A MICROSCOPI C INVESTIGATION OF
PARTICLE-PARTICLE INTERACTIONS IN THE PRESENCE
OF LIQUID BINDERS IN RELATION TO THE MECHANISMS
OF ‘WET’ AGGLOMERATION PROCESSES

Robert James Fairbrother

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University of London

Department of Chemical Engineering
University College London
London WC1E 7JE

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Abstract

Agglomeration of powders by the use of liquid binders is a size enlargement process, important in a range of process industries particularly pharmaceuticals and foods. Traditionally the industries most reliant on such agglomeration have taken system specific approaches to the control and development of their equipment and thus little work has been carried out to study the fundamental microscopic mechanisms. Thus this project has investigated the microlevel phenomena in relation to particle and binder properties with the overall aim of improving understanding and control of macroscopic agglomeration processes.

A novel piece of experimental apparatus has been developed capable of measuring the force of adhesion between particles attached by liquid bridges in both the gas and the liquid phase. The apparatus consists of an optical microscope fitted with an adapted stage, on which two micromanipulators are employed to hold micropipettes, to the ends of which particles are attached. A third micropipette is then used to add bridging liquid between the particles. The force is calculated by measuring how much a pre-calibrated pipette bends as the particles are separated (under piezo-electric control), allowing forces down to $10^{-9}$ N to be resolved. The rupture sequence is captured on video and analysed by image analysis software.

Results have been obtained using spherical glass ballotini particles and a range of liquid binders of various contact angles and viscosities. The behaviour of liquid bridges through their formation, separation and rupture have been observed. The results presented focus on; the relationship between the bridge volume and separation distance between the particles, the geometry liquid bridge menisci adopt depending on the contact angle they make with the solid surface and the experimental measurement of the variation of liquid bridge forces with separation distance from particle contact through to liquid bridge rupture. The total energy to rupture the bridges was then calculated and compared to the bridge volume. A dependence on the square root of the bridge volume was noted and developments were made to a previously derived model. The relationship between the critical separation distance at which liquid bridges rupture compared to the cube root of their volume was also considered and shown to be a reasonable approximation.

The significance of the improvements in the understanding of microscopic interactions to agglomeration arising from this work are considered along with suggestions for future studies.
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<thead>
<tr>
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<tr>
<td>A</td>
<td>Area</td>
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<tr>
<td>$A_0$</td>
<td>Agglomerate coalescence constant</td>
</tr>
<tr>
<td>$B_0$</td>
<td>Agglomerate deformation constant</td>
</tr>
<tr>
<td>C</td>
<td>A bulk liquid phase</td>
</tr>
<tr>
<td>D</td>
<td>A bulk liquid phase</td>
</tr>
<tr>
<td>$D_B$</td>
<td>Bubble spacing</td>
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<td>E</td>
<td>An interfacial region between two bulk liquid phases</td>
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<tr>
<td>$F_{ad}$</td>
<td>Total force due to adsorbed water layers</td>
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<tr>
<td>$F_{pend}$</td>
<td>Total static pendular bridge force</td>
</tr>
<tr>
<td>$F_{sp}$</td>
<td>Force due to the reduced hydrostatic pressure</td>
</tr>
<tr>
<td>$F_{van}$</td>
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<td>$F_{vis}$</td>
<td>Total viscous force</td>
</tr>
<tr>
<td>$F_{\gamma}$</td>
<td>Force due to the surface tension</td>
</tr>
<tr>
<td>$F^*$</td>
<td>Dimensionless force ($=F_{pend}/\gamma R$)</td>
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<tr>
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<tr>
<td>$M_p$</td>
<td>Moisture content of an agglomerate</td>
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**NOMENCLATURE**

<table>
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<td>N</td>
<td>Number of molecules</td>
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<td>Entry suction pressure of an agglomerate</td>
</tr>
<tr>
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<td>Radius of particle</td>
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<td>$U_B$</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>W</td>
<td>Rupture energy of liquid bridge</td>
</tr>
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<tr>
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</tr>
<tr>
<td>$W_c$</td>
<td>Work of cohesion</td>
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<tr>
<td>$X$</td>
<td>$(1 + a^*)$</td>
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<thead>
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<th>Definition</th>
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<td>a</td>
<td>Separation distance between particles</td>
</tr>
<tr>
<td>$a^*$</td>
<td>Dimensionless separation distance ($a/R$)</td>
</tr>
<tr>
<td>c</td>
<td>Rupture energy model constant</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>$d_{3,2}$</td>
<td>Sauter mean diameter</td>
</tr>
<tr>
<td>e</td>
<td>Particle coefficient of restitution</td>
</tr>
<tr>
<td>$h_a$</td>
<td>Characteristic length of surface asperities</td>
</tr>
<tr>
<td>$h_0$</td>
<td>Litshitz-van der Waals constant</td>
</tr>
<tr>
<td>j</td>
<td>Refractive index of the medium</td>
</tr>
<tr>
<td>k</td>
<td>Apparent viscosity</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
</tbody>
</table>
m_p  Mass of agglomerate
n    Flow index
p    Perimeter of plate
r_1 & r_2  Principle radii of curvature of bridge
s    Fractional pore saturation
t_{ad}  Adsorbed later thickness
v_0  Velocity of particle collision
v_n  Velocity of particle
x    Degree of association of liquid

**Greek letters**

α    Chemical potential
β    Half-filling angle for liquid bridge
γ    Surface tension

.γ   Average shear rate
δ    Binder layer thickness on particle
ε    Porosity of agglomerate
ε_m  Maximum strain
μ    Viscosity
θ    Contact angle
ρ    Density
σ_{coh}  Cohesion force of liquid
σ_t  Tensile stress
τ_y  Yield strength
ω    Rotational speed
ψ    Half filling angle of rays entering lens
List of Abbreviations

$G_{cr}^{coal}$ critical agglomerate size for coalescence

$G_{cr}^{def}$ critical agglomerate size at which deformation and breakage will occur

PEC Piezo-electric crystal

LVDT Linear Variable Differential Transducer

RO Reflecto-optic (sensor)

$St_v$ Viscous Stokes number

$St_{coal}$ Coalescence Stokes number
Chapter 1

1. Introduction

Agglomeration, a particle size enlargement process, occurs either by the collision and successful adherence of primary feed particles into discrete granules or by growth centred around a nucleus onto which particles collide and attach themselves to form a layer [1]. Agglomeration processes are used in an appreciable number of industries in the preparation of a wide range of different products. Examples are: fertilisers, ceramics, catalysts, pesticides, minerals, pharmaceuticals, foods (particularly 'instant' products) and detergents, where the common objective is to improve the handling and ease of use of the product. The properties required will govern the selection of the appropriate agglomeration process. In certain circumstances the formation or continued growth of agglomerates is undesirable, for example in grinding and in the transport and storage of powders. In all cases a knowledge of the strength of the resulting agglomerate is required to optimise the production and handling stages. Thus information on particle adhesion and individual particle-particle interactions is of importance in predicting the overall agglomerate strength and its method of formation.
Traditionally the industries most reliant on agglomeration processes have not investigated the fundamentals of the process. Mineral processors have taken an empirical approach and pharmaceutical companies have taken a product formulation approach. Over the last ten years this has started to change and currently there is a large amount of research being carried out internationally on size enlargement which can be considered to be divided into two areas; (i) relating particle and formulation properties such as binder viscosity and interfacial energy, particle size distributions, friction, plasticity, to the bulk agglomeration behaviour, and (ii) the incorporation of these relationships into process scale simulations. This work investigates microlevel phenomena in relation to particle and binder properties with the overall aim of improving the understanding and control of macroscopic agglomeration processes.

Chapter 2 focuses on agglomeration. The first part of the chapter describes the mechanisms of particle-particle adhesion which can be responsible for agglomerate formation. The magnitude and the effect of separation on these adhesion forces is considered. Agglomerate formation is also governed by the type of equipment used for production (section 2.2). For this work it is considered that agglomeration equipment can be divided into four types depending on the mechanism of formation employed [2];

(i). agglomeration by tumbling and other agitation methods
(ii). pressure compaction and extrusion methods
(iii). heat reaction, fusion, and drying methods
(iv). agglomeration from liquid suspensions

For each type adhesion can be brought about by liquid acting as a binder between particles. The final part of the chapter considers the effect on agglomerate formation, structure and strength in relation to the viscosity of the binder, the relative amount present and its surface tension.
In binder-induced agglomeration processes, it is desirable that the binder will wet the desired solids and then to be able to predict how the binder and solid will interact. In order to understand how binders behave, surface chemistry is considered in chapter 3.

Section 3.1 considers the fundamentals of surface chemistry, initially deriving equations through thermodynamic analysis of simple systems and then discussing how different parameters relate to surface tension. In many agglomeration processes, surface active agents (surfactants) are present. Various types of surfactant and the effect they have on solutions is detailed in section 3.2. For example, the addition of surfactants to a system can often lead to a variation with time of the surface tension when an interface is freshly created - the dynamic surface tension. Published data exists for a range of systems [3] and the results for the measured dynamic surface for an ionic surfactant, SDS, at the boundary between dodecane and water are given. A knowledge of dynamic surface tension effects was useful in two ways. First, for the bulk of the work presented in this thesis, only 'pure' bridging liquids were required, thus the ability to be able to detect the presence of surfactant contaminants was desirable (figure A.2). Secondly, when surfactants were added to a pure system to assess the effect on the force exerted by a liquid bridge (section 8.3) a knowledge of the relationship between concentration of surfactant and change in surface tension was necessary to analyse the observed effects. The ability of a liquid to 'wet' a solid surface is vital to the formation of liquid bridges between particles and the influencing factors are detailed in sections 3.3. and 3.4. Section 3.5 gives a brief summary of process applications which exploit surface chemistry effects. Finally (section 3.6) various methods for measuring surface tension and contact angle are tabulated and the theory for the Wilhelmy plate method (used in this work) given.
At present there is a large amount of theoretical work on the nature of the forces between particles attached by liquid bridges (Chapter 4). However, verification of this theoretical work is restricted by the lack of experimental data available in literature concerning liquid bridge forces at varying separation distance. In fact, the only published results available relate to the bridge forces between 3cm diameter spheres [4]. Thus the main aim of this project is to investigate and measure the forces that exist between particles attached by pendular liquid bridges. Recent developments in image processing mean that it has been possible to develop here a novel piece of experimental apparatus capable of measuring liquid bridge forces in both the gas and the liquid phase for particles down to 3μm in diameter. This equipment has been used to obtain results for a range of bridging liquids under different physico-chemical conditions allowing developments in both the fundamental understanding of agglomeration (especially in the area of bridge geometry) and in the modelling of agglomerating systems (Chapter 5).

Chapter 5 starts by looking at two approaches to the modelling of agglomerating systems. The first, adopted by Ennis et al. [5], assumes the viscous forces exerted by binders in agglomerating systems are dominant over static capillary forces. The second, developed by Simons et al. [6] to relate the rupture energy of a single pendular bridge to its volume, considers the static capillary forces (arising from the liquid surface tension and the force exerted by the reduced hydrostatic pressure within a pendular bridge) to be dominant over any viscous dissipation mechanisms. Developments following on from these approaches are then considered.
The second major aim of the project is to validate and develop the model proposed by Simons et al. [6], by a combination of direct experimental measurement and comparison with theory. Chapter 6 details the experimental apparatus and procedure. Here each step in the experimental procedure is explained. The apparatus developed is capable of measuring forces over a wide range (10^{-9} N up to milliNewtons), facilitated by the use and ‘in-situ’ production of glass micropipettes. These micropipettes are made by ‘pulling’ capillary tubing to desired thicknesses, enabling both the force constant and the tip size to be varied. Thus although the production of micropipettes is a task requiring both skill and dexterity, ultimately it allows greater flexibility and it is possible to measure the forces generated by particles over a much wider size range than using conventional force transducers. Viewing of the images and their subsequent processing is carried out by ‘off the shelf’ image analysis hardware and software. The measurement of the surface tensions and contact angles of the bridging liquids are carried out using the Du Nouy-ring and Wilhelmy-plate methods in conjunction with a processor tensiometer.

Results given in Chapter 7 consider five major developments in the understanding of liquid bridges. First, the variation of bridging liquid volume with separation distance, due to movement of liquid around the particles, these observations leading to (secondly) research into the geometries liquid bridges adopt for various liquid-solid contact angles. Thirdly, the measurement of force with separation, the integral of these forces giving (fourthly) the rupture energy of liquid bridge systems. Finally, the critical separation distance at which a liquid bridge will rupture. The significance of these results, there agreement with current agglomeration models and their use in developing new models is then discussed.
Chapter 8 reports on additional investigations carried out during the course of this work that had direct industrial support. In each case it was necessary to make modifications to the equipment or the experimental technique to conduct feasibility studies on the capabilities of the equipment. Three sets of work, the adhesion of ice-crystals, the adhesion of lactose particles and the effect of surfactants on liquid bridges within another liquid, are reported.

Conclusions and recommendations for the direction of future work are presented in Chapter 9, which includes a discussion on how this work relates to other work in the area and how to relate microscopic interactions to macroscopic behaviour of agglomeration processes. Chapter 10 lists all of the references cited in this work.

The appendix is divided into seven sections (A-G). Parts A and B contain surface chemistry data obtained using a Wilhelmy Plate Apparatus. These data were used when analysing the results detailed in Chapter 7.

Details of how the equipment is set-up to directly measure forces are contained in parts C-F. Part C describes the mechanical measurements carried out to determine the force constant of the flexible (force measuring) glass micropipette. In order to non-intrusively control and measure the force on the flexible micropipette a sophisticated electronic control system was developed. Its design, capabilities and control are detailed in part D. The acquisition of data from and output of control functions to the electronics is computer controlled via an A/D board and specially written computer code (part E). The processing of the acquired data and calibration checks that were carried out on the equipment is detailed in part F.

The final part of the appendix (part G) contains a list of the publications, conferences and presentations that have reported on this work.
Chapter 2

2. Agglomeration

Agglomeration can be defined as the action of gathering particulate matter into a ball, mass or cluster [7]. Granulation is a widely used process where agglomeration occurs. A wide variety of industries make use of agglomeration or granulation processes. For example, many pharmaceuticals are produced in high shear agglomerators, fertilisers are produced in drum granulators and many ‘instant’ food products are subject to an agglomeration process, the common objective being to add value to the product by improving its handling characteristics and ease of use.

An agglomerate will form if primary particles collide and adhere to each other. Often agitation is provided to bring about contact between the particles. The strength of the resulting agglomerate is dependent on the following factors [8];

(i). the magnitude and the nature of the adhesive forces between the primary particles
(ii). the particle size distribution
(iii). the number of bonding contact points
(iv). the form of agitation
In comparison to the primary particles the resultant agglomerates have better flow properties, permit dust free operation, have lower tendencies towards sticking together and de-mixing, and can be transported and metered more easily [9].

2.1 The Mechanisms of Particle-Particle Adhesion

The major adhesion mechanisms between particles can be split into those with, and those without, a material bridge in the contact region of the particles [10].

Figure 2.1: Schematic of the major adhesion mechanisms of agglomeration [10].
2.1.1 Solid bridges

Solid bridges can arise when particles come into contact at temperatures high enough to cause the solids to melt (approximately 60% of the absolute melting point [10]), resulting in mutual molecular diffusion at the points of contact to form sintered bridges. Partial melting to form solid bridges can occur when contact points rub together and melt due to the heat of friction and/or the contact pressure. Other mechanisms for solid bridge formation are crystallisation, chemical reaction and deposition of colloidal material [7]. Often liquid binders which solidify over time are added to particulate systems to encourage limited agglomerate growth, i.e. in the granulation of fertilisers. Once the binder hardens, further agglomerate growth ceases and the process can be controlled to yield granules of uniform size and shape. Solid bridges can therefore stabilise such agglomerates once they have formed.

2.1.2 Liquid bridges

Liquid bridges can arise from the adsorption of liquid onto the surface of particles. Initial adsorption causes surface asperities to be smoothed out. This allows a greater area of contact and reduces the effective interparticle separation, causing van der Waals and electrostatic forces to become more significant. Rumpf [8] derived the following equation for the mean bonding force, \( F_{\text{ad}} \), between two touching particles where only absorbed layers are present,

\[
F_{\text{ad}} = \frac{\pi}{2} t_{\text{ad}} d_p \sigma_{\text{coh}}
\]  

(2.1)

where \( t_{\text{ad}} \) is the adsorbed layer thickness and \( \sigma_{\text{coh}} \) is the cohesion force of the liquid forming the adsorbed layer. Turner et al. [11] carried out experiments to calculate \( t_{\text{ad}} \) over a range of humidities. They found that \( t_{\text{ad}} \) had a value of \( \approx 1.4 \text{nm} \) using 83\( \mu \text{m} \) diameter spherical particles. At relative humidities above 65% [11], capillary condensation occurs leading to the formation of discrete bridges.
Currently, work is being carried out using a modified atomic force microscope to further investigate the effect of atmospheric humidity on interparticle force [12]. For this study, ballotini particles mounted on a cantilever spring are brought into contact with a flat surface (to avoid the problems associated with aligning two particles) and the results obtained are then related to particle-particle contact. This type of experiment, although theoretically possible using the experimental apparatus described in chapter 6, has not been carried out in this study. Instead experiments have focused on liquid bridges which formed on the addition of a suitable viscous or adhesive binder, which was capable of wetting the desired particles. A full description of this type of liquid bridge can be found in chapter 4.

2.1.3 Van der Waals forces

Van der Waals forces are short range forces arising, on the microscopic scale, from molecular interactions between the electric fields of permanent and induced dipoles. Their influence is inversely dependent on the separation to the power six \( (1/a^6) \). On the macroscopic scale spontaneous electric and magnetic polarisations result in an electromagnetic field fluctuating within the dispersed solids and the surrounding aqueous medium [13]. Scaling up the van der Waals attraction to macroscopic bodies requires that all pair-wise combinations of intermolecular attraction between two bodies be summed. Such calculations have been performed for several different geometries by Hamaker [14]. An equation for the force of attraction between two spherical particles (radius \( R \)) with a separation distance \( a \), can be given as:

\[
F_{\text{van}} = \frac{h \omega}{2 \pi a^6} \left[ \frac{R_1 R_2}{R_1 + R_2} \right]
\]

where \( h \omega \) is the Lifshitz-van der Waals constant with a value which depends upon the particles’ properties. From this equation it can be calculated that two 5\( \mu \)m particles with a separation distance of 4\( \AA \) (0.4 nm) and an average Lifshitz-van der Waals constant of 10 x 10\(^{-19} \) J will have a van der Waals force of attraction of about 6 x 10\(^{-7} \) N.
2.1.4 Electrostatic forces

Electrostatic forces arise from the interactions between the electrical double layers surrounding charged particles. Substances acquire a surface charge either by preferential adsorption of (potential determining) ions or by the ionisation of surface charged groups when in contact with a polar (e.g. aqueous) medium. This surface charge influences the spatial distribution of nearby ions in the surrounding medium, attracting ions of the opposite charge (the counter-ions) and repelling ions of 'like' charge. However, the excess of counter-ions near the charged surface screen the electrostatic attraction for the counter-ions lying further away from the particle surface and so this results in the formation of an electrical double layer in which the electrical potential falls off rapidly at first (in the Stern layer) and then more slowly with increasing distance (in the diffuse layer), until a uniform charge distribution is met.

Interaction between particles will start as soon as their double layers overlap. The more diffuse the double layer (i.e. in low electrolyte concentrations) the greater the distance between the surfaces of the particles for this overlap to occur. For particles of the same charge sign the result is often an inter-particle repulsion, whilst the reverse is true for particles of opposite signs. If the particles come very close to one another, as in the case of increasing electrolyte concentration, then the van der Waals attraction forces may overcome the repulsion and the particles may agglomerate.

The nature of surface charges can be manipulated by chemical additives to encourage agglomerate formation [15]. Coagulation is the process in which particles are driven together by the addition of an electrolyte to a dispersion, which reduces the potential of the electrical double layer on the particles, thereby allowing close approach and agglomeration. Flocculation, on the other hand, occurs when a low concentration of polymer is added to a dispersion, the polymer molecules adsorbing on to vacant sites on the particle surfaces, resulting in agglomeration either by charge neutralisation or polymer bridge formation.
In addition to the electrostatic and van der Waals forces, magnetic forces may also have
to be taken into account. If a magnetic field exists between two particles, a potential
energy will arise which will either result in a repulsion or attraction, depending on the
orientation of the field to the particles. Recent work [16] has also shown that
magnetised iron powder suspended in a hydrocarbon liquid can be effectively separated
by sedimentation using a two step process. In the first step, ferromagnetic particles are
magnetised and pulled together to form 'particle agglomerates' by the application of a
magnetic field. In the second step, these particle agglomerates settle under gravity and
grow by collision with each other to form 'group agglomerates' which settle at a much
faster rate. It is thought that this work could be applied to the separation of
magnetisable fine micron size catalysts.

The forces of attraction arising from surface charges become insignificant between
particles above around 10\(\mu\text{m}\) in diameter, since the range of such forces are either very
small and require extremely close approach of the particle surfaces for agglomeration to
occur (as in the case of van der Waals attraction) or are too weak at larger separations
(as in the case of diffuse double layers) to have any noticeable effect on non-colloidal
particles. Small particle surfaces will also have smaller (in the absolute sense) surface
asperities, therefore allowing closer approach.

2.1.5 The effect of separation on adhesion forces

The force of adhesion between particles rapidly decreases with increased separation.
Increased separation may be caused by surface asperities. The size and nature of surface
asperities (roughness) can have a major effect on agglomeration. Asperities cause the
minimum separation distance that two particles can attain to be increased. This results
in reduced van der Waals' and electrostatic forces for two major reasons; first, these
short range forces rapidly decrease with increasing separation distance and secondly, it
is mainly the peaks of the asperities which take part in bonding (thus there is a reduced
effective bonding area).
Figure 2.2 shows the separation distance dependence for the various adhesion forces for a sphere-plate interaction [10]. A similar relationship exists for sphere-sphere interactions.

![Figure 2.2: Adhesive forces for a plate-sphere interaction model as a function of separation distance, a [10].](image)
2.2 Agglomeration equipment

Agglomeration equipment can be divided into four types depending on the mechanism of formation employed [2];

(i). agglomeration by tumbling and other agitation methods
(ii). pressure compaction and extrusion methods,
(iii). heat reaction, fusion, and drying methods,
(iv). agglomeration from liquid suspensions

The following section considers examples of the industrial equipment used to bring about agglomeration by the above methods. An understanding of the design, operation, advantages and limitations of industrial equipment is needed in order to develop the fundamental understanding of the microlevel phenomena occurring within them. This has been used to develop ideas on the environments liquid bridges will be formed and ruptured in and the nature of the forces they are subjected to, see for example section 7.1.

2.2.1 Agglomeration by tumbling and other agitation methods

2.2.1.1 Tumbling drum granulation

Tumbling drum agglomerators are used extensively in the process industries. Continuous agglomeration can be brought about by adding binding liquid to a solid feed material while subjecting the mixture to the rolling action of a rotating drum. The agglomerate growth mechanism, rate and final size are dependent on many factors including the feed particle size distribution, the liquid content, the residence time and rotational speed. Many designs of tumbling agglomerator exist (for a comprehensive review see Pietsch [7]), a typical example being the balling drum agglomerator (figure
2.3). Here the tumbling motion causes particles to collide and if the attractive or adhesive forces are high enough coalesce.

![Diagram of balling drum agglomerator](image)

**Figure 2.3:** Schematic of balling drum agglomerator [7].

Fresh material and recycle seeds (nuclei) are fed into the top end of the drum. Initially separation takes place, with fines concentrating at the bottom of the drum. Thus the binding liquid sprayed onto the bed primarily wets the larger coarse particles. These binder coated particles then go onto pick up fines as they travel through the bed. If binder is added over the entire length of the drum, growth will occur throughout and oversized, wet, and relatively loose agglomerates may discharge. If binder is only added for part way along the drum growth towards the discharge end is limited due to lack of binder. Here an equilibrium between size enlargement and size reduction with secondary growth (bonding of fragments) occurs. The material discharged does not contain oversized agglomerates and tends to be more uniform, drier and stronger. Often a curing step takes place to allow solid bridges to form and thus considerable strengthening of the agglomerate.
2.2.1.2 Mixer Agglomerators

Mixer agglomerators are used in many industries, including in the production of pharmaceutical, food and carbon black products. The mixers within these vessels are designed to provide both a rubbing and shearing action to accomplish both mixing and size enlargement. As a result it is possible to process plastic and sticky powder feeds, with the kneading action of the mixer producing denser agglomerates than is possible with the tumbling methods. These mixer agglomerators can be either operated batchwise or continuously. The mechanisms of agglomerate formation vary for each case.

