv = ", tposv];
  Max[tposv]]
```

Determination forces

3.0 2.0 1.5 1.0

> 0.0000 0.0002 0.0004 0.0006 0.0008 0.0010 time[s]

```
fiten[\{h0\_, vplate\_, t\_, \theta\_, vol\_, \gamma\_\}] := 2 Pir2[\{h0, vplate, t , \theta, vol\}] \gamma
flap[{h0_, vplate_, t_, θ_, vol_, γ_}] := Pir2[{h0, vplate, t, θ, vol}]^2
  \gamma (1/r1[{h0, vplate, t, \theta}] - 1/r2[{h0, vplate, t, \theta, vol}])
fcap[{h0_, vplate_, t_, θ_, vol_, γ_}] :=
 fiten[{h0, vplate, t, \theta, vol, \gamma}] + flap[{h0, vplate, t, \theta, vol, \gamma}]
fvis[{h0_, vplate_, t_, \theta_, vol_, \eta_}] :=
 (3 \operatorname{Pi} \eta \operatorname{r2} [\{h0, vplate, t, \theta, vol\}]^{4} vplate) / (16 h[\{h0, vplate, t\}]^{3})
ftot[{h0_, vplate_, t_, \theta_, vol_, \gamma_, \eta_}] :=
 fcap[{h0, vplate, t, \theta, vol, \gamma}] + fvis[{h0, vplate, t, \theta, vol, \eta}]
```

Bridge behaviour for different liquids

```
Water
  water = {\gamma \rightarrow 0.0264, \theta \rightarrow 16.2 Degree,
       \eta \rightarrow 0.001, vol \rightarrow 7.2 * 10^{-16}, h0 \rightarrow 10^{-6}, vplate \rightarrow 2 * 10^{-3};
  tr[{h0, vplate, \theta, vol} /. water]
  0.0010502
  wat = With[{trup = tr[{h0, vplate, 0, vol} /. water]},
     Table[{t, dis[{h0, vplate, t}], h[{h0, vplate, t}], r1[{h0, vplate, t, \theta}],
          r2[{h0, vplate, t, \theta, vol}], fiten[{h0, vplate, t, \theta, vol, \gamma}],
          flap[{h0, vplate, t, \theta, vol, \gamma}], fcap[{h0, vplate, t, \theta, vol, \gamma}],
          \texttt{fvis}[\{\texttt{h0}, \texttt{vplate}, \texttt{t}, \theta, \texttt{vol}, \eta\}], \texttt{ftot}[\{\texttt{h0}, \texttt{vplate}, \texttt{t}, \theta, \texttt{vol}, \gamma, \eta\}],
          (r1[{h0, vplate, t, θ}] + r2[{h0, vplate, t, θ, vol}] - r1[{h0, vplate, t, θ}] *
              Cos[Pi/2-\theta]) \} /. water, \{t, 0, trup, (trup/100)\}];
  wat2 = Prepend[wat, {"t", "dis", "h", "r1", "r2", "fiten", "flap",
       "fcap", "fvis", "ftot", "wetted radius"}];
  Export["water-bridge.xls", wat2];
  With[{trup = tr[{h0, vplate, \theta, vol} /. water]}, LogPlot[
     {r1[{h0, vplate, t, 0} /. water] * 10^6, r2[{h0, vplate, t, 0, vol} /. water] * 10^6},
     {t, 0, trup}, Frame \rightarrow True, FrameLabel \rightarrow {"time[s]", "bridge curvatures [\mum]"},
     PlotLegend \rightarrow {"r1", "r2"}, LegendPosition \rightarrow {1, 0.3}]]
                                                         r1
       10.0
                                                          r2
        7.0
    pridge curvatures [\mu m]
        5.0
```