(a) Batch mixer agglomerators

Batch mixer agglomerators are generally used in low capacity, high value situations such as the production of pharmaceuticals. On reaching equilibrium, batch mixer agglomerators produce agglomerates of uniform size (an equilibrium between size enlargement and disintegration is reached) which is dependent largely on the amount of binder present. However for most production processes the time to reach equilibrium is too long to be economically viable. Also the equilibrium agglomerate is often too large unless very dry, loose agglomerates are made. Therefore most mixer agglomerators are fitted with choppers (also known as intensifiers and turbulisers) in order to reduce the size of agglomerates and allow the fragments to reagglomerate with fines still present.

Pietsch [7] divides the controlled operation of the batchwise mixer agglomerator process into the following steps:

(i). Filling
(ii). Mixing
(iii). Spraying of binder and initial agglomeration
(iv). Agglomeration
(v). 'Chopping'
(vi). Spraying of additional binder and agglomeration
(vii). Repeat(s) of (iv), (v) and (vi)
(viii). Discharge
The properties of the final discharged agglomerate are affected by the duration of each step.

(b) Continuous mixer agglomerators

Continuous mixer agglomerators are used in the production of fertilisers, china clay products and carbon black. They typically process between 20 and 30 tonnes of material per hour, but can go up to several hundred tonnes per hour [2]. Examples include peg granulators and pinmixers (figure 2.4). These consist of a cylindrical shell within which rods ( pegs or pins) attached to a shaft rotate at high speeds. Feed is added, immediately moistened and then the material moves through mixing, pelletising and densifying zones before being discharged as pellets. The control mechanisms possible are limited as compared to those with the batchwise process and as a result granular products from continuously operating equipment feature wider particle size distributions and normally lower apparent density.

Figure 2.4: Schematic of a pinmixer used in the wet-pelleting of carbon black [2].
2.2.2 Agglomeration by pressure compaction and extrusion methods.

2.2.2.1 Pressure compaction

Agglomerates may be formed by the application of very high forces acting on particulates within a defined volume. Commonly used designs are piston, roller, isostatic and extrusion presses along with pelleting machines. If fine powders of plastic materials, which deform under high pressure, are pressed, no binders are required. The forces existing within the resulting agglomerate can consist of van der Waals', valence, interlocking or those caused by partial melting and subsequent solidification. Materials with a low melting point (or any material during hot pressing) can fuse together at grain boundaries to form homogeneous structures. Often the high pressures also cause components of the materials to act as binders, and so very rarely is additional binder needed to bring about agglomeration.

2.2.2.2 Extrusion methods

Extrusion presses and pelleting machines make use of wall friction, causing resistance to flow of plastic materials through bores or open-ended dies [7]. Typical die sizes are between 2 - 30mm [2]. The extrusion equipment is designed to produce shearing and mixing within the material being processed. Often to obtain sufficient plasticity and product strength, binders and / or plasticisers are added to facilitate the process. An extensive review of the equipment available can be found in Pietsch [7].
2.2.3 **Agglomeration brought about by heat reaction, fusion, and drying methods.**

Agglomerates may form when heat transfer takes place to form bonds. Heat may be added to a system to cause drying, fusion or chemical reaction or heat may be removed to cause solidification or crystallisation. Industrial processes employing this technique include the sintering of iron ore, spray drying, prilling and fluidised bed granulation. In the sintering of iron ore, a particle bed is heated until, by atomic and molecular diffusion, sinter bridges develop at the points of contacts between the particles. After cooling, the sinter is crushed into the required particle size. In fluid bed and spouted bed granulation, agglomeration and drying occur simultaneously by spraying liquid feeds onto particles. Growth can occur by both coalescence and layering mechanisms [17]. Extensive work has taken place to understand the fundamental interactions in the beds and thus allow better control of fluidised bed granulators, see for example Schoefer and Wurts [18], and Simons et al. [19].

![Diagram of granulation systems](image)

**Figure 2.5:** Schematic of (a) fluid-bed and (b) spouted-bed granulation system [2].
2.2.4 Agglomeration from liquid suspensions.

Agglomeration of particulate matter contained within a liquid suspension includes flocculation, coagulation and the addition of binding liquids to separate a desired component. An example process where liquid bridges are formed in the initial stages is spherical agglomeration.

2.2.4.1 Spherical Agglomeration

In the spherical agglomeration process, agglomerates are formed by the addition and agitation of a second immiscible liquid (binder) to a solid-liquid suspension, where the solids content can be made up of several different species. The binder is chosen to preferentially wet the desired solid species and cause the formation of pendular liquid bridges between particles. Liquid bridges will form when two particles come into contact and have insufficient relative kinetic energy to overcome the retarding force or strength of the liquid bridge [5]. The correct degree of agitation allows flocculation and then the formation of dense spherical agglomerates. Selective recovery of only one solid component from a mixture can thus be obtained by a knowledge of differences in surface chemistry of the desired component in relation to the other species. Use of this technique allows ultrafine particles (down to 0.1 nm) to be separated. Applications of the process include the recovery of high value solids from waste streams and the agglomeration and benefication of fine coals. At present the process is only applied to situations where the product has a high value and the ore does not respond satisfactorily to other separation techniques. This is because higher amounts of collector (binding agent) are needed than in flotation and the cost of this must be considered [1]. The process can be illustrated as follows:
Spherical agglomeration has been successfully achieved in a wide range of process equipment including various forms of mixers, shaking containers and rotating drums.
2.3 Mechanisms of ‘Wet’ Agglomeration

Agglomeration will take place when colliding particles coalesce and the resulting bonds are stronger than the combined effects of all the separating forces (e.g. elastic, flow, frictional and collision forces).

![Diagram of agglomeration mechanisms](image)

Figure 2.7: Schematic of possible outcomes in agglomeration.

The shear forces within agglomerators which cause particles to come together result in size enlargement and size reduction occurring simultaneously. The growth phenomena are dependent upon many factors such as the density of the tumbling mass and the type of equipment causing agitation of the bed. Sastry and Fuerstenau [21] characterised the mechanisms of agglomeration by deposition (Figures 2.8 - 2.11.). Nucleation occurs when primary particles adhere to form a microagglomerate (figure 2.8), the size
reduction of this microagglomerate (shatter) is seldom observed to occur in well designed agglomerators.

Coalescence (figure 2.9) occurs when two agglomerates come together, deform and join together. Alternatively additional primary particles can attach themselves to larger agglomerates by a layering mechanism (figure 2.10). Finally transfer of material can occur between agglomerates through abrasive forces (figure 2.11).

Figure 2.8: Nucleation of primary particles.

Figure 2.9: Coalescence mechanism of agglomeration.

Figure 2.10: Layering mechanism of agglomeration.
2.3.1 Selection of binder viscosity

Choosing the optimal binder viscosity is rather complex. An increase in binder viscosity in theory favours capture (figure 2.7) and hence increases the rate of growth by nucleation and coalescence. However an increase in binder viscosity also means the liquid mobility is reduced, which has a retarding effect on the consolidation / liquid transport rate which contributes to the coalescence probability. Kristensen and Schaefer [22] investigated the effects of binder viscosity on the growth kinetics of lactose granulated with polyethylenglycols. They reported increases in the viscosity up to 1000 mPas delay the initial granule formation and growth, whilst favouring the rate of growth by coalescence in the massing stage of the process. Above 1000 mPas the binder mobility became too low to enable effective distribution. The effect of viscosity is further discussed in chapter 5.

2.3.2 The effect of liquid content

Along with the characteristics of the liquid, the amount contained within an agglomerate has a large influence on its overall properties. For agglomerates where the bridging liquid perfectly wets the solid (contact angle $\theta=0^\circ$) the following classification, depicted in figure 2.12, has been defined [7].
Figure 2.12: Schematic of liquid distribution in wet agglomerates [7]. (a) Pendular liquid bridge state, (b) funicular region, (c) capillary state, (d) liquid droplet filled with particles.

The pendular liquid bridge state occurs when only small quantities of bridging liquid are present (figure 2.12(a)). On increasing the amount of bridging liquid the funicular state is obtained (figure 2.12(b)), where both liquid bridges and pores filled with liquid are present. Figure 2.12(c) shows the capillary state, where all the pores are filled with liquid and concave menisci are present at the surface of the agglomerate. Figure 2.12(d) represents particles contained within a liquid droplet. These four types of agglomerates all have different physical characteristics, thus the amount of binding liquid added is a factor in controlling an agglomeration process.

Thus the form of the final agglomerated product is dependent upon the relative amount of bridging liquid added. The relationship between the form of the agglomerate (figure 2.12) and the amount of binder present has been summarised by Capes [2] (see Figure 2.13).
State of bridging liquid

Form of product

Preferred agitation equipment
Fluid mixers, high shear mills, pumps
Disk and drum agglomerators shakers
Liquid-liquid contactors
Sedimentation volume (arbitrary units)

0 20 40 60 80 100

Pore vol occupied by bridging liquid, %

Figure 2.13: ‘Wet’ agglomerate form related to amount of binder present [2].

2.3.3 Agglomerate strength

The overall strength of a static agglomerates is dependent upon [20];

- The interfacial tension between the bridging liquid and the continuous suspending liquid phase \( \gamma_{lv} \).
- The three-phase contact angle (figure 2.14).
- The ratio of the volumes of bridging liquid and solid particles.

Figure 2.14: The three-phase contact angle \( \theta \) in solid-oil-water assemblies [20].
Omenyi and Capes [23] state that the maximum negative pressure, or entry suction $P_e$, is given by the following equation,

$$P_e = S_o \left( \frac{1 - \varepsilon}{\varepsilon} \right) \gamma_{LV} \cos \theta$$

(2.3)

and that the tensile stress $\sigma_t$ is given by:

$$\sigma_t = sP_e$$

(2.4)

where $\gamma_{LV}$ is the liquid surface tension

- $\theta$ is the contact angle
- $\varepsilon$ is the porosity of the agglomerate
- $S_o$ is the specific surface of the particles
- $s$ is the fractional pore saturation

Chapters 3 and 4 consider more thoroughly interfacial tension and contact angle effects in relation to particle-particle adhesion. Chapter 5 reviews current literature of the behaviour of agglomerates under process conditions, where energy dissipation can occur through dynamic effects.
Chapter 3

3. Surface Chemistry

In order to develop the fundamental understanding of agglomerating systems it is necessary to understand the chemical and physical parameters which govern the behaviour of gases, liquids and solids. The effects at the boundaries between materials in agglomerates are of major importance in governing their formation and subsequent properties. The surface tension and the shape a liquid surface adopts will affect the behaviour of the liquid bridges and, hence, the adhesive forces developed between the particles. This behaviour can be modified by the presence of surface active agents (known as surfactants).

For a system consisting of two phases, there exists an interfacial region between them. The two phases, which may be a solid and a liquid, a solid and a gas, two liquids or a liquid and a vapour, can be considered as being separated by a surface phase. The atoms at the surface of each phase are subject to a markedly different environment to those in the bulk, as they have an anisotropic distribution of neighbours, which causes the interface to be in a different thermodynamic state to the homogeneous bulk. Thus
molecules tend to move into the bulk of the liquid, causing the surface to contract and it is for this reason that droplets of liquid and bubbles of gas tend to take on a spherical shape. This means the number of molecules at the surface is only a small proportion of those in the bulk. For example, in a spherical droplet of water of volume 1 cm$^3$, only about one in five million of its molecules are at the surface [20]. Thus the number of exposed molecules at the surface is at a minimum and hence the energy of the system is also at a minimum. Traditionally an interface is used to describe all systems, whereas a surface is just for the case of a liquid and a gas.

3.1 Surface Free Energy and Tension

The total free energy $G$ of a system (figure 3.1) consisting of two bulk phases (C and D) separated by an interface (E) is,

$$G = G^C + G^D + G^E \tag{3.1}$$

![Figure 3.1: Schematic of interfacial region (E) between two bulk phases (C & D).](image)

The interfacial region (which is usually only a few molecules thick and whose thickness is exaggerated in the figure) includes all parts of the system that are influenced by surface forces, while the free energies of the bulk phases are calculated on the assumption that they both remain homogeneous right up to the hypothetical geometric surface.
If a small, reversible change occurs in the system, the free energy change $dG$ can be expressed as,

$$dG = dG^C + dG^D + dG^E$$  \hfill (3.2)

For the homogeneous bulk phases, the free energy changes are given by,

$$dG^C = -S^C dT + V^C dP^C + \alpha_1^C dN_1^C + \alpha_2^C dN_2^C + ...$$  \hfill (3.3)

$$dG^D = -S^D dT + V^D dP^D + \alpha_1^D dN_1^D + \alpha_2^D dN_2^D + ...$$  \hfill (3.4)

where $S$, $T$, $V$ and $P$ refer to entropy, temperature, volume and pressure respectively. The term $N$ refers to the number of molecules of a component whose chemical potential is $\alpha$. The subscript refers to component 1, 2, etc.

The surface free-energy change, $dG^S$, must also include a term for the amount of work required to increase the surface area by an amount $dA$, at constant temperature, pressure and composition. The work of surface expansion is resisted by a tension $\gamma$, known as the interfacial tension or when one phase is a gas the surface tension. This reversible work is equal to $\gamma dA$. Thus,

$$dG^E = -S^E dT + V^E dP^E + \gamma dA + \alpha_1^E dN_1^E + \alpha_2^E dN_2^E + ...$$  \hfill (3.5)

As the surface contribution to the volume is negligible, the quantity $V dP$ can be omitted. Summing $dG^C$, $dG^D$ and $dG^S$ gives the total free energy change for the system,

$$dG = -S dT + V^C dP^C + V^D dP^D + \gamma dA + \sum \alpha_i^C dN_i^C + \sum \alpha_i^D dN_i^D + \sum \alpha_i^E dN_i^E$$  \hfill (3.6)
Where \( S = S^C + S^D + S^E \). At constant temperature, pressure and composition equation 3.6 simplifies to,

\[
dG = \gamma dA
\]

or

\[
\gamma = \left( \frac{\delta F}{\delta A} \right)_{T,P,n} = G_E
\]

The interfacial or surface tension, \( \gamma \) (units mN/m = mJ/m^2 = dynes/cm), is a measure of the work required to increase the area of a surface isothermally and reversibly by a unit amount. The term \( G_E \) is the surface free energy per unit volume, expressed in ergs cm\(^{-2}\) (1 erg/cm\(^2\) = mJ/m\(^2\)) and for a pure liquid in equilibrium with its vapour is numerically equal to the surface tension.

### 3.1.1 The Nature of Surface Tension Forces

The forces responsible for surface / interfacial tensions include,

(i). Van der Waals forces. These are small electrostatic attractions arising from dipole-dipole interactions. Van der Waals forces are proportional to \( 1/x^6 \), where \( x \) is the distance between the molecules, thus they are most important at close separations.

(ii). Hydrogen bonding. Arising from spontaneous electric and magnetic polarisations between electronegative atoms (e.g. N, Cl, O) in one molecule and hydrogen atoms bound in another molecule.

(iii). Metal bonds. These are chemical bonds between metal atoms caused by electrostatic attractions between metal ions and electrons.

These forces are not thought to be appreciably influenced by each other and so are assumed to be additive.
3.1.2 Values of Surface Tension

Typical values of surface tension at 293K are given in table 3.1. Most organic and inorganic liquids have surface tensions (at standard conditions) ranging from 15-50 mN/m. Water has a high surface tension value of 72.75 at 20°C because of the strong intermolecular forces associated with hydrogen bonding.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.75</td>
</tr>
<tr>
<td>Fluorocarbons</td>
<td>8-15</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>18-30</td>
</tr>
<tr>
<td>Hexane</td>
<td>18.4</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>27.0</td>
</tr>
<tr>
<td>Polar Organic Compounds</td>
<td>22-50</td>
</tr>
<tr>
<td>Methanol</td>
<td>22.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>22.8</td>
</tr>
<tr>
<td>Aqueous Detergent Solutions</td>
<td>24-50</td>
</tr>
<tr>
<td>Molten Glasses</td>
<td>200-400</td>
</tr>
<tr>
<td>Molten Metals</td>
<td>350-1800</td>
</tr>
<tr>
<td>Mercury</td>
<td>472</td>
</tr>
</tbody>
</table>

Table 3.1: Surface tension values for various types of liquid [24].
3.1.3 Variation of Surface Tension with Temperature.

The work required to increase the area of a surface is equal to the work required to bring additional molecules from the bulk to the surface. This work is done against the attraction of the surrounding molecules. A rise in temperature causes an increase in the kinetic energy of the molecules and thus the attraction between molecules is partially overcome. The surface tension therefore invariably decreases (almost linearly) with increasing temperature, until it no longer exists, at a point known as the critical temperature ($T_c$). The relationship can be described by the empirical equation reported by Katayama and Guggenheim [25],

$$\gamma = \gamma_0 (1 - T/T_c)^{1/9}$$  \hspace{1cm} (3.9)

where $\gamma_0$ is an empirical parameter of the liquid. Data for the variation of surface tension of water against air with temperature is shown in table 3.2.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Surface Tension (mN/m)</th>
<th>Temperature °C</th>
<th>Surface Tension (mN/m)</th>
<th>Temperature °C</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75.60</td>
<td>20</td>
<td>72.75</td>
<td>50</td>
<td>67.91</td>
</tr>
<tr>
<td>5</td>
<td>74.90</td>
<td>25</td>
<td>71.97</td>
<td>60</td>
<td>66.18</td>
</tr>
<tr>
<td>10</td>
<td>74.22</td>
<td>30</td>
<td>71.18</td>
<td>80</td>
<td>62.60</td>
</tr>
<tr>
<td>15</td>
<td>73.49</td>
<td>40</td>
<td>69.56</td>
<td>100</td>
<td>58.90</td>
</tr>
</tbody>
</table>

Table 3.2: Variation in surface tension with temperature for water against air.
3.1.4 Effect of Pressure on Surface Tension

An increase in the pressure of a vapour over a liquid surface causes more gas molecules to be in contact with the surface. These additional molecules exert an additional force on the surface molecules. Thus surface tension decreases with increasing pressure.

3.1.5 Effect of Surface Curvature

Surface tension forces must, at equilibrium, be balanced by an equal and opposite force. This can be illustrated by considering a spherical soap bubble, radius r. A bubble consists of gas inside a thin film of liquid. The film consists of many layers of molecules and those molecules away from both surfaces can be considered to be in the 'bulk'. If the bubble shrinks, more molecules will enter the 'bulk'. However as the bubble shrinks the internal pressure increases until an equilibrium position is reached, with the excess pressure inside the bubble being equal to the force caused by the surface tension.

Initially the surface area of the bubble is $2 \times 4\pi r^2$ (both internal and external surfaces have to be considered) Thus the surface energy of the bubble is $8\pi r^2\gamma$. If the bubble shrinks and the radius is decreased by $dr$, then the change in free surface energy is $16\pi r\gamma dr$. This must be balanced by a pressure difference $\Delta P$ across the film of the bubble. The work against the pressure difference is $\Delta P.4\pi r^2dr$. Equating this work term with the decrease in surface free energy gives,

$$\Delta P.4\pi r^2dr = 16\pi r\gamma dr \quad (3.10)$$

or

$$\Delta P = 4\gamma/r \text{ (for a bubble)} \quad (3.11)$$
Thus, the smaller the bubble, the greater the relative internal pressure compared to the external pressure. Equation (3.11) applies to a bubble having two surfaces (internal and external). However, a liquid drop only has an exterior surface. Thus, the surface area, the surface free energy and the change in surface free energy must be divided by two.

\[ \Delta P = \frac{2 \gamma}{r} \text{ (for a drop)} \]  
\[(3.12)\]

### 3.1.5.1 The Laplace-Young Equation

For a spherical surface, one parameter \( r \) can be used to described the surface. However a surface which is curved, but not spherical, has to be described by two radii of curvature \( r_1 \) and \( r_2 \) (figure 3.2).

![Figure 3.2: Schematic showing the principal radii of curvature at a point X [26].](image)

The pressure difference across the surface is given by the Laplace-Young equation,

\[ \Delta P = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  
\[(3.13)\]
For a sphere $r_1$ and $r_2$ are equal, the Laplace-Young equation simplifies to equation 3.12. For a flat liquid surface, the radii are infinite and $\Delta P = 0$. For a concave liquid surface the pressure inside the liquid tends to be lower than the surrounding medium. For a liquid in equilibrium, $\Delta P$ must be constant over all parts of its free surface or the liquid will flow. As surface tension is constant, it follows that, in the absence of external fields, all liquid surfaces are of constant mean curvature (see chapter 4). For an open film, for example a soap film on a wire frame, $\Delta P$ is necessarily zero. It is also zero for a film pulled between to cylinders open to the atmosphere (see figure 3.3). Here $r_1 = - r_2$ at all points on the surface, although $r_1$ and $r_2$ change from point to point. $R_1$ and $R_2$ represent $r_1$ and $r_2$ at the neck of the bridge.

Figure 3.3: A curved surface with no pressure drop across it [26].
3.2 Surfactants

Surfactants, also known as surface-active agents, are widely used in industries such as pharmaceuticals, waste water treatment, minerals processing and food production. Most domestic cleaning and personal care products contain one, or a combination of, these chemicals, although often only in tiny amounts. They work by being active at some or all of the interfaces in a system.

For the main body of this work only pure bridging liquids have been used. However, it was important to be aware of surfactants’ effect on liquid bridge systems to be able to detect if they were present. Additionally, some preliminary investigations of the effect of surfactants on liquid bridges in liquid media were conducted (section 8.3).

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Figure 3.4: Schematic of surfactant molecules at the surface of water [26].
Generally surfactants are composed of two distinct portions, one of which has sufficient affinity for the solvent to bring the molecule into solution. The other portion is rejected by the solvent, causing the molecule to move to an interface so that at least part of the rejected group is not in contact with the solvent (figure 3.4). For example, in detergency the interaction between water and hydrophobic molecules such as grease is encouraged by the addition of soap acting as the surfactant. The polar group of the surfactant has sufficient affinity for water to cause the soap to be water soluble. The hydrocarbon chain is rejected by the polar water molecules resulting in the concentration of the soap at water-air and water-oil interfaces.

### 3.2.1 Hydrocarbon Oil Soluble Surfactants

Surfactants altering the properties of hydrocarbon oils can be divided into three categories:

(i). Long-chain hydrocarbons with polar groups  
(ii). Fluorocarbon compounds  
(iii). Small molecular weight silicone oils

Long chain hydrocarbons with polar groups lower oil-water interfacial tensions and adsorb to polar surfaces. Typical polar groups are -COOH, -OH, -NH₂, -CONH₂, -SH, -SO₃H, and salts of long-chain carboxylic acids and sulphonates. They do not, however, lower the surface tension.

Short chain fluorocarbons with polar groups are sufficiently soluble in oils to lower both the surface and the interfacial tension. Longer chain fluorocarbons attached to a long hydrocarbon chain are also soluble in oils and lower the surface tension. However they do not lower the interfacial tension at an oil-polar substance boundary.
Silicone oils are generally used as insoluble antifoaming agents. However, those of sufficiently small molecular weights containing only CH$_3$ groups attached to the Si-O backbone are soluble in hydrocarbon oils. They lower the surface tension of the oil as the CH$_3$ group has a lower surface free energy than the CH$_2$ group which predominates in hydrocarbon oils.

### 3.2.2 Water Soluble Surfactants

Water soluble surfactants can be classified into four types:

- **Hydrophobe**
- **Hydrophilic**

#### Anionic

- Anionic surfactants ionise in solution with the long chain carrying a negative charge. Examples are soaps, detergents and sodium dodecyl sulphate (SDS).

\[
\text{C}_{18}\text{H}_{37}\text{-COO}^-\text{H}^+ \quad \text{(Steric acid)}
\]

\[
\text{C}_{12}\text{H}_{25}\text{-O-SO}_3\text{Na}^+ \quad \text{(SDS)}
\]
Cationic surfactants ionise in solution with the long chain carrying a positive charge. There are two general categories; the first consists of long-chain primary, secondary and tertiary amines. These are water soluble only in acidic solution, where they ionise to form a long chain cation and a simple salt anion.

\[ R-\text{NH}_2 \]  
(Primary amine)

The second category consists of quaternary ammonium compounds. These ionise to form long chain cations over the whole pH range. They are synthesised by reacting a tertiary amine with an alkyl halide.

\[
\begin{bmatrix}
    \text{CH}_3 \\
    \text{C}_{18}\text{H}_{37}\text{N} \\
    \text{CH}_3 \\
    \text{CH}_3 \\
\end{bmatrix} + \text{Cl}^- \quad \text{(Quaternary Ammonium Compound)}
\]

Non-ionic surfactants do not ionise in solution and as such are compatible with either anionic or cationic compounds. Examples include fatty acids and sugar esters.

\[ \text{RC(OCH}_2\text{CH}_2)_n\text{OH} \]  
(Fatty acid)

Amphoteric or ampholytic surfactants ionise in solution, with the long chain carrying a positive or a negative charge depending upon the pH of the solution. Examples include long chain amino acids.

\[ (\text{RNH}_2\text{CH}_2\text{COOH})^+\text{Cl}^- \leftrightarrow \text{HCl} + \text{RNHCH}_2\text{COOH} + \text{NaOH} \rightarrow (\text{RNHCH}_2\text{COO})^-\text{Na}^+ \]
3.2.3 The Properties of Solutions Containing Surfactants

The unique behaviour of surfactants comes from the fact that they will orientate to the most energetically favourable state, i.e. hydrophobic parts in hydrophobic regions and polar parts in polar regions. Thus at low concentrations they tend to form layers at interfaces (figure 3.4). However, if the concentration of surfactant is increased, a point known as the critical micelle concentration (CMC) can be reached. Here the surfactant molecules in the bulk of the solution agglomerate into spherical, cylindrical or laminar ‘micelles’ with the non-polar groups clustering together in such a manner that they are surrounded and hidden by the polar groups (see for example figure 3.6). Generally, at concentrations of surfactant above the CMC, surface and interface tensions do not decrease further. The micelles merely act as a reservoir for unassociated surfactant molecules and ions.