```
 \begin{split} & \texttt{watcap} = \texttt{Transpose}[\{\texttt{wat}[[1 ;; \texttt{Length}[\texttt{wat}], 2]] / 10^{-6}, \texttt{wat}[[1 ;; \texttt{Length}[\texttt{wat}], 8]]\}]; \\ & \texttt{watvis} = \texttt{Transpose}[\{\texttt{wat}[[1 ;; \texttt{Length}[\texttt{wat}], 2]] / 10^{-6}, \texttt{wat}[[1 ;; \texttt{Length}[\texttt{wat}], 9]]\}]; \\ & \texttt{ListLogPlot}[\{\texttt{watcap}, \texttt{watvis}\}, \texttt{Joined} \rightarrow \texttt{True}, \\ & \texttt{PlotStyle} \rightarrow \{\texttt{Directive}[\texttt{Thick}, \texttt{Darker}[\texttt{Gray}]], \texttt{Directive}[\texttt{Thick}, \texttt{Dashed}, \texttt{Black}]\}, \\ & \texttt{Frame} \rightarrow \texttt{True}, \texttt{FrameLabel} \rightarrow \{\texttt{"Distance} \ [\mu\texttt{m}]\texttt{"}, \texttt{"Force} \ [\texttt{N}]\texttt{"}\}, \\ & \texttt{PlotRange} \rightarrow \{\{1, 9\}, \{10^{-12}, 5 * 10^{-4}\}\}, \\ & \texttt{BaseStyle} \rightarrow \{\texttt{FontFamily} \rightarrow \texttt{"Arial"}, \texttt{FontSize} \rightarrow 13\}] \end{split}
```

Saturated Sugar Solution

```
satsugar = {\gamma \rightarrow 0.0251, \theta \rightarrow 16.2 Degree,
      \eta \rightarrow 0.215, vol \rightarrow 7.2 * 10^{-16}, h0 \rightarrow 10^{-6}, vplate \rightarrow 2 * 10^{-3};
  sat = With[{trup = tr[{h0, vplate, 0, vol} /. satsugar]},
     Table[{t, dis[{h0, vplate, t}], h[{h0, vplate, t}], r1[{h0, vplate, t, \theta}],
          r2[{h0, vplate, t, \theta, vol}], fiten[{h0, vplate, t, \theta, vol, \gamma}],
          \texttt{flap}[\{\texttt{h0}, \texttt{vplate}, \texttt{t}, \theta, \texttt{vol}, \gamma\}], \texttt{fcap}[\{\texttt{h0}, \texttt{vplate}, \texttt{t}, \theta, \texttt{vol}, \gamma\}],
          fvis[{h0, vplate, t, \theta, vol, \eta}], ftot[{h0, vplate, t, \theta, vol, \gamma, \eta}],
          (r1[{h0, vplate, t, θ}] + r2[{h0, vplate, t, θ, vol}] - r1[{h0, vplate, t, θ}] *
              Cos[Pi/2-\theta]) /. satsugar, {t, 0, trup, (trup/100)}];
  sat2 = Prepend[sat, {"t", "dis", "h", "r1", "r2", "fiten", "flap",
       "fcap", "fvis", "ftot", "wetted radius"}];
  Export["sat_sugar-bridge.xls", sat2];
  satcap = Transpose[{sat[[1;; Length[sat], 2]] / 10^-6, sat[[1;; Length[sat], 8]]}];
  satvis = Transpose[{sat[[1;; Length[sat], 2]] / 10^-6, sat[[1;; Length[sat], 9]]}];
  \texttt{ListLogPlot[{satcap, satvis}, Joined \rightarrow True,}
   PlotStyle → {Directive[Thick, Darker[Gray]], Directive[Thick, Dashed, Black]},
   \texttt{Frame} \rightarrow \texttt{True}, \ \texttt{FrameLabel} \rightarrow \{\texttt{"Distance} \ [\mu\texttt{m}]\texttt{"}, \ \texttt{"Force} \ [\texttt{N}]\texttt{"}\}, \\
    PlotRange → { {1, 9}, {10^{-12}, 5 * 10<sup>-4</sup> } },
   BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 13}]
Glycerol
  glycerol = {\gamma \rightarrow 0.0177, \theta \rightarrow 49.3 Degree,
       \eta \rightarrow 1.420, vol \rightarrow 7.2 * 10^{-16}, h0 \rightarrow 10^{-6}, vplate \rightarrow 2 * 10^{-3}};
  gly = With[{trup = tr[{h0, vplate, θ, vol} /. glycerol]},
     Table[{t, dis[{h0, vplate, t}], h[{h0, vplate, t}], r1[{h0, vplate, t, \theta}],
          r2[{h0, vplate, t, \theta, vol}], fiten[{h0, vplate, t, \theta, vol, \gamma}],
          \texttt{flap}[\{\texttt{h0}, \texttt{vplate}, \texttt{t}, \theta, \texttt{vol}, \gamma\}], \texttt{fcap}[\{\texttt{h0}, \texttt{vplate}, \texttt{t}, \theta, \texttt{vol}, \gamma\}],
          fvis[{h0, vplate, t, \theta, vol, \eta}], ftot[{h0, vplate, t, \theta, vol, \gamma, \eta}],
          (r1[\{h0, vplate, t, \theta\}] + r2[\{h0, vplate, t, \theta, vol\}] - r1[\{h0, vplate, t, \theta\}] *
              Cos[Pi/2-\theta]) \} /. glycerol, \{t, 0, trup, (trup/100)\}];
  gly2 = Prepend[gly, {"t", "dis", "h", "r1", "r2", "fiten", "flap",
       "fcap", "fvis", "ftot", "wetted radius"}];
  Export["glycerol-bridge.xls", gly2];
  glycap = Transpose[{gly[[1;; Length[gly], 2]] / 10<sup>-6</sup>, gly[[1;; Length[gly], 8]]}];
  glyvis = Transpose[{gly[[1;;Length[gly], 2]] / 10^-6, gly[[1;;Length[gly], 9]]}];
  ListLogPlot[{glycap, glyvis}, Joined → True,
   \texttt{PlotStyle} \rightarrow \{\texttt{Directive[Thick, Darker[Gray]], Directive[Thick, Dashed, Black]}\}, \\
    Frame \rightarrow True, FrameLabel \rightarrow {"Distance [\mum]", "Force [N]"},
    PlotRange \rightarrow { { 1, 9 }, { 10^ - 12, 5 * 10^ - 4 } },
    BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 13}]
```