For detergency, the ability of surfactant solutions to dissolve or solubilise water-insoluble materials starts at the CMC and increases with the concentration of micelles. Micelle formation allows the phenomenon of solubilisation to take place. Here organic compounds which would normally be insoluble in water can be ‘dissolved’ as they move into the interior of the micelle. Another mechanism by which detergency proceeds is surfactant absorption onto the surface of an oil droplet, leading to a the stabilisation of an oil-in-water emulsion.
Figure 3.6: Schematic of a sodium dodecyl sulphate micelle [27].
3.2.4 Dynamic Surface Tension

The surface tension of a freshly formed interface, such as at the surface of a pendular liquid bridge between two separating particles, may be quite different from the equilibrium or static value and vary as a function of time if surface active materials are present. The dynamic property of the surface tension is dependent on the instantaneous composition of the surface active materials accumulated on the interface. The value of the surface tension usually decreases monotonically with an increase in the concentration of surfactant adsorbed on the interface until an equilibrium value is reached. A large amount of data for the dynamic surface tension of aqueous surfactant solutions has been published by Rosen and Hua [3], who have also investigated the effects of molecular structure and environment on the dynamic surface tension [28]. Bonfillon and Langevin [29] carried out dynamic surface tension measurements for monolayers of a non-ionic (Triton X100) and an ionic surfactant, sodium dodecyl sulphate (SDS) using a pendant drop apparatus (figure 3.7 and figure 3.8).

The pendant drop apparatus consists of a drop forming system (a needle inside a quartz cell) monitored by a camera connected to an image analyser. Surfactant solution is then injected through the needle to form a drop. The image analyser is used to determine the interface loci. These loci are then compared with theoretical solutions calculated by the Laplace-Young equation and the surface tension is varied to achieve agreement between the experimental loci and theory. Other methods of measuring dynamic surface tension are reviewed by Edwards et al. [30].
Figure 3.7: Dynamic interfacial tension at the interface between dodecane and water with the surfactant SDS present ($c=0.1\text{g/L}$) [29].

Figure 3.8: Dynamic interfacial tension between dodecane and water with SDS in solution with salt (NaCl 0.1 mol/L) present ($c=14\text{mg/L}$) [29].
3.3 The Spreading of a Liquid over a Solid.

A drop of liquid placed on a solid will in most cases spread onto the surface. Whether and how far the liquid spreads is governed by the balance of the attraction of the liquid for the surface and the attraction for itself. In experimental and industrial situations consideration has to be given to the fact that most solid surfaces will be contaminated (usually with grease films, adsorbed vapour or chemisorbed oxide) which may modify their attractive properties. For example, an ordinary sheet of glass such as a microscope slide or a window pane is not completely wetted by water due to an adsorbed grease film. However after vigorous acid cleaning, water will form a continuous sheet over the whole surface.

3.3.1 Contact Angle

A measure of the tendency for a liquid to spread over or wet a solid is known as the contact angle, $\theta$. Rounding up of the liquid (reducing the liquid-solid contact and keeping most molecules in the bulk of the fluid) is balanced against gravity and the reduction in the solid-vapour interface. The lower the contact angle the greater the tendency for the liquid to wet the surface. Thus, complete wetting occurs at a contact angle of zero degrees. A value of $\theta=180^\circ$ would correspond to absolute non-wetting, but is rarely encountered in practice.

Consideration of a liquid drop at rest (sessile drop) on a flat solid surface allows the contact angle to be observed:
Figure 3.9: Schematic of the forces acting upon a liquid drop on a solid surface.

The equilibrium state is attained when the three forces of interfacial tension acting at right angles to the line of contact of the three interfaces and in the planes of the interface are balanced:

\[
\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta
\]  

(3.14)

Rearranging gives,

\[
\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]  

(3.15)

The contact angle is affected by both the chemical and the physical properties of both the liquid and the solid. Thus, from a knowledge of contact angles, predictions can be made about the following [14]:

- wetting
- penetration of porous solids by liquids
- fluid - fluid displacement (as in certain processes of detergency and secondary oil recovery)
- adhesion
- solid surface characteristics (solids may be classified as 'high - energy' or 'low - energy' on the basis of whether or not liquids with relatively high surface tension, such as water, spread with zero contact angle. From this liquids may be used as probes to measure surface energy.
3.3.1.1 Typical values of contact angle

As liquid-solid contact angles are largely dependent on surface contamination wide variations of recorded $\theta$ can be found in literature. Thus it is important for measurements to be carried out for any particular system (see appendix B). Table 3.3 shows some typically quoted values for contact angle.

<table>
<thead>
<tr>
<th></th>
<th>Contact angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water on clean glass</td>
<td>0</td>
</tr>
<tr>
<td>Mercury on glass</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 3.3: Typical values of contact angle.

3.4 The Significance of Contact Angle; Adhesion, Cohesion and Wetting.

Contact angle values can be used to give an indication of the forces of attraction that exist between a liquid and a solid. The work of adhesion ($W_a$) is the work required, per unit area, to separate two substances (e.g. material A from material B - figure 3.10).

This is described by the Dupré Equation.

![Figure 3.10: Schematic of the separation of two substances.](image)
Equation (3.16) can be applied to either two immiscible liquids or a liquid and a clean solid. Applying the equation to a liquid - solid interaction and combining with equation (3.11) gives the work required to separate a liquid with a non-zero contact angle on a solid.

\[ W_{SL} = \gamma_{LV} (1 + \cos \theta) \]  

(3.17)

For situations where the contact angle is zero equation (3.17) becomes,

\[ W_{SL} = 2\gamma_{LV} \]  

(3.18)

Here \( W_{SL} \) is equal to the work of cohesion (\( W_c \)), which is the work required (per unit area) to break a column of liquid into two separate parts, creating two new surfaces (figure 3.11).

**Figure 3.11: Schematic of the separation of a single substance.**

Equation 3.14 can be re-expressed as equation 3.19, which is obeyed by a pure liquid in contact with a smooth, homogeneous, rigid, isotropic solid surface.

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_e \]  

(3.19)

where: \( \gamma_{SV} \) is the solid - vapour interfacial free energy, \( \gamma_{SL} \) is the solid - liquid interfacial free energy, \( \gamma_{LV} \) is the liquid - vapour interfacial tension, \( \theta_e \) the equilibrium contact angle.

The term \( \gamma_{LV} \cos \theta_e \) can be referred to as the 'wetting tension' or 'adhesion tension'.
The value of $\gamma_{SV}$ is not the value of the surface free energy of the pure solid, $\gamma_S$, but is lowered due to adsorption of vapour. This can be described by:

$$\Pi_e = \gamma_S - \gamma_{SV}$$  \hspace{1cm} (3.20)

$\Pi_e$ has the dimensions of energy per unit area (or force per unit length) and is known as the spreading pressure or film pressure of the absorbate. Thus in terms of $\gamma_S$, Young's equation becomes,

$$\gamma_S = \gamma_{LV} \cos \theta_e + \gamma_{SL} + \Pi_e.$$  \hspace{1cm} (3.21)

By analogy with the Dupré equation, the work of adhesion, $W_{SL}$, between a solid and a liquid can then be defined as:

$$W_{SL} = \gamma_S + \gamma_{LV} - \gamma_{SL}$$  \hspace{1cm} (3.22)

Combining equations (3.21) and (3.22) gives,

$$W_{SL} = \gamma_{LV} (1 + \cos \theta_e) + \Pi_e$$  \hspace{1cm} (3.23)

### 3.4.1 Wetting

A liquid will wet another material if its own work of cohesion $W_{LL}$ is less than the work of adhesion between it and the substrate $W_{SL}$. The difference between the two ($W_{SL} - W_{LL}$) is known as the spreading coefficient $\phi$. Thus $\phi$ can be expressed in terms of interfacial energies by consideration of the Dupré equation and remembering $W_{LL} = 2\gamma_{LV}$:

$$\phi = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}.$$  \hspace{1cm} (3.24)

Equation (3.24) gives the equilibrium spreading coefficient and while $\phi$ is positive spreading will occur. Occasionally an interesting phenomenon can be observed when a liquid will initially spread over the surface of a solid and then run back to form a lens. This happens because while the solid surface has an adsorbed vapour layer, $W_{SL}$ is
greater than $W_{LL}$. However as the liquid is favourably adsorbed to the solid surface $W_{SL}$ starts to decrease in relation to $W_{LL}$ and the liquid retreats.

### 3.4.2 Contact Angle Hysteresis

Contact Angle hysteresis can be defined by imagining a liquid front advancing over a solid surface, such as a drop of water running down a window pane:

![Figure 3.12: Schematic of liquid drop on a vertical window pane.](image)

On practically all surfaces there will be a difference between the angle observed after advance, $\theta_a$, and that after retreat, $\theta_r$,

$$H = \theta_a - \theta_r$$  \hspace{1cm} (3.25)

The main reasons for the discrepancy have been identified as [2]:

- Surface roughness (even very smooth surfaces such as freshly cleaved mica have surface heterogeneity).
- Chemical heterogeneity
- A freshly prepared surface can have a very different surface energy, to one which has reached adsorption equilibrium with its surrounding atmosphere.
- Time can also play a part as a solid may dissolve or swell up when on contact with a liquid.
- Elastic distortion of the solid surface.
A liquid can adopt many metastable equilibrium contact angles, however only one represents the global minimum in free energy \cite{12}.

Surface roughness is often caused by the presence of different crystallographic faces on a chemically homogeneous solid or the existence of grain boundaries. One way to quantify the roughness is the roughness ratio:

\[ r = \frac{A}{a} \]  

where: \( A \) is the true area

\( a \) is the projected area on a plane parallel to the apparent surface.

### 3.5 Process Applications using Surface Chemistry Effects

#### 3.5.1 The Flotation of Minerals

Flotation, a process used to separate minerals from the gangue (waste stream), relies on surface chemistry. The process is made possible by the fact that different constituents of an ore tend to float to different extents in water. These differences can be exploited by the addition of certain surfactants known as collectors. Collectors work by adsorbing onto the particles, usually as a monolayer, and making the mineral more hydrophobic and raising the water-on-mineral contact angle. Industrially the ore goes through a comminution stage to produce a fine powder (to minimise weight) which is frothed up with air and water to produce a 'frothing agent stabilised' foam. These frothing agents tend to be oils and help to lower the surface tension of the water. Minerals will tend to stick to the air bubbles within the foam (if the force of surface tension acting at the line of vertical contact of the air, liquid and solid is greater than or equal to the weight of the particle corrected for buoyancy) and can be swept off the top of the water (figure 3.13). For this to work the receding contact angle of the water against the mineral at the air-
water-mineral interface must be greater than zero, otherwise the mineral would be completely wetted and ‘pulled’ down into the bulk water.

![Diagram of froth flotation cell]

Figure 3.13: Schematic diagram of a froth flotation cell.

3.5.2 Waterproofing

For a material to be waterproof it must have a contact angle greater than zero. The value of the advancing contact angle determines whether water will penetrate the material and the receding value how it will run off. For example, in the case of clothing, a coat can be given a wax coating to give it a surface covered in hydrocarbon groups with a contact angle greater than 90 degrees. Glassware can be treated with substances known as chlorosilanes (silanising agents) to render it hydrophobic. These substances are discussed in the materials section.
3.5.3 Wetting Agents

Wetting agents promote, as the name implies, the spreading of a liquid over a solid surface. Here the contact angle must be zero and this can be achieved by either reducing the surface tension $\gamma_{LV}$ or by reducing the interfacial tension $\gamma_{SL}$ or both. These agents usually consist of a hydrocarbon chain with one or more hydrophilic polar groups, thus they are acting as surfactants between the solid and the liquid.

3.6 Surface Tension and Contact Angle Measurement

Several methods have been developed for measuring surface tensions and contact angles. The choice depends on many factors such as the geometry of the system, accuracy required, convenience and cost.

Neumann and Good [2] divided the basic methods up as follows:

- Flat Plate Techniques
  - Sessile Drop or Adhering Gas Bubble
    - Direct measurement of Angle from drop profile
    - Interference Microscopy
    - Measurement of Contact Angles from Drop Dimensions
  - Wilhelmy - Gravitational Method
  - Capillary Rise at a Vertical Plate
  - Tilting Plate Method
  - Reflection Method
• Contact Angle Measurement at a Capillary Tube
  
  Wihelmy Method
  Method of Capillary Rise
  Reflection Method
  Rate of Penetration Method

For the contact angle associated with cylinders, rods, fibres and powders direct measurements are sometimes taken, but often contact angle is calculated from surface tension data.

3.6.1 Wilhelmy - Gravitational Method

In the studies reported here a Wilhelmy-Plate method has been employed to obtain the values of the contact angles of the bridging liquid on the particles.

![Figure 3.14: Representation of vertical plate method for measurement of surface tension and contact angle. Plate extends perpendicular to plane of paper. (a) zero depth of immersion, (b) finite depth of immersion.](image)
The Wilhelmy technique can be described as follows [31]. If a smooth, vertical plane is brought into contact with a liquid, as in figure 3.14(a), a downwards force will be exerted on the plate by the liquid. This force can be calculated from:

\[ f = p \gamma_{lw} \cos \theta \]  

(3.27)

where \( p \) is the perimeter of the plate.

If the plate is immersed in the liquid (figure 3.14(b)), the equation must be modified to include a volume of displaced liquid term, \( V \):

\[ f = p \gamma_{lv} \cos \theta - V \Delta \rho g \]  

(3.28)

where \( \Delta \rho \) is the density difference between the two fluids.

From the above equations (3.27 and 3.28), it can be seen that a knowledge of either surface tension or contact angle allows the other to be calculated. To use the method for contact angle measurement a smooth surface is essential. However for surface tension measurement the plate is often sandblasted or roughened with abrasive to obtain a zero contact angle.

A description of the apparatus used can be found in chapter 6. Advancing and receding conditions can be easily achieved by moving the liquid up and over the plate and then bringing it back down again. To check the contact angle along the plate, the perimeter must remain constant and the surface of the liquid remain free of vibration. If these conditions are met extremely accurate measurements can be taken. The whole process can be easily automated and is especially useful where contact angle changes over time due to the effects discussed in section 3.4.2.
However the method is not without its disadvantages. The plate must have the same composition and morphology on all surfaces, front, back and both sides. This can be difficult to attain. Also swelling, change of solution volume and adsorption of the liquid or its vapour to surfaces can cause problems.
Chapter 4

4. Pendular liquid bridges

This project focuses on systems where liquid binder provides the dominant adhesion force in agglomerates. The initial stages of ‘wet’ agglomeration usually depend on the formation of liquid bridges between particles and these bridges then remain in either liquid or a solidified form in the final agglomerate. The forces developed by liquid bridges are dependent upon the surface tension, the viscosity and the wetting of the solid. These parameters affect the geometry of the bridge formed, the distance at which it will rupture and the energy absorbed in particle-particle collisions. This chapter considers and develops the theories relating to liquid bridges between particles.

Pendular liquid bridges have been subject to numerous investigations (see, for example, Mehrotra and Sastry [32] who give a chronological summary of research investigations up to 1979) in relation to the behaviour of processes incorporating ‘surface-wet’ particles. The attractive forces developed between particles attached by the liquid bridges, may be either capillary or viscous in nature, i.e. static or dynamic, respectively.
Capillary forces usually dominate in cases where the liquid exists as discrete bridges, whereas viscous forces can become significant when the liquid viscosity is very high or at high interparticle velocities [33]. The importance of dynamic forces is considered in more detail in chapter 5 in relation to the modelling of agglomerating systems.

4.1 Static liquid bridges forces

Fisher [34] carried out much of the early work on pendular liquid bridges. He proposed the overall cohesive force between two particles attached by a pendular liquid bridge is a combination of three factors;

(i). The surface tension of the liquid
(ii). The hydrostatic suction (capillary) pressure, generated by the curvature of the liquid meniscus at the fluid(air) / liquid interface.
(iii). Buoyancy and gravity.

Princen [35] showed that buoyancy and gravity only influence the magnitude of the resultant force for relatively large bodies (>1mm in diameter), therefore this factor is ignored in this work.

Figure 4.1 shows two equi-sized particles (radius R) in contact with each other and attached by a liquid bridge. The principle radii of curvature of the bridge are described by \( r_1 \) and \( r_2 \) and the liquid has a half-filling angle (\( \beta \)) with the particle. From Fisher’s assumptions, for a liquid bridge which perfectly wets the particles (contact angle, \( \theta \), equal to zero), the total force (F\(_{\text{pend}}\)) is given by,

\[
F_{\text{pend}} = F_{\gamma} + F_{sp}
\]  

(4.1)

where \( F_{\gamma} \) is the force due to the surface tension
\( F_{sp} \) is the force due to the reduced pressure within the bridge
There are then two approaches to calculating the overall force, the 'neck' approach and the boundary approach.

4.1.1 The 'Neck' Approach

The force due to the surface tension is calculated at the neck of the bridge,

\[ F_y = 2\pi r_2 \gamma \]  \hspace{1cm} (4.2)

as is the hydrostatic force,

\[ F_{sp} = \pi (r_2)^2 \Delta P \]  \hspace{1cm} (4.3)

For liquid bridges with a menisci surface of constant mean curvature, \( \Delta P \) can be calculated from the Laplace-Young equation. Mean curvature is given by,

\[ H = \frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  \hspace{1cm} (4.4)

For pendular liquid bridges \( r_2 \) is considered to be negative and the Laplace-Young equation can be expressed as,

\[ \Delta P = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \]  \hspace{1cm} (4.5)

Substituting equations (4.2-4.5) into equation (4.1) gives,

\[ F_{\text{pend}} = 2\pi r_2 \gamma + \pi (r_2)^2 \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \]  \hspace{1cm} (4.6)
which simplifies to,

\[ F_{\text{pend}} = \pi \gamma \frac{r_2}{r_1} (r_1 + r_2) \]  

(4.7)

A consideration of the geometry of figure 4.1 allows \( r_1 \) and \( r_2 \) to be expressed in terms of \( R \) and the half-filling angle of the liquid bridge, \( \beta \),

\[ r_1 = R(\sec \beta - 1) \]  

(4.8)

and

\[ r_2 = R(1 + \tan \beta - \sec \beta) \]  

(4.9)

Substituting equations (4.8) and (4.9) into (4.7) gives,

\[ F_{\text{pend}} = \frac{2 \pi R \gamma}{1 + \tan (\beta/2)} \]  

(4.10)

4.1.2 The Boundary Approach

Adams and Perchard [33] used a different approach to derive the force equations by evaluating the surface tension and hydrostatic forces at the surface of the particles rather than at the bridge neck. The liquid contact length on the particle surface is \( 2\pi R \sin \beta \), hence the axial component of the surface tension is given by;

\[ F_\gamma = 2\pi R \gamma \sin^2 \beta \]  

(4.11)

The effective area of liquid contact on the particle surface is \( \pi R^2 \sin^2 \beta \) and thus the hydrostatic force is:

\[ F_{sp} = \pi R^2 \gamma \sin^2 \beta \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] \]  

(4.12)

The main effect of this approach is to alter the value of each component, rather than the total force.
By adding the two component forces and again substituting for \( r_1 \) and \( r_2 \), the total force is given by,

\[
F_{\text{pend}} = 2\pi R \gamma \left[ \frac{2r^2 - t + 1}{(1+t^2)^2} \right]
\]

(4.13)

where \( t = \tan (\beta/2) \). A comparison between the methods of Fisher [34] and Adams and Perchard [33] for calculating the interparticle force with varying half filling angle, \( \beta \), at zero separation is shown in figure 4.2.

**Figure 4.2:** Variation of forces with half filling angle, \( \beta \), at zero separation.

The values obtained for figure 4.2 were calculated using particles with a radius of 461\( \mu \)m, attached by a bridging liquid with the surface tension of water (72mN/m). From the figure it can be seen that for small values of \( \beta \) the surface tension force is insignificant and that the total liquid bridge force is approximately constant.
For agglomerating systems the range of interest in liquid bridge half-filling angle is between 0° at 45°, as the coalescence limits for liquid bridges between spheres are 30° and 45° for close-packed and cubic arrangements, respectively [36]. Figure 4.3 shows a schematic of the maximum half-filling angles possible for discrete liquid bridges to remain in ideally packed agglomerates. For bridges within an agglomerate having a large contact angle (>60°) on the particles surface, Coughlin et al. [36] observed that fusion of condensed liquid bridges did not occur.

Figure 4.3: Schematic of maximum half-filling angles allowed for discrete liquid bridges to remain in ideally packed agglomerates [36].
4.2 Finite separations, non zero contact angles and unequal sized particles

In the previous section, only equi-sized particles in contact wet with perfect wetting binders have been considered. Figure 4.4 shows a toroidal pendular liquid bridge with a contact angle, $\theta$, between two unequal sized particles at a separation distance $(a_1 + a_2)$. In certain cases of imperfect wetting it is possible that the formation of a liquid bridge results in a repulsive force being generated [37], although this is an extreme case and will not be considered here.

![Figure 4.4: Schematic showing the effect of a non-zero contact angle between unequal sized particles.](image)

Consideration of the geometry of figure 4.4 allows $r_1$ and $r_2$ to be expressed in terms of separation distances, $a_i$, particle radii, $R_i$, half filling angles, $\beta_i$, and the solid-liquid contact angle, $\theta$:

$$r_1 = \frac{a_i + R_i(1 - \cos \beta_i)}{\cos(\beta_i + \theta)}$$  \hspace{1cm} (4.14)

$$r_2 = R_i \sin \beta_i - [1 - \sin(\beta_i + \theta)]r_1$$  \hspace{1cm} (4.15)
These values can then be inserted into equation (4.7) to give the total capillary force.

### 4.3 The geometry of liquid bridges

Much of the work focusing on modelling agglomeration and investigating liquid bridges has assumed liquid bridges have toroidal geometry. Although it is generally stated that this is an approximation, the results (chapter 7) of this microscopic work and previous macroscopic works (see for example Wolfram and Pinter [38] and Padday [39]) show a range of bridge geometries dependent on the liquid-solid contact angle and the filling angle (beta). Orr et al. [37] investigated the meniscus properties and capillary forces of pendular rings between solids and classified the profiles of axisymmetric menisci of uniform mean curvature in relation to the work of Plateau [40], see figure 4.5. Figure 4.5(a) shows the meniscus at first having nodoidal geometry; here the mean curvature is negative and the pressure inside the meniscus is lower than that of the surroundings. Figure 4.5(b) shows a catenoid which has zero mean curvature; here the pressure inside the meniscus equal that outside. Figure 4.5(c) shows an unduloid section having negative meridional curvature but positive mean curvature. Figures 4.5(d)-(i) show possible geometries with positive mean curvatures, thus the pressure inside the meniscus is higher than that on the outside. Orr et al. [37] also derive equations for the dimensionless mean curvatures, radii and heights for the cases shown.
Figure 4.5: Profiles of axisymmetric menisci of uniform mean curvature [37].
Wolfram and Pinter [38] investigated liquid bridges formed between two horizontal plates immersed in a second liquid. Their system consisted of a pyrex glass top plate and a PTFE bottom plate with water and n-hexane used as the bridging and surrounding liquids (figure 4.6).

Figure 4.6: Images of 250ml liquid bridges between flat plates [38].

Figure 4.6(a) shows a 250ml water liquid bridge surrounded by n-hexane. Figure 4.6(b) shows a 250ml n-hexane liquid bridge surrounded by water. The high contact angles result in an unduloid type geometry being observed. However in these cases the effect of gravity must also be considered [35]. Padday [39] investigated the equilibrium and stability properties of menisci for a range of systems, following on from earlier work he conducted on the profiles of axially symmetric menisci [41]. Within these works the shape properties of bounded menisci such as sessile drops, pendant drops, sessile bubbles and emerging bubbles, and unbounded menisci such as a liquid bridge between two horizontal plates, were investigated. He also identified the shapes that the meniscus of a liquid bridge will form as being either catenoid, nodoid or unduloid. Figure 4.7 shows nodoidal (A) and unduloidal (B and C) geometries.
It is now possible to look at the fundamental physical reasons behind the formation of such shapes in terms of the balances of forces and stability.