```
wattot2 =
        Transpose[{wat[[1;; Length[wat], 2]] / 10^-6, wat[[1;; Length[wat], 10]] * 10^6}];
sattot2 = Transpose[{sat[[1;; Length[sat], 2]] / 10^-6,
                 sat[[1;; Length[sat], 10]] * 10^6}];
glytot2 = Transpose[{gly[[1;; Length[gly], 2]] / 10^-6,
                gly[[1;; Length[gly], 10]] * 10^6}];
ListPlot[{wattot2, sattot2, glytot2}, Joined \rightarrow True, PlotStyle \rightarrow
         {Directive[Lighter[Blue]], Directive[Thick, Dashing[Medium], Darker[Blue, 0.5]],
            \texttt{Directive[Thick, Dashing[Tiny], Darker[Blue, 0.6]]}, \texttt{Frame} \rightarrow \texttt{True},
    \texttt{FrameLabel} \rightarrow \{\texttt{"Distance } [\mu\texttt{m}]\texttt{"}, \texttt{"Force } [\mu\texttt{N}]\texttt{"}\}, \texttt{PlotRange} \rightarrow \{\{1.90, 9\}, \texttt{All}\}, \texttt{PlotRange} \rightarrow \{\{1.90, 9\}, \texttt{All}\}, \texttt{PlotRange} \rightarrow \{\texttt{PlotRange} \rightarrow \{\texttt{PlotRange} \rightarrow \texttt{PlotRange} \rightarrow \texttt{PlotRange
    BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 18}]
wattot = Transpose[{wat[[1;; Length[wat], 2]] / 10^-6, wat[[1;; Length[wat], 10]]}];
sattot = Transpose[{sat[[1;; Length[sat], 2]] / 10^-6, sat[[1;; Length[sat], 10]]}];
glytot = Transpose[{gly[[1;; Length[gly], 2]] / 10^-6, gly[[1;; Length[gly], 10]]}];
ListLogPlot[{wattot, sattot, glytot}, Joined \rightarrow True, PlotStyle \rightarrow
         {Directive[Lighter[Blue]], Directive[Thick, Dashing[Medium], Darker[Blue, 0.5]],
            Directive[Thick, Dashing[Tiny], Darker[Blue, 0.6]]},
    Frame \rightarrow True, FrameLabel \rightarrow {"Distance [\mum]", "Force [N]"},
    PlotRange \rightarrow \{\{1, 9\}, \{5 * 10^{-} 8, 5 * 10^{-} 4\}\},\
    BaseStyle -> {FontFamily -> "Arial", FontSize → 18}]
trupwat = tr[{h0, vplate, θ, vol} /. water]
trupsat = tr[{h0, vplate, θ, vol} /. satsugar]
trupgly = tr[{h0, vplate, θ, vol} /. glycerol]
truptes = tr[{h0, vplate, 16 Degree, vol} /. water]
0.0010502
0.0010502
0.00155392
0.00104921
dis[{h0, vplate, trupwat} /. water]
dis[{h0, vplate, trupsat} /. satsugar]
dis[{h0, vplate, trupgly} /. glycerol]
6.20079 \times 10^{-6}
\textbf{6.20079} \times \textbf{10}^{-6}
8.21566 \times 10^{-6}
```

Effect of different parameters