### 4.3.1 Geometrical patterns

It is well known that a sphere has the least surface area for a given volume and is the most suitable structure for restraining internal forces. The exact nature of these internal forces is immaterial, and they can be made up of nuclear, electrostatic, magnetic, surface tension, elastic, hydrostatic, centrifugal, convective and gravitational components. The type of forces that operate are determined partly by the size, the amount, and the kind of matter, in a given amount of space. To be able to develop expressions for the menisci shapes and thus bridge volumes of static pendular liquid bridges, it is necessary to understand the forms liquids will take when subject to a combination of these forces.
4.3.1.1 Conic Sections

When subjected to unbalancing forces the geometrical patterns of a sphere or a circle are lost. Unbalanced spherical patterns often change to shapes or curves known as conic sections, which were discovered in the fourth century BC by Menaechmus, and more completely investigated by Apollonius in the third century BC. These conic sections are formed by the intersection of a plane and a right circular cone (a solid generated by rotating a right triangle around one of the legs of the 90° angle). Figure 4.8 shows a double cone.

![Figure 4.8: The conic sections](image)

**Figure 4.8:** The conic sections

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Circle</td>
</tr>
<tr>
<td>B</td>
<td>Ellipse</td>
</tr>
<tr>
<td>C</td>
<td>Parabola</td>
</tr>
<tr>
<td>D</td>
<td>Hyperbola</td>
</tr>
<tr>
<td>E</td>
<td>Point</td>
</tr>
<tr>
<td>FG</td>
<td>Straight line</td>
</tr>
</tbody>
</table>
If a plane is sliced through the cone in such a way that the plane is perpendicular to the axis of the cone, the section of the cone is a circle (Figure 4.8 A). If the plane cuts the circular cone obliquely to the axis, the section of the cone is an ellipse (Figure 4.8 B). If the cutting plane is parallel to one of the sides of the circular cone, a parabola is formed (Figure 4.8 C). Alternatively, if the plane intersects each of the two cones, a hyperbola is formed (Figure 4.8 D), and if the cutting plane is tangent to one of the sides of the circular cone, a straight line is formed (Figure 4.8 EF). If the cutting plane is outside the cone, but touches at point E, a point is given (Figure 4.8 E).

### 4.3.1.2 Surfaces of Revolution

Plateau's surfaces of revolution are surfaces of objects that are symmetrical around an axis. They represent examples of other shapes into which conic sections can be transformed. These principles were discovered in 1873 by Joseph Plateau [40]. He found that there are only six types of symmetrical surfaces that can be formed by oil globules or soap bubbles; thus a bubble can be blown up into a sphere, or shaped into a plane surface, cylinder, unduloid, catenoid, or nodoid (see figure 4.9).

![Figure 4.9: Five of the six surfaces of revolution formed by a film of oil or soap.](image)

The five symmetrical surfaces show in figure 4.9 occur when:

a) a soap bubble floating in air forms a sphere
b) a ring dipped in a soapy solution will create a plane surface soap film inside the ring
c) a soap bubble between two rings can be stretched apart until it takes the shape of a cylinder
d) the cylindrical form of the soap bubble is stretched further to give the shape of a catenoid
CHAPTER 4. PENDULAR LIQUID BRIDGES

e) a bubble of oil stretched a proper distance between two rings will cause the lower portion to bulge (due to gravity, surface tension etc.), thereby forming an unduloid structure

All these surfaces are related and can easily slip from one to another. The mathematical relationship between them was first shown by Delaunay in 1841. He proved that the mathematical curves shown in figure 4.10, which are generated as roulettes (curves generated by a point on a curve rolling on another - as when using a spirograph - the dot represents the focal point that traces the roulette pattern) of the conic sections, can be used to create the shapes of figure 4.9.

Figure 4.10: Roulettes of five of the conic sections.

Key:

a) Straight line traced by the centre of the circle.
b) Unduloid traced by one focus of an ellipse.
c) Semi-circle traced by one of the focal points at the end of a straight line.
d) A catenoid traced by the focal point of a parabola.
e) A nodoid traced by the focal point of a hyperbola.
As can be seen in figure 4.11, every ellipse has two axes (AOA' is called the major axis and BOB' is called the minor axis. F and F' are the two focal points and O is the centre). One axis passes through the two focal points, the other axis is at right angles to it and passes through the centre of the ellipse. The more unequal the length of these axes, the greater will be the swings of the undulation of the roulette. If the two axes are equal, the ellipse becomes a circle. The curve created by the rolling centre of a circle is a straight line parallel to the line on which it is rolling. This roulette line, when rotated around the baseline, creates a cylinder. Thus it can be seen that an unduloid changes to a cylinder when the ellipse reduces to a circle. If one axis of the ellipse decreases to zero length but the other axis still has a definite length, then the ellipse is reduced to a straight line with one focus at each end. This generates a roulette of semicircles. These semicircles, in turn, rotate around the baseline to create a series of spherical surfaces.

Figure 4.11: Schematic of an ellipse.
4.4 The rupture distance of liquid bridges

As discussed already, the force exerted by a liquid bridge between particles is dependent on the separation distance between the bodies. However a bridge is only stable up to some critical separation distance, at which point it will rupture. In order to understand how and when a liquid bridge will rupture it is interesting to review the work of Plateau [40], before considering the specific liquid bridge work.

4.4.1 Collapse of Cylindrical Structures

Plateau [40] showed that a cylinder of liquid is not a structure of stable equilibrium if its length is longer than the circumference. A long cylindrical liquid rod (figure 4.12) if it could be assembled and then left by itself, would immediately collapse into a row of equally sized and equally spaced drops.

Figure 4.12: Schematic of a cylinder of liquid. This state cannot exist for long if its length is more than its circumference.

In the above example, the cause of collapse would be due, mainly, to surface tension minimising energy. Plateau was able to show by his experiments that any disturbances formed at distances less than the circumference of the cylinder would result in a configuration as in figure 4.13. There is a very simple law that states that the distance between the centres of the drops is equal to the circumference of the cylinder.
Figure 4.13: Schematic of unduloid column. The liquid cylinder in figure 4.12 can change to the unduloid shape when it is disturbed.

The disturbance would affect the curvature of the outside surface in such a way as to make the surface tension push the bulges (shown in figure 4.13) back and pull the hollows outwardly. If the bulges are further apart than the circumference of the cylinder, then the sharper curvature of the thinner parts will force the liquid in the thinner parts into the parts that are already wider. Thus any such disturbance would cause the bulges to separate still further, or cause the whole thing to break into drops. Before the break-up occurs, the drops are joined by narrow necks of liquid (figure 4.14 top). These narrow necks split themselves up into smaller secondary droplets (figure 4.14 bottom). When dealing with different substances, there will be variations in the actual phenomena observed. These variations are determined by the viscosity, the inertia of the fluid, gravity, etc.

Figure 4.14: Schematic of continuation of break up of the cylinder.
Plateau [40] explained the formation of the smaller beads as follows: When contact is nearly broken between two big spheres, there is still a narrow thin neck. The fluid does not flow easily out of this neck into the larger spheres because of internal friction. This thin cylinder now acts like another cylinder, but of smaller circumference. Therefore, it also breaks up when the length becomes greater than the new, smaller circumference. This length is usually such that it breaks at two points. This leaves an end piece attached to each sphere, which is absorbed, and a small sphere in the centre. Sometimes the same process of formation of a connecting thread is repeated a second time between the small intermediate bead and the larger sphere. In this case, there are two additional beads of still smaller size on each side of the first small one.

4.4.2 Liquid bridge rupture

When the separation distance of a liquid bridge held between two particles is increased the meniscus displaces until a certain critical bridge separation is attained, at which point the bridge becomes unstable and ruptures. From experimental observations the neck diameter at this critical point is greater than zero. Erle et al. [42] and De Bisschop and Rigole [43] both developed numerical evaluation procedures for the stability of liquid bridges in relation to the work of Plateau [40]. They found that there were two solutions of the Laplace-Young equations which converged to a single solution at a critical separation distance. For separation distances beyond this critical value there were no solutions. Erle et al. [42] proposed that if the solutions were expressed in terms of liquid bridge neck diameter, the critical separation distance corresponded to the rupture point. De Bisschop and Rigole [43] stated that as separation distance is increased the half-filling angle (β) decreases continuously and rupture occurs when it reaches a minimum. It was subsequently observed by Mazzone et al. [44] and also in this work that a minimum half-filling angle is indeed reached, but that stable bridges can exist on increasing the separation distance beyond this point with β actually increasing before rupture (see also figure 4.15(b)).
More recently Lian et al. [45] have conducted a theoretical study of the liquid bridge forces between two rigid spherical bodies. They developed the previous work, stating that as well as neck diameter and half-filling angle, mean curvature and total force could also be used as predictive criteria for the critical separation distance. Figure 4.15 shows the results of the work by Lian et al. [45]. The two solutions of the Laplace-Young equation are shown, the solid lines representing the regions with the lower surface free energy and thus the 'stable' regions. Their results are consistent with the work of Mazzone et al. [44] and show good agreement with the experimental work of Mason and Clarke [4]. From figure 4.15(b) it can be seen that theory predicts the observed rise in the half-filling angle before the critical separation distance is reached.

Following on from the solutions shown in figure 4.15, Lian et al. [45] derived a simple relationship between the rupture distance and the bridge volume. By plotting dimensionless volume ($V_b^*$) against the dimensionless rupture distance ($a_1 + a_2^* = (a_1 + a_2)/R$) they proposed the following relationship,

$$a_1 + a_2^* = (1 + 0.5\theta)^{3/2}V_b^*$$  \hspace{1cm} (4.16)

where $\theta$ is the solid-liquid contact angle expressed in radians.
Figure 4.15: Stable (——) and unstable (ΔΔ) numerical solutions of the Laplace-Young equation at different dimensionless separation distances for a range of dimensionless liquid bridge volumes and a zero contact angle expressed in terms of (a) the dimensionless neck radius, (b) the half-filling angle, (c) the dimensionless mean curvature, and (d) the dimensionless total liquid bridge force [45].
4.5 The Bridge Volume

To calculate the volume of a liquid bridge from a two dimensional image it is necessary to characterise the line $C_1HC_2$ (see figure 4.16) and perform a volume of revolution integration around the $x$-axis (assuming an axisymmetric liquid bridge - this is a reasonable assumption for liquid bridges between small particles - see for example Princen [35]). The volume of the liquid bridge is then obtained by subtracting the volumes of the segments of the spheres obtained by rotating the arcs $C_1D_1$ and $C_2D_2$ around the $x$-axis.

4.5.1 The Toroidal Approach

Previously it has been assumed that a pendular liquid bridge has the geometry of a toroid [6] and a combination of two dimensional measurements with volume of revolution integration have been used to calculate the bridge volume based on the approximation originally derived by Jacques et al.[46]. Figure 4.16 shows the centres of two spheres $A_1$ and $A_2$ which are points on the $x$-axis. The spheres’ radii are given by $R_1$ and $R_2$. The $y$-axis intersects the $x$-axis at the point $B$ and the separation between the spheres is given by $a_1 + a_2$. $r_1$ gives the radius of the arc $C_1HC_2$.

The general expression for the arc $C_1HC_2$ is given by;

$$x^2 + (y-j)^2 = r_1^2 \quad (4.17)$$

The expressions for the arcs $(C_iD_i)$ formed by the spheres are given by,

$$(x-(R_i+a_i))^2 + y^2 = R_i^2 \quad (4.18)$$

where $i=1$ or 2.
By using volume of revolution integration of the form,

\[ V = \int_{a}^{b} \pi y^2 \, dx \quad \text{where} \quad y = f(x) \]  

(4.19)

it is possible to calculate the volume of the toroid formed by rotating the arc \( C_1H \)\( C_2 \) about the x-axis through one revolution. The volume of the liquid bridge is then obtained by subtracting the volumes of the segments of the spheres obtained by rotating the arcs \( C_1D_1 \) and \( C_2D_2 \) around the x-axis. Thus rearranging equation 4.17 in terms of \( y \) gives,

\[ x^2 + (y-j)^2 = r_1^2 \]  

(4.17)

\[ (y-j)^2 = r_1^2 - x^2 \]

\[ y-j = \pm(r_1^2 - x^2)^{0.5} \]

\[ y = j \pm (r_1^2 - x^2)^{0.5} \]  

(4.20)
This equation for \( y \) describes the whole circle and from consideration of the geometry of figure 4.16 the arc \( C_1HC_2 \) is given by,

\[
y = j - (r_1^2 - x^2)^{0.5}
\]

(4.21)

\[
y^2 = j^2 - 2j(r_1^2 - x^2)^{0.5} + r_1^2 - x^2
\]

(4.22)

And rearranging equation (4.18) in terms of \( y^2 \),

\[
(x-(R_i+a_i))^2 + y^2 = R_i^2
\]

(4.18)

\[
x^2 - 2(R_i + a_i)x + (R_i + a_i)^2 + y^2 = R_i^2
\]

\[
x^2 - 2R_ix - 2a_ix + R_i^2 + 2a_iR_i + a_i^2 + y^2 = R_i^2
\]

\[
y^2 = 2R_ix + 2a_ix - 2a_iR_i - a^2 - x^2
\]

(4.23)

Thus the volume of half the liquid bridge \( V_i \) can be given by integrating with respect to \( x \), between \( x=0 \) and \( x=f \) for the bridge and \( x=a \) and \( f \) for the segments.

\[
V_i = \pi \int_0^f \left[ j^2 - 2j(r_i^2 - x^2)^{0.5} + r_i^2 - x^2 \right] dx - \pi \int_a^f \left[ 2R_ix + 2a_ix - 2a_iR_i - a^2 - x^2 \right] dx
\]

(4.24)

and the total volume calculated from \( V=V_1 + V_2 \).

Integration of equation (4.24) gives [47],

\[
V_i = \pi \left[ j^2x - 2j \left( \frac{x(r_i^2 - x^2)^{0.5}}{2} + \frac{r_i^2}{2} \arcsin \frac{x}{r_i} \right) + r_i^2x - \frac{1}{3}x^3 \right]_0^f
\]

\[
-\pi \left[ R_ix^2 + ax^2 - 2aRx - a^2x - \frac{1}{3}x^3 \right]_a^f
\]

(4.25)

by consideration of the geometry of figure 4.16, \( \sin k_i = f/r_i \), therefore \( \arcsin f/r_i = k_i \).

(For this equation to be valid \( r_i > f \)) and \( (r_i^2 - x^2)^{0.5} = f \cot k_i \).
Thus:

\[ V_i = \pi [ j^2 f - j f^2 \cot k - j r_j^2 k_i + r_i^2 f - \frac{1}{3} f^3] - \pi [R_i^3 (1 - \cos \beta_i)^2 - \frac{R_i^3}{3} (1 - \cos \beta_i)^3] \] (4.26)

where

\[ j = r_1 + r_2 \]
\[ k_i = (\pi/2) - \beta_i - \theta \]
\[ f = a_i + R_i (1 - \cos \beta_i) \]

This equation is the same as that derived by Lian [48] numerically,

\[ V_i = \pi \left[ (r_1 + r_2)^2 x_{ci} + r_1^2 x_{ci} - \frac{x_{ci}^3}{3} - (r_1 + r_2) \left( x_{ci} \sqrt{r_1^2 - x_{ci}^2} + r_1^2 \arcsin \frac{x_{ci}}{r_1} \right) \right] - \frac{\pi R_i^3}{3} (1 - \cos \beta_i)^2 (2 + \cos \beta_i) \] (4.27)

where,

\[ i=1,2 \] and \[ x_{ci} = a_i + R_i (1 - \cos \beta_i) \] (equivalent to \( f \))

### 4.5.2 Catenoidal Approach

For certain liquid bridge systems the bridge has catenoidal geometry (see the results chapter). Thus it is useful to modify the toroidal approximation to give a more accurate calculation of the liquid bridge volume. Since a volume expression for catenoidal bridge geometry is not available in the literature, the following derivation was developed in this work.

A catenoid can be described by finding the equation of the catenary line (see figure 4.17) and rotating it around the x-axis. The general form of the equation of a catenary is;

\[ y = b \cosh \left( \frac{x}{b} \right) \] (4.28)

the effect of the value of 'b' can be see in figure 4.17.
Thus the general expression for the arc $C_1HC_2$ (figure 4.16) becomes,

$$y = r_2 \cosh \left( \frac{x}{r_2} \right)$$

(4.29)

A catenoid is a minimum surface, meaning it has zero mean curvature ($H=0$ - equation 4.4). The expressions for the arcs $(C_iD_i)$ formed by the spheres remain the same and are given by,

$$(x-(R_i+a_i))^2 + y^2 = R_i^2$$

(4.30)

where $i=1$ or 2.

Again, by using volume of revolution integration of the form,

$$V = \int_a^b \pi y^2 \, dx$$

where $y = f(x)$

(4.31)

the volume of the bridge can be calculated,

$$V = \pi \int_{r_2}^{r} r^2 \cosh^2 \left( \frac{x}{r_2} \right) \, dx$$

(4.32)

Now, $\cosh 2x = 2 \cosh^2 x - 1$ [47] and therefore,
\[ \cosh^2 x = (\cosh 2x + 1)/2. \quad (4.33) \]

Substituting into equation 4.32 gives,

\[ V = \pi \int_0^{r_2} \frac{r^2 \cosh \left( \frac{2x}{r_2} \right) + 1}{2} \, dx \quad (4.34) \]

and

\[ V = \frac{\pi}{2} \int_0^{r_2} r^2 \cosh \left( \frac{2x}{r_2} \right) + 1 \, dx \quad (4.35) \]

\[ V = \frac{\pi r_2^2}{2} \left[ \frac{r_2}{2} \sinh \left( \frac{2x}{r_2} \right) + x \right]_0^f \quad (4.36) \]

\[ V = \frac{\pi r_2^3}{4} \left[ \sinh \left( \frac{2x}{r_2} \right) + x \right]_0^f \quad (4.37) \]

Thus half the volume \( V_i \) is given by,

\[ V_i = \frac{\pi r_2^3}{4} \left[ \sinh \left( \frac{2x}{r_2} \right) + x \right]_0^f - \pi \left[ R_i x^2 + ax^2 - 2aR_i x - a^2 x - \frac{1}{3} x^3 \right]_0^f \quad (4.38) \]

(\text{using } \sinh 0 = 0) and finally,

\[ V_i = \frac{\pi r_2^3}{4} \left[ \sinh \left( \frac{2f}{r_2} \right) + f \right] - \pi \left[ R_i^3(1-\cos \beta_0)^2 - \frac{R_i^3}{3}(1-\cos \beta_0)^3 \right] \quad (4.39) \]

### 4.6 Dynamic effects

The previously stated force equations are valid for static liquid bridges. However in most agglomeration processes, such as spherical agglomeration and binder granulation, dynamic effects play an important role. Here the viscosity (whether it be Newtonian or
non-Newtonian), the dynamic surface tension of the binder (section 3.2.4) and any
dynamic contact angle effects (due to hysteresis - section 3.4.2) have to be considered
along with the kinetic energy of colliding particles. Adams and Perchard [33] applied
lubrication theory to derive the following expression for the viscous force,

\[ F_v = \frac{3\pi \mu (R^*)^2 v_n}{a} \]  (4.39)

where \(1/R^* = 1/R_1 + 1/R_2\), \(\mu\) is the viscosity of the liquid, \(v_n\) is the relative velocity
between the two spheres and \(a\) is the total separation between the spheres.

In this derivation they assumed the viscous separation force for the two solids attached
by the liquid bridge arises from the radial pressure flow of the liquid. They state that the
inverse of this phenomenon, in which solid surfaces are pressed together, is known as
'squeeze film' and is of considerable importance in lubrication theory.

However, in their derivation Adams and Perchard [33] made several assumptions which
the results presented in this thesis (chapter 7) and those presented by other workers (see
for example [49] and [50]) have shown to be invalid. For example they state that the
constant volume requirement of a pendular liquid bridge means that during particle
separation the contact area must decrease. The results of this work (section 7.2) have
shown pendular bridge volumes are not always constant and the contact area (effectively
the half filling angle) can decrease with increased separation, but then can increase with
changes in bridge geometry (section 7.3).

More recently, additional work has focused on the modelling of agglomerating systems.
By their nature agglomerating systems are dynamic and it is felt the theories developed
for these cases more closely match the experimental results and observations of this
work. Chapter 5 considers different approaches to analysing dynamic agglomerating
systems.

Dynamic effects of individual liquid bridges are reported upon later in this work.
Section 7.2 examines changes in liquid bridge volume with separation between particles,
a previously unreported phenomenon. Section 7.3 examines the relationship between binder on solid contact angle and bridge geometry, theoretically examined in section 4.3.
Chapter 5

5. Modelling of Agglomerating Systems

Improvements in the fundamental understanding of individual particle-particle interactions will improve the modelling of agglomeration processes as a whole. However, adapting the theories of interparticle forces between pairs of equal spheres to multi-body agglomerates, whose constituent particles are spheres or otherwise, is no trivial task and it is therefore perhaps not surprising that many workers have taken the empirical approach to modelling based on experience and experimental data. Many useful models have been developed in this way, several of which form crucial stages in the design procedures of commercial equipment, such as thickeners and fluidised bed granulators.

A key process where “wet” agglomeration takes place is that of granulation, used extensively in the mineral, pharmaceutical and fertiliser industries. A great deal of research has focused on determining which of the many process variables, such as the
size, size distribution and shape of the solid(s), the surface tension and the viscosity of the binder, the wetting of the solid by the liquid (contact angle), geometry and speed of the drum or impeller etc., should be used as predictive criteria for successful operation of granulators. However, the mechanisms of granulation in relation to these parameters are still poorly understood and the initial choice of equipment and subsequent manipulation of the process conditions to optimise granulation is still largely empirical and system-specific [15].

Recently there have been efforts to bring together a cross section of disciplines and industries dealing with agglomeration processes in order to share ideas and develop the fundamental understanding of agglomeration phenomena which can be utilised in the design and optimisation of agglomeration processes. Work published by Ennis et al. [5], who developed a dimensionless Stokes number relating granule collisional kinetic energy to the viscous dissipation brought about by interstitial binder, and by Simons et al. [6], who developed a model relating the energy required to rupture a single liquid bridge solely to its volume, have done much to improve the understanding and provoke further work on the fundamentals of agglomeration. At the Agglomeration and Size Enlargement session of the First International Particle Technology Forum (Denver, 1994), Sastry [51] presented a process based approach to the development of industrial granulation plant operation procedures, combining fundamental principles with operating experience (Figure 5.1).

The work presented in this thesis is concentrated on the understanding of the areas in the top part of figure 5.1. The current state and future needs of industrial agglomeration equipment have been assessed through published literature and personal communication with both manufacturers and end users of agglomeration equipment. The following sections (5.2 and 5.3) review the seminal work of Ennis et al. [5] and Simons et al. [6]. In the final parts of the chapter the current literature is reviewed.
Figure 5.1: Representative interfaces between process engineering and a typical granulation plant [51].
5.1 The ‘Ennis’ Approach

For a full description of a ‘wet’ agglomeration process it is important to be able to predict the initial agglomeration behaviour, i.e. whether collisions between wet particles will give rise to rebound or ‘capture’. Thus Ennis et al. [5] investigated the forces involved in the collision between two spherical particles (radius, R), surface-wet with a layer of binder (thickness, δ), in an attempt to develop the fundamental understanding of granule growth (figure 5.2). Both capillary and viscous dissipation mechanisms were considered, however it was shown that the latter effectively dominated the surface tension effects provided the binder was well dispersed and sufficiently viscous. By considering the energy dissipation in the coming together of the liquid layers and any subsequent formation of a dynamic pendular bridge, Ennis et al.[5] developed expressions for the minimum velocity required for the particles to rebound. A viscous Stokes number for two identical spheres (radii R) colliding was defined as,

\[ St_v = \frac{2mv_0}{3\pi\mu R^2} = \frac{8\rho v_0 R}{9\mu} \]  

(5.1)

where \( v_0 \) is the velocity of particle collision, \( m \) is the mass and \( \mu \) the viscosity.

It was stated that for rebound to occur the Stokes number must exceed a critical value, \( St_v^* \).

\[ St_v^* = \left[ 1 + \frac{1}{e} \right] \ln \left[ \frac{\delta}{h_a} \right] \]

(5.2)

where \( h_a \) represents some characteristic length of surface asperities and \( e \) is the particle coefficient of restitution with the presence of binder (thickness \( \delta \)). This is calculated by assuming the initial rebound velocity which is equal to \( ev_a \), where \( v_a \) is the velocity of each approaching particle upon reaching a separation distance \( h_a \) from each other.
In any agglomerator, there will be a range of particle velocities and possibly a maldistribution of binding liquid, giving rise to a distribution of operating Stokes number, $St_v$. Whether this distribution falls above or below $St_v^*$ will govern the rate and mechanisms of agglomerate growth in so far as success of particle collisions in terms of rebound or "capture" are concerned. Three granulation regimes were defined according to the magnitude of $St_v$ in comparison to $St_v^*$.