```
testing = {γ → 0.0264, θ → 16.2 Degree,

η → 1, vol → 7.2 * 10<sup>-16</sup>, h0 → 10<sup>-6</sup>, vplate → 2 * 10<sup>-3</sup>;

■ Contact angle

thetalist = Range[0 Degree, 50 Degree, 20 Degree]

{0, 20°, 40°}
```

```
c = Table[
     trup = tr[{h0, vplate, thetalist[[i]], vol} /. testing];
     ParametricPlot[{dis[{h0, vplate, t} /. testing] / 10^-6,
        ftot[{h0, vplate, t, thetalist[[i]], vol, \gamma, \eta} /. testing] * 10^6},
       {t, 0, trup}, PlotRange \rightarrow {All, {0, All}}, AspectRatio \rightarrow 0.8,
       PlotStyle → Directive[Thick, ColorData[1, i]]],
     {i, Length[thetalist]}];
  legendth = Table[{Graphics[{ColorData[1, i], Thick, Line[{{0, 0}, {1, 0}}]}],
       thetalist[[i]]}, {i, Length[thetalist]}];
  GraphicsGrid[legendth, ImageSize \rightarrow 50]
  Show[c, FrameLabel \rightarrow {"Distance[\mum]", "Total force [\muN]"},
   Frame \rightarrow True, PlotRange \rightarrow {{1.90, 9}, All},
   BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 12}, AspectRatio \rightarrow 1]
Interfacial tension
  itenlist = Range[0.01, 0.05, 0.01]
  \{0.01, 0.02, 0.03, 0.04, 0.05\}
  iten = Table[trup = tr[{h0, vplate, 0, vol} /. testing];
     ParametricPlot[{dis[{h0, vplate, t} /. testing] / 10^-6,
        ftot[{h0, vplate, t, \theta, vol, itenlist[[i]], \eta} /. testing] * 10^6},
       {t, 0, trup}, PlotRange \rightarrow All, AspectRatio \rightarrow 1,
       Show[iten, FrameLabel \rightarrow {"Distance[\mum]", "Total force [\muN]"},
   PlotRange \rightarrow {{1.90, 9}, All}, Frame \rightarrow True,
   BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 12}, AspectRatio \rightarrow 1]
  legenditen =
    Table[{Graphics[{ColorData[1, i], Thick, Line[{{0, 0}, {1, 0}}]}] itenlist[[i]]},
     {i, Length[itenlist]}];
  GraphicsGrid[legenditen, ImageSize \rightarrow 50]
  iten = Table[trup = tr[{h0, vplate, \theta, vol} /. testing];
     ParametricPlot[{dis[{h0, vplate, t} /. testing] / 10^-6,
        fiten[{h0, vplate, t, 0, vol, itenlist[[i]]} /. testing] * 10^6},
       {t, 0, trup}, PlotRange \rightarrow All, AspectRatio \rightarrow 1,
       PlotStyle → Directive[Thick, ColorData[1, i]]], {i, Length[itenlist]}];
  Show[iten, FrameLabel \rightarrow {"Distance[\mum]", "Total force [\muN]"}, PlotRange \rightarrow All,
   Frame \rightarrow True, BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 12}, AspectRatio \rightarrow 1]
Viscosity
  vislist = {0.001, 0.1, 1}
  \{0.001, 0.1, 1\}
  vis = Table[trup = tr[{h0, vplate, θ, vol} /. testing];
     ParametricPlot[{dis[{h0, vplate, t} /. testing] / 10^-6,
        ftot[{h0, vplate, t, \theta, vol, \gamma, vislist[[i]]} /. testing] / 10<sup>-6</sup>},
       {t, 0, trup}, PlotRange \rightarrow {All, {0, All}}, AspectRatio \rightarrow 1,
       PlotStyle → Directive[Thick, ColorData[1, i]]], {i, Length[vislist]}];
  legendvis =
    Table[{Graphics[{ColorData[1, i], Thick, Line[{{0, 0}, {1, 0}}]}], vislist[[i]]},
      {i, Length[vislist]}];
  GraphicsGrid[legendvis, ImageSize \rightarrow 50]
```

```
Show[vis, FrameLabel \rightarrow {"Distance[\mum]", "Total force [\muN]"},
PlotRange \rightarrow {{1.90, 9}, All}, Frame \rightarrow True,
BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 15}, AspectRatio \rightarrow 1]
```

Now, in order to calculate the force of adhesion (Ftot (t = 0)), the data for viscosity of sugar solutions vs.concentra - tion can be imported :

```
concvisc = Import["sucrose-viscosity-concentration.xlsx"];
```

```
cv = concvisc[[1]];
```

```
viscon = cv[[2;; 69, 1;; 3]]; viscon // TableForm;
```

Force of adhesion increase with viscosity of sugar

```
viscosity = viscon[[1;; 48, 3]];
concentration = viscon[[1;; 48, 1]];
```

```
force = With[{vis = viscosity}, Table[ftot[{h0, vplate, 0, θ, vol, γ, vis} /. water]]];
force // TableForm;
```

data = Transpose[{concentration, force * 10^6}];

table = {concentration, viscosity, force};

Export["force-viscosity-sat-sugar.xls", table];

```
ListPlot[data, PlotRange → {{0, 70}, {8.5, 11.5}}, Frame → True,
Joined → True, PlotStyle → Directive[Thick, Darker[Gray]],
FrameLabel → {"Sucrose concentration [g/100g of solution]", "Force (t=0) [µN]"},
BaseStyle -> {FontFamily -> "Arial", FontSize → 13}, AspectRatio → 1]
```

Volume of the bridge

```
volist = {1.4 * 10<sup>-16</sup>, 3.6 * 10<sup>-16</sup>, 7.2 * 10<sup>-16</sup>, 1.5 * 10<sup>-15</sup>}
```

```
\{1.4 \times 10^{-16}, 3.6 \times 10^{-16}, 7.2 \times 10^{-16}, 1.5 \times 10^{-15}\}
```

volist1 = {"Vr=0.005", "Vr=0.01", "Vr=0.02", "Vr=0.05", "Vr=0.1"}

m = Table[

```
trup = tr[{h0, vplate, \theta, volist[[i]]} /. testing];

ParametricPlot[{dis[{h0, vplate, t} /. testing] / 10^-6,

ftot[{h0, vplate, t, \theta, volist[[i]], \gamma, \eta} /. testing] * 10^6},

{t, 0, trup}, PlotRange \rightarrow All, AspectRatio \rightarrow 0.8,

PlotStyle \rightarrow Directive[Thick, ColorData[1, i]]],
```

{i, Length[volist]}];