(i). $St_v \ll St_v^*$ non-inertial regime (all collisions successful)
(ii). $St_v \approx St_v^*$ inertial regime (some collisions successful)
(iii). $St_v \gg St_v^*$ coating regime (no collisions successful)

For fine powders, growth often occurs by all three of the above mechanisms, proceeding through them as agglomerate size and $St_v$ increase. Quantifying where the boundaries of the regimes occur depends on gaining a knowledge of all the variables. According to Ennis, in the case of a drum granulator with a rotational speed of $\omega$ the relative agglomerate velocities are of the order of $v_o = 2R_A \omega$, where $R_A$ is the agglomerate radius. Adetayo et al. [52] estimated the agglomerate velocities to be $v_o = \alpha R_D \omega$, where $R_D$ is the radius of the granulator and $\alpha$ is a constant. Substituting Ennis's expression into (5.1) the critical Stokes number can be defined as:
\[ S_{tv}^* = \frac{16\rho R_A'^2 \omega}{9\mu} \]  

(5.3)

where \( R_A' \) is the mean agglomerate radius.

In order to relate their model to granulation processes, Ennis et al. [5] assumed granules to be non-porous, surface-wet, solid spheres with elastic, or near elastic, behaviour on collision. In reality, granules will either plastically deform on impact, fracture or break-up, leading to growth by either coalescence or crushing and layering. In certain conditions, granules will also be surface-dry. Nevertheless, the approach represents a significant step in focusing on the governing parameters in agglomerate formation in the presence of liquid binders.

### 5.2 The Rupture Energy Model

Simons et al [6] took a different approach to Ennis [5] in developing a model to provide an approximate value of the rupture energy of pendular liquid bridges. They stated that the viscous forces do not always dominate and considered the rupture energy of a liquid bridge to be the integral of the quasi-static capillary forces with respect to separation distance, between the limits of zero (particles in contact) and the critical separation distance (rupture). However, to calculate this would be an arduous process since a non-trivial integral is obtained as the constant bridge volume means that the half-filling angle, \( \beta \), varies with separation distance. Thus a simple expression for the energy required to rupture a pendular liquid bridge was derived.

#### 5.2.1 Development of the Rupture Energy Model

By expressing the principle radii of curvature of a bridge \( r_1 \) and \( r_2 \) (see figure 4.4) in terms of dimensionless half-separation distances (\( a^* = a/R \)):

\[ r_1 = R[(1+a^*)\sec \beta -1] \]  

(5.4)
\[ r_2 = R[1+(1+a^*)\tan \beta - (1+a^*)\sec \beta] \quad (5.5) \]

and substituting into Fisher’s expression for the total capillary force,

\[ F_{\text{pend}} = \pi \gamma r_2 \left[ \frac{r_1 + r_2}{r_1} \right] \quad (5.6) \]

an expression for the total pendular liquid bridge force at varying separations was obtained:

\[ F_{\text{pend}} = \pi \gamma R(1+X \tan \beta - X \sec \beta) \left[ \frac{X \tan \beta}{X \sec \beta - 1} \right] \quad (5.7) \]

where \( X=(1+a^*) \).

The integral of this equation is the half rupture energy, \( W \):

\[ W = \pi \gamma R^2 \int_{X_{\text{min}}}^{X_{\text{max}}} \left[ X \tan^2 \beta \cos \beta + \sin^2 \beta + \frac{\sin^2 \beta}{X \sec \beta - 1} - X \tan \beta \right] dX. \quad (5.8) \]

The lower limit \( X_{\text{min}} \) can be taken as 1 (particles in contact) and the upper limit \( X_{\text{max}} \) can be calculated from Lian’s cube root of the volume expression \((2a = \frac{3}{2} \sqrt[3]{V_b})\). However, as stated above, the half-filling angle \( \beta \) is a function of separation distance. So Simons et al. [6] set out to show that over full separation \( \beta \) could be assumed to be constant.
Figure 5.3: The variation of beta with dimensionless separation distance (a*/a*max) for various dimensionless volumes (V/R^3).

From figure 5.3 it can be seen that beta has a maximum value at particle contact and then reaches a minimum with increased separation until increasing slightly before rupture. It can also be seen that the overall change in beta from contact to rupture decreases with decreasing dimensionless volumes.

As stated, in agglomerating systems the coalescence limits for liquid bridges between spheres are 30° and 40° for close-packed and cubic arrangements respectively. Thus Simons et al. stated, as a first approximation, that β was independent of a*. This approximation was verified by comparing the dimensionless force calculated using constant values of beta with those calculated using beta values obtained from the volume equation of Jacques et al. [46]. Figure 5.4 shows a comparison of the two methods.
Figure 5.4: Comparison of dimensionless force using constant and varying values of bridge half-filling angle, $\beta$. 
It was considered that there was sufficient agreement between the two to assume that beta was constant. Thus equation (5.8) was integrated:

\[ W = \pi \gamma R^2 \left[ \frac{X^2}{2} (\tan^2 \beta \cos \beta - \tan \beta) + X \sin^2 \beta + \tan^2 \beta \cos^3 \beta \ln(X \sec \beta - 1) \right]^{X_{\text{max}}}_{X_{\text{min}}} \]  

Values obtained from this expression were compared with those obtained by applying Simpson’s rule to the plots shown in figure 5.4. Table 5.1 shows the dimensionless rupture energies \( W^* = W/\gamma R^2 \) calculated by both Simpson’s rule and from equation (5.9) and the percentage difference between the values. It is clear that the difference decreases with increasing bridge volume.

<table>
<thead>
<tr>
<th>( V_b^* )</th>
<th>( \beta )</th>
<th>W* (equ)</th>
<th>W* (Simpson')</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>16.5°</td>
<td>0.31</td>
<td>0.33</td>
<td>-6</td>
</tr>
<tr>
<td>0.005</td>
<td>9.2°</td>
<td>0.13</td>
<td>0.15</td>
<td>-13</td>
</tr>
<tr>
<td>0.001</td>
<td>5.4°</td>
<td>0.06</td>
<td>0.07</td>
<td>-14</td>
</tr>
</tbody>
</table>

Table 5.1: Comparison of dimensionless rupture energy \( W^* \) values.

A simple expression for the energy required to rupture a liquid bridge was then derived by plotting \( \ln W^* \) against \( \ln V^* \). This plot shows a linear relationship which can be characterised by the equation:

\[ W^* = c V_b^{0.5} \]  

where \( c = 1.8 \). Thus a good approximation of the rupture energy of a liquid bridge can be made with a knowledge of bridge volume, particle size and the binder’s surface tension. However the model, as it stands, only considers equi-sized spheres wet with a binder giving a zero contact angle in a static situation. In addition, as only the static capillary forces have been considered for the model, it is not applicable to higher states of liquid saturation, where viscous dissipation mechanisms dominate as the air-liquid interface disappears.
The relationship derived by Simons et al. [6] has important implications in the modelling of agglomerates held together by pendular bridges. For instance, work by Abdel-Ghani et al. [53] using compacts formed from glass ballotini showed that the fracture of agglomerates can be described by fracture mechanics analysis. Here the stored strain energy released during crack extension provides the energy to extend the crack. In agglomerates where the adhesion forces are due to liquid bridges, crack extension occurs by rupture of the bridges. Hence it is useful to have a simple means of calculating the energy absorbed in this process. It is important to point out here that, whilst the rupture energy of liquid bridges scales with the fracture energy of agglomerates, the absolute contribution to the fracture energy is modest compared with the frictional energy dissipated due to the relative displacement of the primary particles during fracture.

5.3 Predicting and controlling agglomerate formation

The formation of agglomerate has arbitrarily been divided into three stages by Litster et al. [54] as:

(i). Binder distribution, wetting and nucleation
(ii). Consolidation and granule growth
(iii). Attrition and breakage

They state that two classes of granule growth have been observed depending on whether the granules are deformable or not (figure 5.5). For weak systems with a narrow size distribution of coarse particles granules grow steadily with time. The granules formed in this type of system are deformable and coalesce easily. The deformability of the granules allows energy to be absorbed and resist separating forces within the granulator. As a result, often no maximum size is reached. The growth rate increases with increased liquid content.
The second type of granule growth defined by Litster et al. [54] occurs in strong, non-deformable systems (fine particles, wide size distribution) with slow rates of consolidation. Here, after initial nucleation, there is a period of little or no growth (defined as the induction period), followed by a period of rapid growth when liquid is squeezed to the granule surfaces. With increasing liquid content the length of the induction period decreases [55]. A maximum size of granule is reached when the torque exerted on the granules by the agglomerator prevents further coalescence.

Figure 5.5: The influence of deformation on granule growth behaviour [54].
Having identified these two mechanisms of granule growth Litster et al. [54] proposed that granule growth behaviour is a function of the system’s liquid binder saturation and rate of consolidation (which is proportional to granule deformability). They state at very low concentrations of binder, particles will either remain as separate entities or form nuclei due to Van der Waals interactions, but will not grow any further. At slightly higher liquid saturations, either nuclei will form which will not grow, or for weak, highly deformable systems a non-granular ‘crumb’ material will be produced [56]. For medium amounts of binder, deformable granules will grow steadily, whilst slowly consolidating, low deformation granules will have an induction period. At high levels of liquid binder, all systems grow rapidly. At very high liquid contents, a slurry is formed (figure 5.6).

![Diagram](image)

**Figure 5.6:** Granule growth regime map proposed by Litster et al. [54].
5.3.1 The addition and distribution of the binding liquid.

Many factors influence the rate and type of initial nucleate formation. These include;

(i). the method of binder addition
(ii). the initial mixing distribution of the binder with the bulk powder
(iii). the time span over which the binder spreads onto the granular surface and / or penetrates into the pores of the powder
(iv). the type of agitation

Methods of binder addition in a high shear mixer agglomerator were investigated by Knight et al. [57]. A low viscosity (81mPas) polyethylene glycol binder (melting point 43-46°C) was used with 4μm to 23μm calcium carbonate particles. The contact angle of the binder on the solid was found to be 60 degrees. Three techniques were used to add the binder;

(i). Pour on. Molten binder was poured directly onto the solid. Mixing then commenced
(ii). Spray-on. Molten binder was sprayed onto the powder with the impeller already rotating.
(iii). Melt-in. The binder was added as solid flakes to the surface of the powder. Mixing was then started. They estimated (from torque and temperature measurements) that melting occurred in just under 3 minutes.

They found that when liquid was poured on the distribution of the liquid is produced solely by the action of mechanical mixing. Spraying the liquid on gave small droplets of liquid distributed throughout the powder, the mechanical mixing then produced a more uniform liquid distribution. The melt-in method was found to give a non-uniform liquid distribution and was dependent on the mechanical mixing. They stated that although initially the liquid distributions differ for the different addition methods, ultimately they all depend on prolonged mechanical mixing to give uniform binder distribution.
Knight et al. [57] suggested that, on mixing of a liquid with a powder, initially drops of liquid are surrounded by powder. Further mixing causes liquid to be transferred to the dry powder, with the liquid wetting the powder (assuming good wetting characteristics) and then formation of small granules takes place. They observed that the liquid wets all of the powder rapidly. From these observations they propose that in the early stages of mixing there is a bimodal distribution of agglomerate sizes.

Litster et al. [54], however, argue that the degree of binder dispersion indicates the quality of the mixing between the powder and the binder fluid, and is reflected directly in the nuclei and product size distribution. In cases where all particles are coated with equal amounts of binder, there will be a narrow size distribution. When the binder is unevenly distributed throughout the solid, some granules will become more saturated than others resulting in their preferred growth.

In order to achieve uniform binder dispersion, Litster et al. [54] state that is desirable to have a large spray area, small binder droplets, low viscosity binders and good agitation of the binder through the solid. They propose that there are four controlling steps in binder dispersion and agglomerate nucleation (figure 5.7):

2. *The impact of the droplet on the powder surface.* On hitting the powder the binder droplet may break into smaller droplets.
3. *The dispersion of the binder by wetting, capillary and gravitational effects.*
4. *The dispersion of the binder by applied shear forces.*
Depending on the balance of these factors they then propose there are three types of binder wetting and nucleation regimes:

(i). *Fast dispersion regime*. Occurs with low viscosity binders with good wetting characteristics. The size of the binder droplets controls the nucleate size.

(ii). *Intermediate regime*. Here clumps of unevenly distributed binder form (as observed by Knight et al. [57]) when the binder addition rate exceeds the binder dispersion rate.

(iii). *Slow dispersion regime*. This behaviour occurs with high viscosity binders causing the binder dispersion to be slow and controlled by the applied shear forces of agitation.

Tardos et al. [58] developed the work of Ennis et al. [5] by investigating the critical parameters and limiting conditions in binder granulation of fine powders. The aim of the work being to present a general theoretical and practical framework of binder granulation that takes an agglomeration process from binder selection and testing to granule formation, growth and consolidation and finally to granule deformation and breakup.
They also used the Stokes number analysis to determine the outcome of a collision between two binder coated particles;

\[
St_{coal} = \frac{\text{initial kinetic energy}}{\text{dissipated energy in the bridge}}
\]  

(5.11)

expressed numerically (equation 5.1) as;

\[
St_{coal} = \frac{2mv_0^2}{2F_{vis}\delta} = \frac{8\rho v_0 R}{9\mu}
\]  

(5.12)

where \(\rho\) is the particle density, \(m\) is the mass of the particle, \(\delta\) is the thickness of the liquid layer, \(\mu\) is the surface viscosity of the binding liquid and \(F_{vis}\) is given by;

\[
F_{vis} = \frac{3\pi \mu v_0 R^2}{4\delta}
\]  

(5.13)

They also define an equivalent size for two unequal particles as;

\[
\frac{2}{R} = \frac{1}{R_1} + \frac{1}{R_2}
\]  

(5.14)

In order to be able to use the above equations it is necessary either to measure or accurately predict the value of the relative velocity \(v_0\). Tardos et al. [58] state this is a complex task as the powder flow field in a mixer is very complicated and industrial drum, pan and high shear mixers have different internals such as paddles which render the flow field difficult to model. Particle motion in fluidised beds is also extremely complex due to bubble and wall effects. They do, however, state that as a rough estimate the relative velocity between particles can be taken as;

\[
v_0 = \gamma R = 18U_B R/D_B \Delta^2
\]  

(5.15)

where \(\gamma\) is the average shear rate in the mixer, \(U_B\) is the bubble velocity, \(D_B\) is the bubble spacing and \(\Delta\) is the dimensionless bubble spacing. The first expression is for all mixers, the second is for fluidised beds.
5.3.2 Agglomerate consolidation

Agglomerate consolidation takes place when bridges within an agglomerate are viscous or deformable or if the agglomerate is plastic and malleable. In these cases external compressive and shear forces tend to push particles together and reduce the apparent density of the agglomerate. After binder has been added to a particulate system the agglomerates formed (in both high and low shear agglomerates) are often porous. Knight and Seville [59] proposed that the porosity of the agglomerate can take two forms. For certain systems, 'macro-pores' of air, with a size significant larger than that of the constituent particles, are present in the agglomerate. Mixing causes this air to be released or the pores compressed. For other systems, the liquid does not fill all the space between the particles. Here the pore size is smaller or of a similar size to that of the constituent particles. Mixing causes particles to pack more closely together and the air to be expelled until liquid completely fills the agglomerate. At this stage further close packing of the particles causes binder to be extruded to the surface of the agglomerate and it at this point the agglomerate growth rate is at its maximum.

The role of binder viscosity in agglomeration has recently been the subject of research as a result of the work of Ennis et al. [5] and Simons et al. [6]. Ennis et al. [5] proposed that in the collision of granules the viscous forces prevent rebound and allow granules to stay in contact long enough for coalescence to occur. It may also be the case that agglomerates deform, causing most of the energy to be dissipated in the liquid rather than in the particles rebounding. If deformation does take place the energy can be absorbed by viscous, surface tension or frictional forces. Both Ennis et al. [5] and Simons et al. [60] suggest that the process of compaction of the agglomerate nuclei may actually be retarded by viscous forces. Industrially used binders vary in viscosity and may be non-Newtonian.
Iveson et al. [61] investigated the effects of binder viscosity and binder content on agglomerate consolidation using a 0.3m diameter granulation drum with glass ballotini particles and glycerol-water mixtures as the binder. They developed on the work of Ennis et al. [5] and stated that agglomerate consolidation during tumbling is controlled by the balance between the different mechanisms that resist granule deformation: interparticle friction and viscous dissipation. They found that with decreasing particle size the rate of consolidation decreased. This occurs as decreasing the particle size increases the specific area of particles and increases the resistance to granule deformation by both interparticle friction and viscous dissipation. As the amount of liquid binder was increased the effect of interparticle friction decreased but the viscous losses became more significant. They concluded that the effects of binder viscosity and liquid content are highly interactive and unless the balance between the two mechanisms is accurately known for a given system, the effects of changes to binder parameters on agglomeration behaviour cannot be predicted.

Keningley et al. [62] studied the effects of the viscosity of the binder on agglomeration carried out within a high shear mixer (impeller tip speed 10m/s). Various sizes (8-230 μm diameter) of non-porous calcium carbonate particles and poly(dimethylsiloxane) silicone oils with viscosities in the range 0.001-56 Pa s were used. The minimum viscosity to form granules was found to be 10mPa s for a 8μm powder, 100mPa s for 50μm and 80μm powders and 1 Pa s for a 230μm powder. For the binders with viscosity below 1 Pa s, the consolidation time was independent of viscosity. They proposed that the surface tension forces dominated under these conditions and that consolidation was opposed by frictional forces caused by the capillary pressure (as proposed by Ouchimaya and Tanaka [63]). For binders with viscosities above 1 Pa s, the data presented was consistent with increasing binder viscosity retarding the rate of compaction of agglomerates, although this was not a linear relationship. They concluded that it is the impact strength of agglomerates which is the critical factor in determining whether or not agglomerates survive in a high shear mixer.
It was shown by an order of magnitude analysis of the impact resistance of agglomerates that frictional forces produced by the action of surface tension are too small to make a significant contribution, but that forced viscous flow within the agglomerate can, with high viscosity binders, give a high impact resistance. An equation for the maximum strain ($\varepsilon_m$) was developed as;

$$\varepsilon_m^2 = \frac{1}{540} \frac{\varepsilon^3}{1 - \varepsilon^2} \frac{\rho_D u_0 d_{3.2}^2}{\mu}$$

where $\varepsilon$ is the porosity of the agglomerate, $\rho_D$ is the density of the agglomerates, $u_0$ is the agglomerate impact or collision velocity, $d_{3.2}$ is the Sauter mean diameter and $\mu$ is the binder viscosity. They considered that to prevent fracture the maximum strain must stay below some critical value, taken to be 0.1.

Tardos et al. [58], using their velocity equation (5.15), stated that it is possible to calculate limiting (critical) agglomerate sizes for the point when the process crosses over the different granulation regimes, where $St_{coal} = St^*_{coal}$:

$$G_{cr}^{coal} = \left(9 \mu S_{t_{coal}}^*/8 \rho \gamma \right)^{\frac{1}{2}} = A_0 / \gamma^{\frac{1}{2}}$$

They propose rapid agglomerate growth occurs below the critical agglomerate size $G_{cr}^{coal}$, while above this critical size growth slows considerably, as coalescence of larger particles stops at the critical point where $St_{coal} = St^*_{coal}$. The slow growth region occurs when small particles (with a small critical Stokes number) bind to larger particles or agglomerates by the layering mechanism. The slow growth region occurs as long as fines are present and there is sufficient binder.
The $A_0 / \dot{\gamma}^{\frac{1}{2}}$ term of equation 5.17 states that the critical agglomerate size is approximately proportional to a constant ($A_0$) divided by the square root of the average shear rate in the agglomerator and since the value of the critical Stokes number is not available for most agglomerations, this is the most information that can be extracted from the above model. To be able to use the model as a predictive tool for detailed calculations, a value of the critical Stokes number has to be estimated from theoretical considerations or obtained by direct measurements [58].

### 5.3.3 Attrition and breakage

After the rapid growth stage of consolidation, deformable agglomerates exist which can grow slowly by layering (see above) or can deform and break. Tardos et al. [58] define a dimensionless Stokes number which relates the kinetic energy applied to the agglomerate to the internal energy resisting deformation:

\[
S_t^{\text{def}} = \frac{\text{externally applied kinetic energy}}{\text{energy required for deformation}}
\]  

expressed mathematically,

\[
S_t^{\text{def}} = \frac{m_p \dot{v}_0^2}{2V_p \tau(\gamma)}
\]

where $m_p$ and $V_p$ are the mass and the volume of the agglomerate respectively and $\tau(\gamma)$ is the stress in the agglomerate. They state that the stress in the agglomerate can be calculated from the Herschel-Bulkley model:

\[
\dot{\tau}(\gamma) = \tau_y + k \gamma^n
\]

where $\tau_y$ is the yield strength, $k$ is the apparent viscosity and $n$ is the flow index. They assume that the apparent viscosity is negligible compared to the yield strength, thus,
\[ \tau(\dot{\gamma}) = \tau_y \]  \hspace{1cm} (5.21)

By taking \( v_0 = R \dot{\gamma} \) (equation 5.15) the deformation Stokes number becomes:

\[ St_{def} = \rho G^2 \dot{\gamma}^2 / 2\tau_y \]  \hspace{1cm} (5.22)

From this Tardos et al. [58] derive a critical agglomerate size for the point at which deformation and breakage will occur.

\[ G_{cr}^{def} = (2\tau_y St_{def}^* \rho)^{1/2} / \dot{\gamma} = B_0 / \gamma \]  \hspace{1cm} (5.23)

where \( B_0 \) is a constant. Thus in this case the critical agglomerate size is inversely proportional to the average shear rate.
6. Experimental apparatus

To improve and develop the fundamental understanding of agglomeration, it is necessary to obtain data on the behaviour of individual particles coming together and becoming attached in the presence of liquid binder. As many agglomerates are formed initially from sub 250μm particles it is desirable to obtain data in the mixed colloidal, non-colloidal particle size range (i.e. < 250μm). Previous work [4] obtained data for macroscopic (3cm diameter) particle-particle interactions. Thus the basis for this project was that there was a lack of data for microscopic particles and advances in electronics and image analysis made it possible to design and commission a novel piece of experimental apparatus capable of measuring forces between microscopic particles and recording, visually, the geometries liquid bridges attain under a range of conditions.

The experimental equipment consists of an Olympus BX60 optical microscope fitted with an adapted stage, on which two micromanipulators are employed to hold micropipettes, to the ends of which particles are attached. A third micropipette is then used to add a measured amount of bridging liquid between the particles. The force is
calculated by measuring how much a pre-calibrated pipette bends as the particles are separated (under piezoelectric control), allowing forces down to $10^{-9}$ N to be resolved.

This equipment enables the liquid bridge forces between particles to be measured with both gas and liquid as the surrounding bulk medium. The rupture sequence is captured on video and image analysis software is used to measure the volume of the bridge, the separation distance at which the bridge ruptures and the variation of the half filling angle with separation distance.

![Schematic of the equipment layout.](image)

**Figure 6.1:** Schematic of the equipment layout.

### 6.1 The adapted stage

The apparatus (see figure 6.2) capable of measuring the forces between microscopic particles attached by pendular liquid bridges was designed by Dr. L.R. Fisher of the University of Bristol, Physics Department. The design is based on equipment used during the 1980's to measure the adhesion between biological cells (see for example Bowers et al.[64]).
Figure 6.2: Photograph of the microscope stage.

KEY
A Flexible pipette - piezo-electrically controlled micromanipulator.
B Reflecto-optic following micromanipulator
C Oil feed micromanipulator
D Static pipette micromanipulator

Initially a straight micropipette with a particle attached to one end, is clamped onto the static pipette micromanipulator (D) with the particle being placed under the objective lens of the microscope. Fine adjustment in all three dimensions is achieved using the individual plane micrometers of the micromanipulator.
The second particle, attached to a pre-calibrated flexible micropipette, is then placed under the objective in contact with the first particle (figure 6.3). Again, fine adjustment can be made using the micrometers of the micromanipulator. This micromanipulator also incorporates a 30μm expansion piezo-electric crystal (PEC), which allows the pipette to be driven remotely (see below).

Because piezo-electric crystals exhibit non-linear expansion and hysteresis with respect to applied voltage, a Linear Variable Differential Transducer (LVDT) is fitted to monitor the PEC’s expansion.

To form the bridge, binder liquid is fed through a third micropipette (mounted on micromanipulator C) onto the particles. To achieve a constant, bubble free, flow of oil, the micropipette is pre-loaded with oil before mounting.

When a suitable bridge has been formed the particles are separated by applying a signal causing the PEC to expand. The force of the liquid bridge causes the flexible pipette to bend, with the bend being proportional to the force.

Figure 6.3: Schematic of the adapted stage.
To calculate the bending moment, the fourth follower micromanipulator monitors the tip of the pipette via a mirror. To control the optical follower a reflecto-optic (RO) sensor is used to linearly detect the position of the edge of the mirror in its field. The RO sensor (developed for reading bar codes on shop goods) works by transmitting a beam of light and measuring how much is reflected back. The output from the sensor, when focused on the edge of the mirror, is 0 volts. Movement onto the mirror causes an increase in the output voltage and movement away a decrease. To keep the sensor focused on the edge of the mirror, control electronics are used to drive a second 15μm expansion PEC. The expansion is measured by a LVDT. The difference between the output of the two LVDTs is used to calculate the bending moment and thus the force.