```
legendvol =
```

```
\label{eq:GraphicsGrid[legendvol, ImageSize \rightarrow 50, Spacings \rightarrow \{0, 0\}, Alignment \rightarrow \{Right, Center\}, \\ AspectRatio \rightarrow 0.6, BaseStyle -> \{FontFamily -> "Arial", FontSize \rightarrow 13\}]
```

```
Show[m, FrameLabel \rightarrow {"Distance [\mum]", "Total force [\muN]"},
PlotRange \rightarrow {{1.90, 11}, All}, Frame \rightarrow True,
BaseStyle -> {FontFamily -> "Arial", FontSize \rightarrow 13}, AspectRatio \rightarrow 1]
```

Bridge dimensions - Toroidal approximation

Using the toroidal approximation, the bridge meniscus is described by a circular arc. Therefore the volume of the bridge can be determined as the volume obtained by rotating a circular arc of radius r1 around the Y axis. Since the geometry of the particles are 2 plates (or two paralelepipeds) the volume of the particles does not need to be substracted. (If the particles were circular, for example, then the volume of the particles immersed in the liquid would need to be substracted.)

The volume of the bridge V:

$$\begin{aligned} 2 \int_{0}^{h} Pi \left(r1 + r2 - \sqrt{r1^{2} - x^{2}} \right)^{2} dx \\ \text{ConditionalExpression} \Big[\\ 2 \pi \left[-\frac{1}{3} h \left(h^{2} - 6 r1^{2} + 3 r1 \sqrt{-h^{2} + r1^{2}} - 6 r1 r2 + 3 \sqrt{-h^{2} + r1^{2}} r2 - 3 r2^{2} \right) - \\ r1^{2} (r1 + r2) \operatorname{ArcTan} \Big[\frac{h}{\sqrt{-h^{2} + r1^{2}}} \Big] \Big], \\ \left(h \neq 0 \& r1 \neq 0 \& \left(\operatorname{Re} \Big[\frac{r1}{h} \Big] = 0 \right) || \operatorname{Re} \Big[\frac{r1}{h} \Big] \geq 1 \Big] \Big) || \operatorname{Re} \Big[\frac{r1}{h} \Big] \leq -1 || \frac{r1}{h} \notin \operatorname{Reals} \Big] \\ \text{From geometrical relationships:} \quad \operatorname{ArcTan} \Big[\frac{h}{\sqrt{-h^{2} + r1^{2}}} \Big] = Pi/2 - \theta \\ \text{Then, solving the equation above to r2:} \\ g = \operatorname{Solve} \Big[2 \pi \left(-\frac{1}{3} h \left(h^{2} - 6 r1^{2} + 3 r1 \sqrt{-h^{2} + r1^{2}} - 6 r1 r2 + 3 \sqrt{-h^{2} + r1^{2}} r2 - 3 r2^{2} \right) - \\ r1^{2} (r1 + r2) (\theta) \Big] = \operatorname{vol}, r2 \Big] \\ \Big\{ \Big\{ r2 \Rightarrow \frac{1}{6 h \pi} \Big[-6 h \pi r1 + 3 h \pi \sqrt{-h^{2} + r1^{2}} + 3 \pi r1^{2} \theta - \sqrt{3 \pi} \\ \sqrt{4 h^{4} \pi - 12 h^{2} \pi r1^{2} + 3 h^{2} \pi (-h^{2} + r1^{2}) + 6 h \operatorname{vol} + 6 h \pi r1^{2} \sqrt{-h^{2} + r1^{2}} \theta + 3 \pi r1^{4} \theta^{2}} \Big] \Big\}, \\ \Big\{ r2 \Rightarrow \frac{1}{6 h \pi} \Big[-6 h \pi r1 + 3 h \pi \sqrt{-h^{2} + r1^{2}} + 3 \pi r1^{2} \theta + \sqrt{3 \pi} \\ \sqrt{4 h^{4} \pi - 12 h^{2} \pi r1^{2} + 3 h^{2} \pi (-h^{2} + r1^{2}) + 6 h \operatorname{vol} + 6 h \pi r1^{2} \sqrt{-h^{2} + r1^{2}} \theta + 3 \pi r1^{4} \theta^{2}} \Big] \Big\} \Big\} \end{aligned}$$