The separation of particles and monitoring of the LVDTs is computer controlled via an analogue to digital interface. The code for the program can be found in Appendix E. The set up procedure for the LVDTs and details of their accuracy and control is presented in Appendix D and Appendix F.

### 6.2 Pipette Preparation

The micropipettes are produced from 100mm lengths of 1.1mm O.D., 0.76mm I.D. borosilicate glass tubing (Supplier: Plowden and Thompson Ltd., Dial Glass Works, Stourbridge, West Midlands DY8 4YN.)

A pipette puller (figure 6.4) is used to produce the micropipettes by means of two nichrome wire heating elements. The relative positions of these elements to the borosilicate tubing allow micropipettes (figure 6.5) of varying size (length and diameter) and stiffness to be produced.
The borosilicate capillary tubing is passed through the jeweller’s four jaw chuck at the
top of the puller, down through the top melting element and the bottom cutting element.
The chuck is then tightened around the tubing. The bottom of the capillary tubing is
then attached to the plunger by placing a small piece of silicone capillary tubing around
the glass and pushing the top of the plunger (which is a Gilson pipette tip) onto the
tubing. The frictional force between the two keeps them attached.

A voltage is then applied across the top heating element. This element consists of a
0.5mm diameter nichrome wire wound 5 or 6 times to produce a cylinder of around
6mm O.D. and 7mm in length. Ideally the turns should not be separated by more than
the thickness of the wire. The amount of current flowing through, and thus the
temperature of the element can be varied by a potentiometer on the power supply. The
temperature of the element should be adjusted so the glass starts moving, at a constant
rate, after around 15 seconds. Through extensive production of pipettes the time of 15
seconds seems to provide the correct rate of melting in the glass. The rate of descent of
the plunger is controlled by a small capillary at its base that provides for the egress of
air. By attaching different lengths of flexible capillary tubing it is possible to control the
rate of descent.
Towards the end of the plunger’s descent a lip on the top of the plunger engages a microswitch. This stops the current flowing to the top heating element and starts current flowing through the bottom cutting wire. This 0.25mm O.D. nichrome wire element consists of one turn around and as close to the glass as possible. Again the current to the element is varied via a potentiometer on the power supply. The temperature should be adjusted so that the cut takes around 10 seconds.
6.2.1 Attaching particles to micropipettes

After suitable micropipettes have been produced, it is necessary to attach them to and achieve a stable bond with the particles. To do this the micropipette is mounted in the static pipette micromanipulator and a piece of silicone capillary tubing is placed on the large end to which a syringe is attached. On the stage a clean microscope slide is placed onto which the desired particle (section 6.4) has been positioned along side a drop of Araldite glue. Initially the end of the micropipette and an edge of the glue are focused under the objective. The micropipette is then placed just inside the drop and glue is sucked up the tube by applying a vacuum via the syringe (Figure 6.6). When sufficient glue has entered the micropipette, it is removed and the slide is moved to bring the desired particle into focus. By touching the micropipette against the particle a small amount of glue will flow and the application of suction causes the particle to bond to the pipette. The bond is then left for at least 24 hours to cure.
6.2.2 Pipette bender

The pipette bender (figure 6.7) allows a predetermined length of glass to be bent at an angle to the main body of the micropipette. This is achieved by placing the pipette over a 0.5mm O.D. section of heated nichrome wire and allowing the end of the pipette to fall under its own weight until the desired angle is reached. Adjustments can be made to the horizontal and vertical position of the wire, the angle of the stage and its proximity to the element. The first bend must be a right angle followed by 10mm of glass which fits with the geometry of the RO device relative to the micromanipulator. This is all that is required for gas phase work. For liquid phase work additional bends allow the micropipette to be placed inside the dish holding the liquid media.
6.2.3 Measurement of the pipette force constant.

By hanging a known weight over the 90° bend of the flexible micropipette and measuring the displacement the force constant can be calculated. This is achieved by mounting the pipette in the static pipette micromanipulator, focusing and noting the fine focus micrometer reading. The weight is then placed over the bend, the pipette brought back into focus and the micrometer reading again noted. A calibration curve of deflection against force for the pipette is then plotted (Appendix C).
6.3 Viewing the image

6.3.1 The Olympus BX60 Microscope

The Olympus BX60 microscope employs the UIS (universal infinite system) optical system and can be used for both transmitted and reflected light illumination.

Figure 6.8: Photograph of Olympus BX60 Microscope
Coarse and fine adjustment is facilitated by the adjustment knob, which is calibrated in microns. Four objective lenses (5x, 10x, 20x and 50x) allow liquid bridges between particles down to 3μm (limit of optical microscopy) in diameter to be viewed. The maximum size of particle is limited by the field of view. The field of view with the 5x objective is 4.4mm. Information about the characteristics of each objective is printed on the casing (figure 6.9).

![Microscope Objective Lens](image)

**Figure 6.9: Illustration of microscope objective lens.**

Table 6.1 provides a summary of each objective. The numerical aperture (N.A) is a numerical measure of the light gathering power of an objective. It is defined by the expression \( j \sin \psi \), where \( j \) is the refractive index of the medium between the objective lens and the specimen and \( \psi \) is the half angle of the cone of rays entering the lens. The working distance (W.D.) is the free distance between the objective front lens and the upper surface of the specimen when the latter is in focus.
Optical character of MPlan Objectives | With WH10X (FN22) eyepiece
---|---
Mag | N.A. | W.D.(mm) | Resolution (μm) | Total mag. | Depth of focus (μm) | Field of View (mm)
5x | 0.1 | 19.6 | 3.36 | 50x | 97.5 | 4.4
10x | 0.25 | 10.6 | 1.34 | 100x | 18.4 | 2.2
20x | 0.4 | 1.3 | 0.84 | 200x | 6.09 | 1.1
50x | 0.75 | 0.38 | 0.45 | 500x | 1.42 | 0.44

Table 6.1: Characteristics of the objectives.

### 6.3.2 Capturing the Image

The observation tube of the microscope allows the image to be viewed directly or via a video camera. Usually the light path is split, 20% for the binocular eyepieces and 80% for the camera, although if brighter observation is required 100% can be directed to either. For direct viewing the observation tube allows both the interpupillary distance and the diopter to be adjusted. One eyepiece also contains a micrometer divided into one hundred units.

The camera (a JVC S-VHS colour video camera) is attached to the observation tube via an U-TV1X video attachment and an U-CMAD C Mount adapter. The camera has a resolution of 752 (H) x 582 (V) pixels. The Y/C output of the camera is connected to the S-VHS input of the video.

The images obtained from the camera are recorded using a Panasonic S-VHS video recorder. This allowed a rupture sequence to be recorded and then played back frame by frame to allow measurements to be taken via an image processor.
Individual frames from the video are viewed on the computer screen and captured using a video image viewing computer package Screen Machine (supplier Fast Electronic GmbH). This consists of an internally fitted board and a software package, allowing conversion of analogue images into standard digital image formats.

![Figure 6.10: Liquid bridge image captured using Screen Machine software.](image)

### 6.3.3 Processing the image

After the image is captured using the Screen Machine package, it is analysed using another package, PC/Image (supplier Foster Findlay Associates Ltd). Of the wide range of digital output formats Screen Machine can produce, the most suitable for PC/Image is a 256 shades of grey TIFF. It is then possible to measure distances, angles and curvatures directly from the screen. Figure 6.11 shows the lines drawn (binary file) on top of an image of a liquid bridge.

![Figure 6.11: PC/Image generated binary file engraved on liquid bridge image.](image)


6.3.4 Calibration

6.3.4.1 Eyepiece calibration

This can be achieved by the use of a calibration graticule fitted internally in the left eyepiece. Direct measurement allows the eyepiece to be calibrated.

<table>
<thead>
<tr>
<th>Objective lens</th>
<th>1 eyepiece graticule unit equals</th>
</tr>
</thead>
<tbody>
<tr>
<td>5x</td>
<td>20µm</td>
</tr>
<tr>
<td>10x</td>
<td>10µm</td>
</tr>
<tr>
<td>20x</td>
<td>5µm</td>
</tr>
<tr>
<td>50x</td>
<td>2µm</td>
</tr>
</tbody>
</table>

Table 6.2: Eyepiece graticule calibration.

6.3.4.2 PC_Image

In order that any data produced from images analysed is useful, the pixel size is calibrated for all the magnifications used. The pixels are not necessarily square thus, a built in calibration function of PC_Image allowed an image of a calibration graticule to be loaded and the size of each pixel in both the x and y axes to be calculated. The X and Y values can be seen to be equal (table 6.3), this is achieved by maintaining a constant aspect ratio through capture and analysis (governed by the initial aspect ratio of the camera 752(h) x 582(v)). Distances (in microns) and angles can then be measured directly from the screen.

<table>
<thead>
<tr>
<th>Objective lens</th>
<th>microns/pixel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>5x</td>
<td>1.66</td>
</tr>
<tr>
<td>10x</td>
<td>0.83</td>
</tr>
<tr>
<td>20x</td>
<td>0.42</td>
</tr>
<tr>
<td>50x</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 6.3: PC_Image pixel calibration
6.4 Materials

Lead glass ballotini were used as model particles as they are spherical, non-elastic and inexpensive. A range of particle sizes below 250μm in diameter were used both in untreated and silanised form. Untreated glass has a hydrophilic nature which is readily altered using a silanising agent to produce a hydrophobic surface. The silanising agent used was supplied by BDH as a 2% solution of dimethyldichlorosilane in octamethylcyclotetrasiloxane:

```
Glass surface

Si - OH

dimethylchlorosilane

Cl
\[\text{Si} - \text{CH}_3\]

Cl

\[+ 2\text{H}_2\text{O}\] (Hydrolysis)

\[\text{Si} - \text{OH}\]

\[\text{HO} - \text{Si} - \text{CH}_3\]

\[+ 2\text{HCl}\]

(Chemical reaction)

\[\text{Si} - \text{O} - \text{Si} - \text{CH}_3\]

\[+ 2\text{H}_2\text{O}\]
```

Figure 6.12: Silanisation reaction.
Silanisation has the benefit that, in addition to cleaning the surfaces of unknown contaminants, it also prevents the formation of adsorbed water layers and therefore eliminates the effects on interparticle cohesion by ambient humidity [53]. However, care must be taken during silanisation in order to prevent alteration of the nature of the surface due to the build up of multilayer films of silanising agent.

### 6.4.1 Method of Silanisation

Figure 6.12 represents the silanisation reaction taking place on the surface of glass. To silanise ballotini the following method was employed. First to ensure the glass surface was clean and grease free, the ballotini was placed in a beaker and washed with acetone. The ballotini was then separated from the acetone using a Buchner funnel and placed in a clean beaker. The silanising agent (a 2% solution of dimethyldichlorosilane in octamethylcyclotetrasiloxane) was then added. To ensure an even contact of the agent with all ballotini surfaces a magnetic stirrer was used to agitate the mixture. The reaction was considered to be complete after a few minutes and again the ballotini was separated using a Buchner funnel. In order to remove any surplus silicone residues an alcohol solution (in this case propanol) was used to wash the ballotini. Finally the ballotini was dried in an oven.

### 6.4.2 Bridging liquids

Hydrocarbon oils, Dow Corning 200 series silicone fluids, glycerol and glycerol / water mixtures were used as the bridging liquids. The use of dodecane between silanised glass particles provided a stable bridge which did not evaporate. Shorter chain hydrocarbons tended to evaporate with time.
The silicone oils were used as the bridging liquid did not tend to evaporate, gave a range of viscosities, and were easily characterised. However, they had the disadvantage that the particle-liquid boundary was hard to distinguish since they have a similar refractive index to the glass particles.

Water and glycerol/water mixtures were again easily characterised and gave a range of contact angles on the particles. Surface tension and contact angle data for these systems can be found in appendix A and B respectively.
6.5 The Measurement of Surface Energy and Contact Angle

Measurements of the bridging liquid surface energies and the contact angles they made with solids were carried out using a Kruss K12 processor tensiometer, which employs the Du Nouy-ring and the Wilhelmy-plate methods.

The apparatus consists of a measuring unit and a processor unit which is connected via a serial port to a computer to log the data. A schematic of the measuring unit is shown in figure 6.13.

Figure 6.13: Schematic of measuring unit of the Kruss K12 processor tensiometer.
Key for figure 6.13:

1. Plate - perimeter of which should be constant
2. Thin rod
3. Electrobalance
4. Recorder of downwards force
5. Beaker
6. Liquid
7. Movable platform (with thermostatically controlled bath)
8. Screw to allow movement of platform
9. Motor
10. Clamp (for coarse adjustment) and support
11. Lid to minimise evaporation

6.5.1 Preparation for measurements.

6.5.1.1 Cleaning the sample vessel

An ISO standard for the ring and plate methods states that the sample vessel (key 5) should be cleaned with chromo-sulphuric acid, boiled for a period of time in distilled water and finally flamed with a Bunsen burner. However, chromo-sulphuric acid is hazardous and therefore in most cases it was indeed sufficient to clean the vessel with a proprietary detergent and water, followed by rinsing with acetone and finally flaming.

6.5.1.2 Handling and cleaning of rings and plates

The ring and the plate were handled by their shafts to both minimise the chances of damage and to minimise contamination of the measuring surfaces. The ring and plate were cleaned after every measurement.
After measurement of an aqueous solution the cleaning procedure was as follows; rinsing with warm tap water, rinsing with distilled water, annealing to red hot with a Bunsen out any subsequent measurements.

After measurement of an organic solution the cleaning procedure was as follows; rinsing with a suitable organic solvent, rinsing with acetone, rinsing with distilled water, annealing to red hot with a Bunsen burner. Again the ring or plate was allowed to cool to room temperature before carrying out any subsequent measurements.

The annealing stage is important to remove any residues (especially organic) which remain after the rinsing procedure. However, care must be taken not to allow the ring or plate to become white hot as this could damage them.

6.5.1.3 Preparation of tensiometer and peripheral equipment

Initially the sample liquid was poured into the beaker and placed inside the thermostat vessel. The ring or plate was then inserted into the electrobalance (at this stage the electrobalance was locked). Next the lock on the electrobalance was loosened and the plexiglass doors of the tensiometer closed. The tensiometer processor and computer software was now loaded. The temperature control for the thermostat bath (if used) was now set and allowed to equilibrate. Next the thermostat vessel was moved up until the ring or plate was just above the liquid surface. The computer data acquisition program was then used to acquire the surface chemistry data (shown in appendix A & B).
Chapter 7

7. Results and Discussion

Experimental results have been obtained using glass ballotini in the size range 10\(\mu\text{m}\) to 100\(\mu\text{m}\) radius. These ballotini were used either in their ‘natural’ state or after silanisation. A range of bridging liquids (dodecane, glycerol, glycerol/water mix, silicone oils and water) have been used to give a range of surface tensions, viscosities and contact angles for the liquid bridge.

As the commissioning of the experimental apparatus (chapter 6) was not completed until two years of the project had elapsed the nature of the experiments changed throughout. Initially it was decided to investigate the critical separation distance at which a liquid bridge ruptures and to correlate any relationship between this distance and the volume of the bridge (section 3.4.2). However these results proved inconclusive. Whilst carrying out this work movement of the bridging liquid in and out of the bridge from around the particles was observed. Thus this movement and its explanation became the focus of the work.
Section 7.2 reports and examines the movement of bridging liquid in both the formation (7.2.1) and separation stages (7.2.2) of liquid bridges. As a range of binding liquids were investigated the movement was found to be dependent upon the tendency of the bridging liquid to wet the particles and the micropipettes holding the particles. The geometries liquid bridges adopt was also found to be dependent upon the contact angle the binder made with the particle surfaces (section 7.3).

Concurrently, the apparatus was being commissioned to measure the forces developed by liquid bridges between particles (section 7.4). Initially this was carried out using the image processing software by direct measurement of the bend of the pipette from the screen. In this technique the micromanipulator holding the flexible pipette remains static and the 'static' micromanipulator is manually adjusted to give the range of interparticle separations. Thus, by noting the initial position of the particle attached to the flexible micropipette, the amount of bend (and hence the force) can be calculated for all separations. With the delivery of the stage electronics it became possible to measure all forces automatically and in a non-invasive manner. However the direct measurement technique offers advantages when large volumes of bridging liquids are used leading to separations outside the range of the electronic following equipment.

Observations about the effect of separation on the bridge half-filling angle are reported in section 7.5. Low contact angle systems behave as predicted by previous theory (section 4.4.2), whereas high contact angle systems show a different trend.

From the force separation data the energy required to rupture the liquid bridge was calculated using the trapezium rule. This rupture energy was then related to the bridge volume (section 7.6) in order to develop on a previously derived model [6]. The model has applications in the analytical and numerical modelling of the formation, deformation and fracture of agglomerated particulates, where it is impractical to calculate the energy to rupture single bridges directly.
For example, it may be calculated that for a certain moisture content (section 7.2.1.2) an agglomerate is attached via pendular bridges and the number of bonds calculated. For crack propagation, it has been postulated that the macroscopic rupture energy of a compact may be obtained by appropriate summation of individual bond energies [65], although this approach has been shown to be problematic where bulk deformation can absorb energy away from the crack tip [53]. Similarly, for granule formation it is postulated here that the rupture energy of single liquid bridges can in some way be scaled up to the macroscale energy of the granulation process. The measured force as compared to the force predicted by the ‘neck’ (section 4.1.1) and ‘boundary’ (section 4.1.2) theories was also considered.

Finally the critical separation (rupture) distance of the liquid bridge was compared with the bridge volume (section 7.7). The ability to predict the distance at which a liquid bridge ruptures is required to calculate the total rupture energy. Also if it can be shown that mechanical disturbances to an agglomerate cause strains below the critical separation value, it is possible that the liquid bridges will recover the integrity of the particle assembly and the deformation energy will be absorbed. The data is compared with the theoretical critical separation predictions given by a model developed by Lian et al. [45] (section 4.4.2).

Section 7.8 is a general discussion of the significance of these results to the verification and development of both liquid bridge and agglomeration theories.
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7.1 Mechanisms of liquid bridge strain

A major part of the project was taken up in the commissioning and development of the experimental apparatus (as described in chapter 6) used to observe the behaviour of and measure the forces developed by liquid bridges between particles from particles contact to the critical separation distance at which the bridge ruptures. The mechanical parts of the stage were built and commissioned before the electronic control system could be designed. The stage itself is flexible enough to allow manual or computer controlled experiments to be conducted.

It can be considered that disruption to a liquid bridge can occur by one or a combination of three mechanisms (figure 7.1). The particles can be pulled directly apart, a shear force can be applied or a rotational force can cause the particles to separate. Although the apparatus is designed to measure the separation by pulling the particles directly apart, several experiments were carried out to observe the effect of shear on a liquid bridge (see sections 7.3.3 and 8.3).

Figure 7.1: Mechanisms of liquid bridge strain.
7.2 Variation of bridge volume

Previous studies have assumed the volume of a liquid forming a bridge between two particles remains constant. In the course of the work presented here observations have been made that show movement of liquid into the bridge on its formation and movement out on increased separation between the particles. The tendency of the liquid to flow into and out of the bridge is related to the contact angle it makes with the solid and the rate at which it does so is dependent upon its viscosity.

7.2.1 Liquid bridge formation

Experimentally the addition of binder to form a bridge can be carried out in three ways:

(i). Two ‘dry’ particles can be brought together and then the third pipette can be used to add binder to form the bridge at zero (or close to zero) separation.

(ii). Two particles can be precoated with binder and then brought together.

(iii). One particle can be precoated with binder and then be brought together with a ‘dry’ particle.

7.2.1.1 Direct addition

In case (i) the volume of liquid added and the contact angle it makes with the solid particles, or in the case where massive amounts of liquid are added, has lead to some interesting observations. Recently the method of addition of binders to agglomerators [57] and the binder’s behaviour once subjected to the forces within an agglomerator has been of research interest. Although at this stage it is not possible to draw any firm conclusions about how adding liquid with a micropipette compares to spraying in, melting in, or pouring in of binder to agglomerators, some analogies can be made.
7.2.1.1.1 Addition of small amounts of binder

If small amounts of a binder showing good wetting on the particle surface are added the binder is observed to come between and move around the two particles and then flow down the micropipettes (figure 7.2). This is particularly interesting in the case of a dodecane binder wetting silanised ballotini particles held with non silanised micropipettes. The measured contact angles using the Wilhelmy plate apparatus of dodecane on glass are for the silanised coverslip 16.6° advancing and 12.5° receding and perfect wetting, 0°, for the unsilanised coverslip. Thus in this case it is energetically favourable for the binder to wet the pipette rather than the particle. Only after a certain volume of dodecane has been added is the formation of a liquid bridge possible. It has been considered that at this point the pipette is saturated (figure 7.6 shows ‘dry’ particles and micropipettes - figure 7.7 shows the saturated micropipette).

It believed that these observations may be significant to agglomeration of heterogeneous mixtures of particles where it is important to maintain a homogeneous mixture; for example, in the production of pharmaceuticals where it is common to have a small amount of active ingredient contained within a bulk material. Here differences in the wetting characteristics of the binder have to be considered in order to determine its expected distribution within the powder. The observations are also consistent with the theory of selective agglomeration of one type of particle from a mixture, as in recovery of one component in the spherical agglomeration process (section 2.2.4), where the binder is required only to wet the desired particle species.
If small amounts of high contact angle binder are added very different behaviour is observed. The binder forms discrete droplets on the surface of the particles, rather than spreading over them and the micropipettes (figure 7.16). Through formation, separation and rupture the volume of the liquid bridge remains constant.

7.2.1.1.2 Addition of large amounts of binder

When a large amount of bridging liquid is forced out of the micropipette very quickly and over the particle, it is felt analogies can be drawn with dry particles initially making contact with binder droplets. For low contact angle cases the particles can be contained entirely within a liquid droplet (figure 7.3).
For higher binder-on-particle contact angles, it has been found that rather than the particles being contained within a liquid drop they tend to stay at the surface of the drop. This is consistent with observations reported by other workers [66] relating to the production of pharmaceuticals using high contact angle binders. This work has shown that during the initial stages of agglomeration a structure similar to that of figure 7.4 (left) is observed.

![Figure 7.4: Particles on the edge of a binder droplet.](image)

Figure 7.4 (right) shows a silanised ballotini particle being pulled away from the edge of a glycerol / water mix droplet. The Wilhelmy - plate measured contact angles in this case are 95.3° advancing and 77.9° receding (appendix B). It can be seen that only half the ballotini particle has been wet by the binder. As the particle is being pulled away from the liquid droplet it can be considered that the contact angle observed is showing the receding value. Willett [67] and Schubert [50] have both theoretically determined that for certain process situations the contact angle will not be constant. As predicted by contact angle hysteresis theory (section 3.4.2) the contact angle the binder makes on the particle surface as the particles approach each other is larger than the contact angle as the particles are separated. Since the liquid is not retracing its original path as it recedes, the process is not thermodynamically reversible. A long equilibrium time (unlikely to occur in process situations) would be necessary to determine an equilibrium position. Thus, the wetting behaviour of the solid surface in such cases is governed by the dynamic contact angle.
7.2.1.2 Precoated particle formation

In cases (ii) and (iii) where one or both particles are binder coated and brought together and the binder on solid contact angle is low (<20°), a period has been observed where liquid flows around the particle(s) and into the bridge. It is possible to observe the formation of the bridge in real time. In case (iii) liquid moves around the dry particle to cause this to become binder coated also. This rate of formation seems, as would be expected, to be viscosity dependent. These observations agree with the model proposed by Schaafsma et al. [68] for agglomerate growth. Their work proposes that agglomerate growth can be divided into two stages.

Initially, fast growth takes place by wetting of particles by a binder droplet, leading to the formation of a saturated agglomerate filled with binder solution. An analogy can be drawn here with the binder covered particle and pipette. Schaafsma et al. [68] report that that this step happens very quickly and our observations agree with this as it is not possible to observe the spreading rate of the binder on ‘dry’ particles in real time (figure 7.6 shows ‘dry’ particles - figure 7.7 shows particles and pipettes wet with dodecane). Consideration of surface chemistry would also support these observations as this is simply wetting of a solid surface (see chapter 5) under favourable conditions.

To consider whether an agglomerate is saturated, a qualitative description of agglomerate structure in relation to liquid content has been considered in section 2.3.2. The three structures identified are pendular, funicular and capillary. The final structure is then related to pore volume occupied by bridging liquid (figure 2.13). Flemmer [69] developed a quantitative description of the three states for randomly packed equal sized spheres. He stated that the moisture content of an agglomerate, $M_p$, is defined as;

$$M_p \% = \frac{V_l}{V_s + V_l + V_g} \times 100$$  (7.1)
An agglomerate can be considered to be saturated at moisture contents above the upper limit for the pendular state (which corresponds to the lower limit of the funicular state). Flemmer calculated this upper limit to be at a moisture content value of 13.6%.

The second stage proposed by Schaafsma et al. [68] is initiated by liquid transport from the initial agglomerate to the free particles surrounding the agglomerate (figure 7.5). If the surface of the agglomerate is sufficiently saturated, free particles can reach the liquid phase (analogous to the contacting of binder coated particles) and a liquid bridge can be formed. They propose that during growth binder drains from the voids inside the agglomerate to the newly wetted pores formed by the attached particle at the surface of the agglomerate, and assume this drainage step is the rate-limiting process for growth due to the resistance of the liquid flow (see figure 7.8 showing binder coated particles on initial contact and figure 7.9 showing an equilibrium liquid bridge between the particles which has taken six seconds to form). This agrees with experimental observations in this work on 200 series silicone fluids, which showed a viscosity dependence of liquid flow into a pendular bridge (table 7.1). Here, three fluids having viscosities of 5cS, 50cS and 200cS, Wilhelmy plate measured surface tensions of 19.22mN/m, 20.37mN/m and 20.86mN/m and contact angles of below 20° showed that the rate of flow into the bridge was directly dependent upon the viscosity. The driving force for the liquid flow is the capillary pressure difference between the pores inside the agglomerate and the pores with the lower saturation near the surface of the agglomerate.
Figure 7.5: Limits of saturated agglomerate growth (after [68]).

Table 7.1: Formation time for silicone liquid bridges between two equi-sized particles

<table>
<thead>
<tr>
<th>Silicone fluid</th>
<th>Calculated volume (μm³) of bridge at zero separation</th>
<th>Time to form bridge (seconds)</th>
<th>Volume/time</th>
</tr>
</thead>
<tbody>
<tr>
<td>5cS</td>
<td>2267</td>
<td>0.81</td>
<td>2798</td>
</tr>
<tr>
<td>5cS</td>
<td>1671</td>
<td>0.66</td>
<td>2531</td>
</tr>
<tr>
<td>50cS</td>
<td>4792</td>
<td>3.41</td>
<td>1405</td>
</tr>
<tr>
<td>50cS</td>
<td>3277</td>
<td>2.16</td>
<td>1517</td>
</tr>
<tr>
<td>50cS</td>
<td>4082</td>
<td>2.89</td>
<td>1412</td>
</tr>
<tr>
<td>200cS</td>
<td>7586</td>
<td>9.96</td>
<td>761</td>
</tr>
<tr>
<td>200cS</td>
<td>819</td>
<td>0.58</td>
<td>1412</td>
</tr>
<tr>
<td>200cS</td>
<td>1321</td>
<td>2.43</td>
<td>543</td>
</tr>
<tr>
<td>200cS</td>
<td>1891</td>
<td>2.57</td>
<td>735</td>
</tr>
</tbody>
</table>
Table 7.1 shows the time of formation for liquid bridges when two silicone 200 series fluid coated particles (radii 23.3 and 23.2μm) were contacted. Three viscosities were used; 5cS, 50cS and 200cS. The volume divided by time column shows that the lower the viscosity the quicker the binding liquid flows into the bridge. The rate at which the binding liquid flows into the bridge is not constant, but is at its greatest on initial contact. This is due to the pressure difference being at a maximum when the principal radii of curvature $r_1$ and $r_2$ are small and also the amount of binder to be transported around the particles. This is illustrated by the second result for the 200cS fluid, in this case only a thin binder layer was present and the bridge was seen to form at a rapid rate.

![Figure 7.6: Two silanised ballotini held with micropipettes.](image)
Figure 7.7: Two silanised ballotini wet with dodecane.

Figure 7.8: Two silanised glass ballotini particles covered with a dodecane liquid binder on initial contact.
7.2.2 Liquid bridge separation

Results have shown that as separation distance increases for low contact angle systems the volume of the bridging liquid between the particles decreases. The rupture of a dodecane liquid bridge is shown in figures 7.10-7.12 and some examples of the measured change of volume with separation distance for silicone fluid systems are shown in figure 7.13. These examples have been selected from a much larger set of quasi-static measurements using different initial bridge volumes and a range of viscosities. However, the scatter of the data was such that no dependence of viscosity on the volume change behaviour could be elucidated. Hence, the data shown in figure 7.13 has been selected for clarity only and no relationship with viscosity should be inferred. Although the change in the volume seems from the figure to be more marked as viscosity increases, it should be noted that the initial bridge volumes are not the same.

From the video footage of the rupture sequence, liquid can be seen to be moving over the particles and out of the bridge in the case of the two equal sized particles. It is
interesting to note for the unequal sized particles liquid only appears to move over the smaller particle. It is believed this phenomena occurs as a result in changes in the internal pressure of the liquid bridge relative to the surrounding fluid and is a function of liquid bridge geometry. This is considered in more detail in section 7.3.1. For high contact angle systems no movement of bridging liquid is observed.

Figure 7.10: Two silanised glass ballotini particles with a dodecane liquid bridge.

Figure 7.11: Two silanised glass ballotini particles with a dodecane liquid bridge, frame before rupture.
Figure 7.12: The two particles several frames after rupture.

Figure 7.13: Variation of experimentally calculated liquid bridge volume with separation distance between two silanised ballotini particles ($\approx 23 \mu m$ radii) wet with silicone fluids.
7.3 Liquid Bridge Geometries

Most recent theoretical studies have assumed that the bridge has the geometry of a toroid. This assumption is made because it simplifies the calculation of the liquid bridge volume (see Jacques et al. [46]) and it provides a reasonable approximation of the principal radii of curvatures (section 4.5.1).

The geometries that liquid bridge menisci can adopt has previously been investigated by Orr et al. [37] and is reviewed in section 4.3. Experimentally the geometry a liquid bridge adopts has been found to be dependent upon the contact angle the binder makes with the solid surface. Nodoidal, catenoidal and unduloidal geometries have been observed, corresponding to negative, zero and positive relative pressures respectively.

It has been found that for nodoidal bridge geometries the toroidal approximation is suitable and simplifies calculations. However for catenoidal and unduloid bridge geometries the approximation is not so satisfactory. An expression for catenoidal bridge geometries was developed and is given in section 3.5.2. For unduloid geometries it was not possible to develop an expression based on a single equation and further work is required to develop relationships between contact angle, dimensionless bridge volume and dimensionless separation in order to allow a numerical computer analysis to be performed. Experimentally, it is possible to measure the principle radii of curvature of an unduloid liquid bridge directly from captured images, so it was possible to make direct comparisons with the forces predicted by the neck and the boundary theories (equations 4.7 and 4.12).
7.3.1 Low contact angle systems

For experimentally observed low contact angle systems the torroidal approximation has proved inaccurate as at separation distances close to rupture the neck of the bridge is seen to 'thin' (see figure 7.14(b)). Therefore it is proposed that the geometry of the bridge at this point is in fact a catenoid.

![Image of liquid bridge geometry](image)

**Figure 7.14: 3D Schematic of observed changes in liquid bridge geometry from particle contact (a), bridge necking (b) and rupture (c to d).**

Considering the geometry of the bridge to be catenoidal, rather than toroidal, allows the movement of bridging liquid to be explained. Recall equation (4.6):

\[
F_{\text{pend}} = 2\pi r_2 \gamma + \pi(r_2)^2 \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right)
\]  

Equation (4.6) states that the total force is a combination of the force due to the surface tension (1st term) and the reduced hydrostatic pressure within the bridge (2nd term).

For the low contact angle experimental system described here, a binding-liquid layer exists all around the particles and onto the pipettes (which could be regarded as adjacent particles in a multi-particle agglomerate - figure 7.2). This liquid acts as a reservoir of bridging liquid and must be at atmospheric pressure. Thus, it follows when equilibrium conditions are attained between two static particles that, since there is a continuum of binder, the bridge must also be at atmospheric pressure. Catenoidal bridge geometry means that the bridge meniscus is of zero mean curvature \((r_1 = r_2, \text{i.e. } \Delta P = 0)\). Thus for these systems the total force is given by only the first term of equation (4.6) i.e. \(F_{\text{pend}} = 2\pi r_2 \gamma\). This agrees with experimentally acquired data and has previously been discussed by Orr et al. [37] for the case of a sphere and a plate.
7.3.2 High Contact Angle Systems

Figure 7.15(a) shows a schematic representation of two particles covered with a binder with a large liquid-on-solid contact angle (i.e. non-perfect wetting). When these two particles are brought together to form a liquid bridge a different kind of bridge geometry is observed 7.15(b). This geometry is that of an unduloid. For these cases the theoretical torroidal equations overestimate the force, due to inaccuracies in the predictions of the principal radii of curvature. Initially this overestimation of the force lead to larger rupture energies being predicted than those being measured experimentally.

Further computational work is required to develop a general expression for the volume and principal radii of an unduloid liquid bridge taking account of the contact angle, half-filling angle and the separation distance. For these situations no change in bridge volume is observed and there is very little change in the half-filling angle (β) of the liquid on the solid. If the particles are pushed together the bridge will start to 'bulge' outwards (similar to that shown in figure 7.18 & 7.19) and repulsive forces are experienced. On particle separation (figure 7.20) a general decrease in the gradient of the undulation is observed until bridge rupture occurs. It is thought these observations (combined with those discussed in section 7.2.1) have implications on the most efficient way of wetting solids in granulation processes. For example, when spraying the binder onto the powder it is necessary to consider the droplet size in relation to the particle size (figure 7.4 and figure 7.15). Alternatively, when the binder is poured onto the powder how the fluid will wet the solids and the geometries likely to be formed on agitation need to be considered.
7.3.3 The effect of shear on geometry.

Although the apparatus is not designed to measure shear forces, observations of the effect of shear on liquid bridges will aid the understanding of macroscopic agglomeration processes and will enable more realistic computer simulations to be developed.

7.3.3.1 Low contact angle systems

The application of a shear force to binders showing good wetting causes liquid to move around the particles and the axisymmetric nature of the liquid bridge is maintained.

This has implications in the modelling of deformation of agglomerates and the absorption of collision energy, where it appears that part of the energy transfer occurring can be attributed to the wetting and de-wetting of the particle surfaces. This effect would also be applicable for any rotation of particles, which could for example occur to particles at the edge of agglomerates.
7.3.3.2 High contact angle systems

Figure 7.17 shows two silanised ballotini pre-coated with a glycerol binder (Wilhelmy plate measured contact angles 90.6° advancing and 89.7° receding). The separation between the particles is decreased until a liquid bridge forms (figure 7.18). At this stage the particles moves down as a result of a shear force caused by the unsymmetrical nature of the bridge. No movement of binder is observed around the left hand particle’s surface. Therefore the adhesive force of the binder to the solid at the top left of the bridge combined with the energy required for the binder to wet the particle at the bottom of the bridge must be greater than the forces existing within the liquid bridge due to its unsymmetrical configuration. Additional wetting of the right hand particle appears to take place. The balance of these forces with the positive pressure within the bridge prevent the bridge taking on catenoidal geometry as with the low contact angle systems.

Figure 7.17: Silanised ballotini coated with glycerol binder.

Figure 7.18: Glycerol binder between silanised ballotini.
Figures 7.19 shows compression being applied to the liquid bridge. Only a small movement of binder is observed over the right hand particle. The bridge is seen to bulge out more (the internal radius of curvature decreases, thus the pressure difference increases; $\Delta P = \gamma/r$). At this stage the bridge is exerting a repulsive force on the particles.

![Image of compressed glycerol binder between silanised ballotini.](image)

**Figure 7.19: Compressed glycerol binder between silanised ballotini.**

Figure 7.20 shows the bridge at a larger separation distance. Here the half-filling angles have decreased the curvature of the bridge has become unduloidal.

![Image of glycerol binder between silanised ballotini at larger separation.](image)

**Figure 7.20: Glycerol binder between silanised ballotini at larger separation.**

Figure 7.21 shows the bridge with a shear force applied by moving the right hand particle ‘downwards’ relative to the picture. A small movement of bridging liquid is observed around both particles, but the unsymmetrical nature of the bridge suggests strain within it.
Figure 7.21: Shear force applied to glycerol bridge.

Figure 7.22 shows the last stable frame before rupture. Thinning of the bridge close to the smaller particle can be observed.

Figure 7.22: The shear glycerol bridge close to rupture.

Figure 7.23 shows the particles after rupture. The binding liquid has returned to the original position on the larger particle. There has been a slight movement around and transfer of binder to the smaller particle.
7.3.4 Energy dissipation through contact angle hysteresis

It has been proposed through theoretical examination of liquid bridges by Willett et al. [67] that in certain cases a liquid bridge will have a different configuration depending on whether the particles are approaching each other or whether the separation distance between them is increasing, this effect occurring as a result of contact angle hysteresis. The examination proposed that when particles approach each other the bridge bulges out, since the advancing contact angle is high. Conversely, when particles separate the bridge takes on a pendular shape as the contact angle ‘flips’ to the lower receding value. The forces are therefore higher on separation due to the reduced pressure force component and thus the energy to separate is greater than to approach.

For the dodecane and silicone oil work carried out in this study no flip in contact angle has been observed. These are the low contact angle systems where movement of bridging liquid occurs (section 7.2).
For the high contact angle work carried out here (glycerol and glycerol/water binders),
the effect was not observed either. Observations showed that geometry did change with
separation, but this appeared to be a function of separation distance rather than whether
the particles were approaching or separating at any particular instance. For this work it
should be noted that there was not a large difference between the advancing and
receding contact angle values obtained on the ballotini particles (see figure 7.18-7.22).
More experimental investigation is required on the theoretical postulation of Willett et
al. [67], but it seems likely that for their theory to be valid for high contact angle
systems there would need to be movement of bridging liquid around the particles, which
has not been observed here to occur (see section 7.3).
7.4 Force versus separation data.

Force versus separation data was obtained in two ways; initially by direct measurement of the bend in the pipette using the image analyser and latterly, using computer software controlling the stage electronics.

In the direct measurement technique, the micromanipulator holding the flexible pipette remains static and the 'static' micromanipulator is manually adjusted to give the range of interparticle separations. Thus, by noting the initial position of the particle attached to the flexible micropipette, the amount of bend (and hence the force) can be calculated for various separations (see figure 7.24).

![Direct measurement of bend](image)

**Figure 7.24: Schematic of direct measurement technique.**

The direct measurement technique is limited by the accuracy of the image analyser. For instance, using a 20x microscope objective, each computer pixel has a characteristic length of 0.42 microns (see table 6.3). Thus using this technique the accuracy of the force measurement is limited by this factor and the pipette force constant (see appendices C and F).
A typical force versus separation plot obtained by the direct measurement method is shown in figure 7.25.

![Graph showing force versus separation for glycerol/silanised liquid bridge.](image)

Figure 7.25: Plot of force versus separation for a glycerol liquid bridge between two silanised glass ballotini particles (radii 25.4\(\mu\)m and 31.58\(\mu\)m) obtained using direct measurement technique.

It can be seen from figure 7.25 that data points were only obtained for 11 separations. As each point required a manual measurement to be taken this was a laborious process. With the delivery of the stage electronics it became possible to measure all forces automatically and in a non-invasive manner (chapter 6 and appendices C-F). However the direct measurement technique was still used when large volumes of bridging liquids were added leading to separations outside the range of the electronic following equipment.

The force curves obtained were compared with the forces predicted by both the ‘neck’ and the ‘boundary’ theories. Figure 7.26 shows such a comparison for a force curve for unsilanised glass ballotini wet with a glycerol / water binder.
Figure 7.26: Variation of force with separation for two unsilanised ballotini (28.9 & 22.72 µm radii) wet with 50% water / 50% glycerol mix.

This system has an advancing contact angle of 59.6° and a receding contact angle of 40.8° and unduloid bridge geometries are observed. In this case the forces predicted directly by toroidal theory are shown. It can be seen that at small separations there is an overprediction as compared with the measured force. This is caused by the outward bulge of the bridge (as shown in figure 7.18) resulting in the reduced pressure component of the overall force causing a separation force rather than an attractive force between the particles (toroidal theory assumes that the half filling angle would increase and the geometry would be maintained). As separation between the particles is increased the theoretical and measured values converge. This is as a result of the predicted principal radii of curvature becoming close to those actually adopted by the bridge.

In the case where the image analyser is used to directly measure the radii of curvature good agreement is found between measured and theoretical values. This is as expected for any surface of constant mean curvature.
The trendlines inserted through figures 7.25 and 7.26 are exponential in nature, as at this stage it was assumed that the decay of force with separation took this form. However, the more accurate force curves which could be obtained by the control electronics proved this assumption only to be valid for certain criteria, based on the ratio of the bridge volume to the volume of the particles. Further literature research [50] found theory which agreed with these observations (figure 7.27). It can be seen in cases where a large liquid bridge is present (relative to the size of the particles) that the force curve decays more slowly with separation.

Figure 7.27: Theoretical dimensionless adhesion force $F^* (=F/\gamma R)$ of a liquid bridge between two equal spheres against the dimensionless separation $a^*$ ($=a/R$). The parameter, $\varphi$, is the volume of the liquid bridge divided by the volume of the spheres [50].
The value of the force used to calculate the dimensionless adhesion force is that given by the ‘neck’ method (section 4.1.1). Results of force predicted by the ‘boundary method’ only differ slightly (section 4.1.2). In the bulk of this work only the forces predicted by the ‘neck’ method are shown as it was felt these were more accurate, as they do not depend on accurate measurement of the half-filling angle. They only depend on the principal radii of curvature at the neck and in cases where the particles used were not spherical (see for example work on lactose (section 8.2)) there was no need to define a characteristic radius.

Figure 7.28 shows electronically obtained experimental force data compared with theory (as predicted by the ‘neck’ method) for a 200cS silicone oil binder on silanised glass ballotini. The value of $\varphi$ is 0.14, thus a steady decrease in force is predicted by the theory shown in figure 7.27. It can be observed that at zero separation the value of the force is seen to increase with no separation up to a value of just under 1$\mu$m, this corresponds to the pipette being driven away but the two particles staying in contact, until the bend in the pipette provides enough force to cause separation. Then at separation distances of up to approximately 0.45 $\mu$m the force is seen to rise and then slowly decay until the critical separation distance is reached at just over 16$\mu$m.
Figure 7.28: The variation of the measured force with separation distance for silanised ballotini particles wet with a 200cS silicone oil binder.

As commented on above and also reported by Mazzone [44] the maximum force seems to be at a small, but non-zero, separation distance. Although for our apparatus judging where particle contact occurs is an arbitrary decision made by microscopic observation, the low contact angle experimental results seem to support this phenomenon. It seems sensible to suggest that as two binder coated particles approach each other a separation distance must be reached where the volume of the bridge decreases as binding liquid is squeezed out. When a small separation is introduced between the particles the principal radii of curvature remain constant thus liquid flows into the middle of the bridge and the overall force increases.

From figure 7.28 it can be seen there is good agreement with the force equations when using directly measured values for the principal radii of curvature and (as shown in section 7.6) the rupture energy model. The assumption made in the derivation of the model of a constant half-filling angle appears to be valid for nodoidal and catenoidal bridge geometries as the most important factor in the total force is the change in the internal radius of curvature ($r_2$) as the neck of the bridge 'thins'.
7.5 Variation of the bridge half-filling angle with separation.

Through this work the values of the half filling angle with separation have been noted. It has been observed for low contact angle systems (where movement of bridging liquid is observed) that from zero separation the value decreases with increased separation, but then can increase slightly close to and at the point of rupture as the neck of the bridge thins and bridging liquid flows back around the particles. This agrees with the observations of Mazzone et al. [44] and the theoretical work of Lian et al. [45] (section 4.4.2). In contrast for high contact angle systems (where no movement of bridging liquid is observed) the value of the half filling angle shows a decrease up to the critical separation distance (figure 7.29). After rupture the value increases again to accommodate the liquid droplet on the particle.

![Graph showing the variation of the half filling angle with separation for experiments with a glycerol binder between two silanised ballotini particles (radii 25.4 and 31.6\(\mu\)m).](image)

Figure 7.29: The variation of the half filling angle with separation for experiments with a glycerol binder between two silanised ballotini particles (radii 25.4 and 31.6\(\mu\)m).
7.6 Rupture energies

The rupture energy of a liquid bridge is given by the integral of the forces between particle contact and bridge rupture. The area under the curve of the experimental plots of the force versus separation, from particle contact to bridge rupture, gives the total energy required to rupture the liquid bridge.

The total energy was calculated using the trapezium rule. The dimensionless rupture energy was then calculated \( W^* = \frac{W}{\gamma R^2} \) along with the dimensionless volume \( V^* = \frac{V}{R^3} \). In the cases where a change of bridge volume was noted the maximum measured volume was used. By considering the relationship between the rupture energy and the bridge volume to be of the form;

\[
W^* = cV_b^{*m}
\]

and taking natural logarithms gives,

\[
\ln W^* = m \ln V_b^* + \ln c
\]

The gradient of plots of \( \ln W^* \) versus \( \ln V_b^* \) can be seen to give the value of \( m \) and the intercept gives \( \ln c \). Simons et al. [6] stated that the rupture energy was proportional to the square root of the bridge volume, thus \( m=0.5 \) and assigned a value to \( c \) of 1.8 for the half rupture energy and thus \( c=3.6 \) for the total rupture energy.

Figure 7.30 shows \( \ln W^* \) plotted against \( \ln V_b^* \) for all the experimental data obtained in the course of this project and the relationship as given by the rupture energy model.
Figure 7.30: In $W^*$ against In $V^*$ for all experimental data.

As can be seen there is a large spread within the data and it is not possible to draw any firm conclusions, although a linear relationship does seem apparent. However, by examining the results for silicone fluids between two equi-sized particles (23.3μm radii), a relationship can be observed (see figure 7.31).

Figure 7.31: In $W^*$ against In $V^*$ for 200 series silicone oils (5, 50 and 200cS) between equi-sized particles (23.3μm radii).
The data plotted in figure 7.31 shows reasonable agreement with the premise that rupture energy is proportional to the square root of the bridge volume ($m=0.5378$) and gives an intercept of 0.9371. Thus $c$ has a value of 2.55 ($\ln c = 0.9371$), lower than the 3.6 predicted by Simons et al. [6].

Willett et al. [67] have theoretically analysed the rupture energy model and suggested a relationship between contact angle and the value of the rupture energy constant ($c$). The relationship is of the form:

$$c = \frac{2}{0.45} - 0.080 + 0.30^2$$

(7.4)

The relationship was obtained by curve fitting and assumed liquid bridges of constant volume. The proposed relationship is plotted in figure 7.32.

![Figure 7.32: Proposed relationship between rupture energy constant and contact angle [67].](image)

From figure 7.32, it can be seen that for contact angles of around 20°, $c$ is expected to have a value of approximately 4.4, higher than both the Simons et al. [6] prediction and that measured experimentally here. It is felt more experimental data is needed to satisfactorily develop the rupture energy model, particularly for cases of high contact...
angle where bridge geometries have a marked effect on the forces developed between the particles.

### 7.7 Comparison of measured and theoretical separation distance

The critical separation distance at which a liquid bridge ruptures has been subject to numerous theoretical investigations. Lian et al. [45] reviewed these (section 4.4.2) and showed that for a liquid bridge between two particles at close separations there are two solutions of the Laplace-Young equation. As the separation distance is increased the two solutions converge until they become equal; for further increases in separation no solutions exist. By plotting dimensionless volume \( V_b^* \) against the dimensionless rupture distance \( ((a_1 + a_2)^* = (a_1 + a_2)/R) \) they proposed the following relationship,

\[
(a_1 + a_2)^* = (1 + 0.5\theta)^3 V_b^*
\]  

(4.16)

where \( \theta \) is the solid-liquid contact angle expressed in radians. This relationship was investigated for all the binders used in this work and the results are shown in figure 7.25. The value of the receding contact angle was used in equation 4.16, since the particles were completely wetted by the bridging liquid and were being separated. The values used were as given in table 7.2.

<table>
<thead>
<tr>
<th>System</th>
<th>Measured receding contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane-silanised ballotini</td>
<td>12.5°</td>
</tr>
<tr>
<td>50/50 water/glycerol-unsilanised ballotini</td>
<td>40.8</td>
</tr>
<tr>
<td>Glycerol-silanised ballotini</td>
<td>89.7°</td>
</tr>
<tr>
<td>200cS silicone fluid</td>
<td>16.7°</td>
</tr>
<tr>
<td>50cS silicone fluid</td>
<td>18.1°</td>
</tr>
<tr>
<td>5cS silicone fluid</td>
<td>15.2°</td>
</tr>
</tbody>
</table>

Table 7.2: Values of receding contact angle used in equation 4.16.
In the low contact angle cases, where movement of bridging liquid was observed, the measured volume of the bridge used was the value obtained at the point of rupture, i.e. the CSD.

![Comparison of measured and theoretical CSDs](image)

Figure 7.25: Comparison of experimentally measured and theoretically predicted rupture distances for liquid bridge systems.

As can be seen from figure 7.25 good agreement is found between theory and the experimentally measured values for the critical separation distance of a liquid bridge. This is to be expected as the theory reviewed in section 4.4 has been developed with the assumption that with particles below 1mm gravity can be ignored and that the fundamental principles governing bridge stability apply. This has been confirmed to be valid by investigations on the stability of columns of liquid under zero gravity conditions in space by NASA on board the first Spacelab flight [70].
7.8 General discussion

The apparatus developed in this project has been shown to be capable of measuring a range of forces between particles of various sizes attached by liquid bridges. The whole life cycle of a liquid bridge from formation (however that may be (see section 7.2.1)) through disturbances and increased separations to rupture may be observed.

As discussed in Chapter 5, improvements to the overall understanding of agglomeration have to come from a variety of sources (a good illustration of these being that of figure 5.1). It is felt that the major strength of this work comes from the ability to observe, measure and characterise interactions taking place between industrially (and therefore academically) relevant sized and shaped particles.

Observations of the actual behaviour of liquid and particle systems can be used to improve both the mechanistic models (chapter 5) and the computation models being developed by many other workers (see for example [71], [72] and [73]). In the formation stage of an agglomerate the observations made here on the method of binder addition and the effect of contact angle on the tendency of the binder to spread through a particulate mass or to remain as discrete droplets should allow more accurate predictions to be made. Future work using this equipment will also be able to experimentally measure and observe process situations and relate them to agglomerate formation using a recently commissioned high shear mixer agglomerator. It is felt that this will allow more detailed conclusions to be drawn by taking and analysing samples at various stages during the agglomeration process.

It has also been shown that liquid bridges behave in various ways when subjected to a disruptive force depending on the nature of this force and the tendency of the liquid to wet the particle surface. Most previous models have assumed a ‘straight’ pull to cause liquid bridge rupture, whereas in fact shear and rotational disruptions will often occur under process conditions. Current work by Khan and Tardos [74] is investigating the
stability of wet agglomerates in granular shear flows, developing on the work of Ennis [5] (section 5.1). For low contact angle systems a liquid bridge will move around particles to absorb shear stresses, thus energy is absorbed through de-wetting and wetting of the particles surface. It has been observed for high contact angle systems that often the stresses existing within a liquid bridge subject to shear are not enough to cause these de-wetting and wetting effects, thus an unsymmetrical liquid bridge exists. As for a static liquid bridge the force is dependent upon the surface tension, it seems sensible to suggest that for high contact angle systems having a higher binder surface tension than those observed here, that this unsymmetrical effect may not be observed. Alternatively it may be that larger shear forces are required to observe the effect. Khan and Tardos [75] report that their critical Stokes number, where aggregation starts is a direct function of the Capillary number, i.e. it varies with surface tension and its effect of 'pulling' the particles together. They also state that the view of the process of agglomeration depending on mainly the Stokes number (as by Ennis [5]) appears to be rather simplistic and in need of improvement.

In a population balance modelling study of granulation, Adetayo et al. [71], having identified two stages of agglomerate growth in the granulation of materials with a wide size distribution, developed a model with a sequential two stage kernel, the first stage being rapid and described by the non-inertial regime of Ennis (section 5.1), the second requiring a size dependent kernel and being much slower and agglomerate deformation becoming important. The work of Adetayo et al. [71] and other population balance modelling approaches helps to improve the simulation of agglomeration for a given set of conditions. However, due to the complexity and lack of knowledge of the forces involved in agglomeration processes, it has only been possible to develop growth kernels with semi-empirical adjustable parameters. The observations of sections 7.1-7.3 and the direct measurements of 7.4-7.7 can all be used to develop population balance models by better definition of the growth kernel.

The growth of an agglomerate is often a balance between the breaking of weak bonds and the formation of stronger bonds. Other work relating to this project [76], investigated the change in torque of a Rushton turbine mixer when a binding liquid was
added to a particulate mass, the amount of liquid added being sufficient to cause the formation of only pendular liquid bridges. The end point of granulation was considered to occur when all the liquid was homogeneously distributed and that each particle had become attached to its neighbours via pendular liquid bridges. The difference in energy required to mix the dry and wet powder was then compared to the total rupture energy of the liquid bridges, calculated from an approximation of the total number of bridges within the particulate mass. Good agreement was obtained. Previous work by Kendall [65] on crack propagation postulated that the macroscopic rupture energy of a compact may be obtained by appropriate summation of individual bond energies, although this approach has been shown to be problematic where bulk deformation can absorb energy away from the crack tip [53]. If the rupture energy model is considered to be accurate it should be possible to relate the energy required to form and deform agglomerates in this kind of high shear environment to the number of bonds and their nature in terms of geometry and viscosity. This would then represent the first step in relating microscopic phenomena to macroscopic behaviour.

The energy required to form, deform and rupture liquid bridges is also of use in the area of fluidisation, for instance, in determining the role of interparticle forces on catalysts used in the cracking of oil [77]. Previously, Simons et al. [60] examined the mechanisms behind defluidisation, where a fluidised bed suddenly becomes static due to an increase in interparticle forces. This can be considered to be a dynamic change from a mobile to a static bed. Simons et al. [60] found a direct correlation between the extra kinetic energy required for fluidisation due to the presence of free liquid and the energy required to rupture liquid bridges. Further research work to be undertaken at UCL will carry out a more extensive study into the mechanisms of defluidisation due to the presence of free liquid in order to develop predictive models for the behaviour of fluidised beds in applications where free liquid can exist.
Chapter 8

8. Additional investigations

Throughout the course of this work, additional studies were carried out where there was direct industrial interest. These pieces of work involved modifications to the microscope stage or the production of micropipettes with different geometries, in addition to the use of particles other than glass ballotini.

8.1 The adhesion of ice crystals

In collaboration with Unilever Research and The University of Bristol a feasibility study was undertaken to discover whether the micropipette manipulation technique could be adapted to measure the forces required to separate ice crystals in environments similar to those found in ice cream.
Two model environments were chosen. The first was n-decane (chosen as a readily available Newtonian fluid), this was used primarily because the experiments were expected to be simpler than in the second (viscous, sticky, non-Newtonian) model environment, concentrated sucrose solution (which more closely represents ice cream). However, in the course of the experiments it turned out that sucrose solutions were easier to work in than n-decane, although it was shown that the micropipette technique could be used to measure ice crystal adhesion in both environments.

8.1.1 Experimental apparatus and method

The apparatus consisted of a stage similar to that described in chapter 6. Achieving and maintaining low temperatures was the major modification required to conduct the experiments. In the initial experiments, a cylindrical aluminium support wrapped in a copper cooling coil was used as a base for a petri dish containing the model solutions. The cooling medium was liquid nitrogen, passed intermittently through the coil. As the experimental technique was developed, a refrigerated thermostat (Lauda Model RM20S Compact Low Temperature Thermostat) was purchased and used to pass a propylene glycol/water mixture through the coil. This proved inadequate to cool the liquid in the Petri dish to below 0°C, and so a cooling coil directly immersed in the Petri dish (figure 8.1) was used instead, permitting temperatures of -10°C to be achieved with a temperature of -20°C for the circulating fluid. The performance could have been improved by adding insulation to the dish.

Initially the experimental method consisted of the “standard” micropipette approach. That was to cool the model solution until ice crystals appeared (floating at the surface), pick up an ice crystal at the tip of each pipette, touch the ice crystals together and then measure the force required to pull them apart, by moving the micromanipulator supporting the flexible micropipette in a direction to separate the particles. If the particles were adhering, the base of the pipette would move but the tip would not - that
is, the pipette would bend, and would continue bending until the force generated was 
sufficient to pull the particles apart. At this stage a jump was observed, the magnitude 
of the jump together with the calibrated stiffness of the pipette giving the force required 
to separate the particles.

The n-decane system suffered from interference due to the formation of spherical 
crystals at the air/decane interface by condensation of atmospheric water vapour. This 
problem was far from negligible, since the ice crystals so formed attached themselves 
tenaciously to the pipette tips and interfered with almost every measurement that was 
attempted.

Hydrophobising of the pipette tips failed to cure the problem, as did passing a curtain of 
dry nitrogen over the surface. Eventually, it was found that the problem could be 
overcome by enclosing the dish in a close-fitting polythene curtain into which dry 
nitrogen was passed at a positive pressure. Slots in the curtain permitted passage and 
manipulation of the micropipettes without affecting the efficacy of the approach, no 
adventitious ice crystals being observed after a period of two hours (without the curtain, 
they appear within minutes).

At this stage it was considered that the major experimental problems associated with the 
measurement of ice crystal adhesion forces in n-decane had been overcome.

For both n-decane and sucrose media, the solution was cooled by immersion of a copper 
cooling spiral (Figure 8.1). Ice crystals first formed at the point where the cooling spiral 
entered the solution, with the ice front progressing around the spiral. This advancing 
front invariably progressed to the stage where it was interfering with the shaft of the 
flexible pipette.
After trying several designs to overcome this problem (all unsuccessful), it was decided to forgo the rigid pipette completely, replacing it with a freezing loop, simply using the flexible pipette to pick ice crystals off a layer of the ice front, and then measuring the adhesion of these crystals to those in the original layer. First attempts at this failed, since a thick layer of ice developed with no free or loose crystals. The main reason for this was the very high temperature difference between the freezing coil and the sugar solution. Even when a single crystal was picked off successfully, it melted as soon as it was moved more than a few micrometers from the surface.

**Figure 8.1: Ice front on cooling coil.**

This problem was overcome by returning to the original cooling spiral, but modifying the flexible pipette configuration so that crystals could be picked off the inside of the spiral. In this new configuration, the flexible shaft passed vertically through the air/solution interface, instead of being entirely immersed in the liquid.
The approach described was successful in a surprising way. A crystal "picked off" from an ice front formed in 40% aqueous sucrose solution at -5°C acted as a nucleus for further growth, making it relatively easy to perform the experiments. Two problems remained, however - the fact that the ice crystal layer thickness continually increased as the experiment progressed, and the irreproducibility of the nucleation of ice crystals at the pipette tip.

Both of these problems were overcome, and force measurements could be made on a routine basis. The principal features of the experimental technique were to set the thermostat temperature such that the equilibrium position of the advancing ice front was close to the pipette tip. Minor adjustments of the temperature then permitted manipulation of the crystallisation in this front. Each experiment was started with the pipette clear of the solution surface and filled with water. Once the ice front was established, the pipette was lowered into the measurement position. At -5°C, the temperature used for the experiments reported below, the water in the pipette remained supercooled but unfrozen, providing two possibilities for ice crystal formation at the tip:

(i). Touching of the tip to the ice front produced nucleation of a small "hexagonal" crystal at the tip (Figure 8.2).

(ii). Extrusion of a small drop of water from the tip, which then froze in the form of a sphere (Figure 8.3).

Results obtained from this technique are given in Tables 8.1 and 8.2, which shows both the reproducibility and the effects of varying the experimental conditions. All of the results shown are for ice crystal adhesion in 40% w/w aqueous sucrose solution at -5°C. The force constant for the pipette used was 8.45μN/μm.
CHAPTER 8. ADDITIONAL INVESTIGATIONS

'Hexagonal' Ice Crystal Adhesion

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Jump Distance(µm)</th>
<th>Detachment force (µN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.8</td>
<td>193</td>
</tr>
<tr>
<td>2</td>
<td>19.7</td>
<td>166</td>
</tr>
<tr>
<td>3</td>
<td>19.0</td>
<td>161</td>
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<tr>
<td>4</td>
<td>14.5</td>
<td>123</td>
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<tr>
<td>5</td>
<td>23.5</td>
<td>199</td>
</tr>
<tr>
<td>6</td>
<td>22.5</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 8.1: Experimental results for 'hexagonal' ice crystal adhesion.

These experiments concerned the "edge-on" adhesion of a crystal at the pipette tip with different crystals in the ice front. They demonstrate the reproducibility that can be achieved with the technique.

Figure 8.2: Contact of nucleated 'hexagonal' ice crystal (held with a micropipette - tip size 25µm) with ice front.
### ‘Spherical’ Ice Crystal Adhesion

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Jump</th>
<th>Detachment</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.3</td>
<td>146</td>
<td>Small contact area for exps. 1-4</td>
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<tr>
<td>2</td>
<td>8.7</td>
<td>74</td>
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<td>3</td>
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<td>4</td>
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<td>86</td>
<td></td>
</tr>
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<td>5</td>
<td>20.8</td>
<td>176</td>
<td>Contact region flattened to give larger contact area</td>
</tr>
<tr>
<td>6</td>
<td>19.7</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>36.3</td>
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<td>Contact region further flattened</td>
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<td>8</td>
<td>33.6</td>
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<td>48.0</td>
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<td>Point contact (same for 9&amp;10)</td>
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<td></td>
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<td>11</td>
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<td>654</td>
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<td>Different point contact</td>
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<td>57.0</td>
<td>482</td>
<td>Different point contact (same for 13-16)</td>
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<td>14</td>
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<td>466</td>
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<tr>
<td>17</td>
<td>29.4</td>
<td>248</td>
<td>Point contact</td>
</tr>
<tr>
<td>18</td>
<td>77.2</td>
<td>652</td>
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<td>19</td>
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<td>520</td>
<td></td>
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<td>20</td>
<td>81.3</td>
<td>687</td>
<td>New contact point (same for 20-23)</td>
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<td>21</td>
<td>85.5</td>
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<tr>
<td>22</td>
<td>77.8</td>
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<td>23</td>
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<td>561</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>39.8</td>
<td>336</td>
<td>New contact point (same for 24-26)</td>
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<td>25</td>
<td>38.1</td>
<td>322</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>32.0</td>
<td>270</td>
<td></td>
</tr>
</tbody>
</table>

**Table 8.2: Results for spherical ice crystal adhesion.**

These results again demonstrate the reproducibility of the technique, and also illustrate that there are differences in adhesion forces that required more detailed information about the effective contact area, that in this study were not fully developed as information gained from the microscopic observation only characterised the contact in terms of the two dimensional geometry.
Figure 8.3: Contact of nucleated 'spherical' ice crystal (held with a micropipette -
tip size 25\(\mu\text{m}\)) with ice front.

8.2 The adhesion of lactose particles

In collaboration with a PhD student sponsored by Rhone Poulenc Rourer a feasibility study was undertaken to discover whether the micropipette manipulation technique could be adapted to measure the forces required to separate lactose particles in environments similar to those found in high shear mixers used in the production of pharmaceuticals. No modifications were made to the equipment. It was shown that the apparatus could be used to measure these forces.

Various sizes of lactose particles were wet with water and a water bridge was formed between them. Of particular interest in the production of pharmaceuticals in high shear mixers is the effects of using binders with a high solid contact angle. As can be seen from figure 8.4 the shape of lactose particles vary considerably. Thus as with the ice-crystal work the geometries of the liquid solid contact are difficult to predict. Figure 8.5 shows a water liquid bridge between the particles. This work will be developed further by the Rhone Poulenc Rourer student undertaking a 15 month project.
Figure 8.4: Two ‘dry’ lactose particles.

Figure 8.5: Water liquid bridge between lactose particles.
8.3 Liquid phase work

The experimental apparatus is designed to be able to measure the force of adhesion between particles in both gas and liquid phase continuous media. The work presented in this thesis concentrated on obtaining results in the gas phase, however during the course of the project a small number of liquid phase experiments were conducted in order to assess the viability of measuring forces in situations similar to those found in detergenty where shear forces are combined with detergents to remove particulate matter from clothes (i.e. washing machines).

To conduct liquid phase work it was necessary to purchase a water immersion objective for the microscope. A 20x objective having the correct refractive properties and being capable of being submerged in water was used. A petri dish was placed on the microscope stage and filled with water. In order to allow the particles to be submerged in this dish a more complex micropipette geometry was devised (figure 8.6). It was also necessary to attach the silver foil mirror to the right angle of the micropipette with a water insoluble glue. A hydrocarbon liquid bridge (decane) was then formed between two particles.

The electronics were set up to cause the separation distance between the particles to slowly increase and decrease at a rate of approximately one oscillation per second (simply a matter of making small changes to the C code presented in appendix A). A surfactant was then added to the liquid solution to observe any changes in the bridge behaviour, geometry and force. It was found that with the addition of a small quantity of surfactant solution (in this case washing up liquid) the observed forces decreased. In this investigation the possibility of measuring shear forces in the liquid phase was also investigated. To apply a shear force the 'static' micromanipulator was used to move the particle tangentially. Here the bridge was seen to be pulled around the particle whilst retaining its pendular shape (see section 7.3.3).
Figure 8.6: Schematic of side view of flexible micropipette geometry for liquid phase work.

This investigation concluded that the measurement of force in the liquid phase in the presence of surfactants is possible and it is hoped further funding will be obtained to continue this work.
Chapter 9

9. Conclusions

This thesis has focused on improving the understanding of agglomeration through the investigation of individual particle-particle interactions when joined by liquid bridges. This has been achieved through microscopic observation of particles followed by image analysis and the measurement of forces by a specially commissioned piezo-electric crystal driven apparatus.

9.1 The apparatus

Although the experimental apparatus that has been commissioned and developed over the course of the project has only been used for measuring forces between particles attached by liquid bridges it was designed and developed to ensure maximum flexibility for future work.
The maximum size of particle that can be used is limited by the effective capture area of the image analyser; when using a 5x objective and the 0.5x camera tube the maximum field of view is 4.4mm. The minimum capabilities of the equipment are governed by the limits of optical microscopy and are therefore in the region of 1μm. Unlike designs which rely on force transducers, the equipment is capable of measuring a large range of forces, governed by the pipette force constant. By varying the force constant of the glass micropipettes, forces down to 10⁻⁹ Newtons and as high as 1 Newton have been measured. The use of another material for the production of the flexible pipette showing different elastic properties would allow larger force ranges to be measured. For the measurement of forces where only a small ‘bend’ of the pipette takes place the piezo electric driven control electronics are used.

The control electronics can in theory measure a bend in the pipette of up to 18μm at a 18μm separation (total driven side movement 36μm). However, when the piezo electric crystals approach their limits of contraction and expansion unpredictable behaviour has been noted. Thus to ensure accurate readings it is recommended that the crystals are operated 10% either side of the manufacturers quoted travel distances, thereby giving the electronics the capability of measuring bends of up to 15μm at 15μm separations. Pipette bends greater than 15μm may be obtained by direct measurement using the image analyser. The apparatus has been shown to be effective not only in the measurement of liquid bridge forces but also, with minor modifications in the measurement of a whole range of other interparticle forces (see chapter 8).

9.2 Liquid bridges

The commissioning and development of the experimental apparatus made up a large part of the project before direct measurements were possible, due to its novelty. However, improvements in the understanding of liquid bridges between particles have been made to several areas.
9.2.1 Change of volume

Previous studies assumed the volume of liquid forming a bridge between two particles remained constant. The work presented in this thesis reported observations of movement of liquid into bridges on their formation and movement out on increased separation between the particles. The tendency of the liquid to flow into and out of the bridge was observed to be dependent upon the binder-solid contact angle and the rate of movement dependent upon the binder’s viscosity. This phenomena was then related to a mechanistic model of agglomeration proposed by Schaafsma et al. [68]

9.2.2 Geometry

The geometry a liquid bridge meniscus adopts has been shown and experimentally observed to be directly dependent upon the binder liquid-solid contact angle. When static the meniscus has constant mean curvature. Nodoidal, catenoidal and unduloidal geometries have been observed. Previously it has been assumed that the pressure within a liquid bridge is ‘reduced’ with respect to the surrounding environment. For nodoidal (most closely representing the toroidal geometry assumption made by many workers) this is true, however for catenoidal geometries there is no pressure difference and for unduloidal geometries the pressure within the bridge is greater than that in the surrounding environment.

9.2.3 Force

The force between two particles attached via a liquid bridge has been successfully measured in both gas and liquid phase continuous media. Measurements of force versus particle separation distance were obtained for various binding liquids between a range of particle sizes. By direct measurement of the principal radii of curvature of the bridge reasonable agreement was found with theoretically predicted forces.
It was noted that the maximum force occurred at a small, but non-zero separation distance, due to binding liquid being ‘squeezed’ out at close separations. Experimental work focused on gas phase experiments. It is hoped a future project will focus on liquid phase experiments where the presence of surfactants and dynamic surface tension effects become of greater significance.

9.2.4 Rupture Energy

The total energy required to separate two particles attached by a liquid bridge from particle contact to bridge rupture was termed the rupture energy. The rupture energy is given by the area under the force versus separation curves and was calculated using the trapezium rule. This energy was then compared with the maximum calculated volume of the liquid bridge and used to verify a previously developed [6] rupture energy model, which stated that the rupture energy was proportional to the square root of the bridge volume. Good agreement was found with this theory (given the assumptions made in its derivation) and the experimental data was used to make a reduction to the value of the model’s rupture energy constant. Further experimental data is required to assess and extend the model for high contact angle systems.

9.2.5 Rupture distances.

The distance at which a liquid bridge ruptures was compared to its volume. A model previously developed by Lian et al. [45] stated the critical separation distance at which a liquid bridge will rupture is proportional to the cube root of its volume. A correction for contact angle is included in their model and the results presented here showed good agreement with their theory.


9.3 Agglomeration

Improvements to the overall understanding of agglomeration have to come from data obtained from a variety of microscopic and macroscopic sources combined with theoretical modelling work (see figure 5.1). The results presented in this thesis and its associated work contribute by supplying measurements and observations carried out on previously only theoretically described systems.

Prior to this work data from the direct observation of the behaviour of liquid bridges was unavailable between particles below 100µm in radius. Chapter 5 summarises approaches to modelling agglomerating systems and a discussion of the significance of these results to agglomeration research is detailed in section 7.8. Many observations have been made which tie into current theories of agglomeration. In addition, observations of the movement of bridging liquid on both formation and separation, along with the effect of shear forces on liquid bridges should enable more realistic models to be devised.

9.4 Future Work

The addition of a video recorder capable of capturing more than 25 frames per second would enable the exact changes in liquid bridge geometry and the point of rupture to be observed. Also a frame by frame time stamp would allow greater accuracy in calculating rates of binder movement. Observations on binder movement may also be aided by the addition of a tracer dye.

Modifications to the electronics of the equipment would allow a larger range of experiments to be carried out. By upgrading the piezo electric crystals larger separation distances could be measured non intrusively.
Also, or alternatively, the addition of a PEC-LVDT system capable of giving larger separations could be fitted to the static micropipette micromanipulator. A facility such as this would allow particles to be driven away from the flexible pipette in a non-intrusive manner, being especially useful in the sudden breakage type experiments (as with ice crystals) where bodies remain attached until sudden fracture occurs. Thus a single glass micropipette could be used for a wide range of forces as bends up to the field of view of the microscope could be measured.

9.5 Final remarks

A novel piece of experimental apparatus has been developed to observe and measure all aspects of liquid bridge behaviour resulting in improvements being made to both liquid bridge and agglomeration theories. It has been shown that the apparatus can be used to measure other types of interparticles forces. Further work, using the apparatus described here, is now being carried out to measure liquid bridge forces between particles immersed in a second immiscible liquid.
10. References


Appendix A

A.1 Surface tension data

Data for the surface tension of the bridging liquids used was obtained using a Kruss K12 processor tensiometer. Measurements were carried out using the Wilhelmy-plate method (as described in Chapter 6) and a platinum plate. The plate is 19.9mm wide and 0.2mm thick, thus the total perimeter is 40.2mm. The plate is roughened, so it is assumed that all liquids have a contact angle of zero on the plate. Thus the equation,

$$f = p\gamma_w \cos \theta$$  \hspace{1cm} (3.27)

Simplifies ($\cos 0^\circ = 1$) to;

$$f = (40.2 \times 10^{-6}) \gamma$$  \hspace{1cm} (A.1)

A series of 100 measurements were taken and the results plotted against time, the measurement being repeated three times. For a pure bridging liquid the surface tension remained constant throughout (figure A.1). For a bridging liquid containing surface active agents a decrease in the surface tension was observed with time (i.e. a dynamic surface tension effect - figure A.2). For the force experiments carried out in this work, only pure bridging liquids were used. When it was evident the sample was
contaminated with surfactants, new solutions were produced and the equipment was thoroughly cleaned to remove all impurities.

**Figure A.1:** Example of surface tension measurement of pure liquid.

**Figure A.2:** Example of surface tension measurements for liquid containing surfactants.
The surface tension data was then tabulated;

<table>
<thead>
<tr>
<th>Bridging liquid</th>
<th>Temperature (°C)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>21.0</td>
<td>24.33</td>
</tr>
<tr>
<td>Reverse Osmosis Water</td>
<td>22.4</td>
<td>72.11</td>
</tr>
<tr>
<td>50/50 glycerol/water</td>
<td>21.4</td>
<td>55.64</td>
</tr>
<tr>
<td>Glycerol</td>
<td>21.4</td>
<td>52.8</td>
</tr>
<tr>
<td>Silicone oil 200/5cS</td>
<td>20.6</td>
<td>19.22</td>
</tr>
<tr>
<td>Silicone oil 200/50cS</td>
<td>24.1</td>
<td>20.37</td>
</tr>
<tr>
<td>Silicone oil 200/200cS</td>
<td>24.6</td>
<td>20.86</td>
</tr>
</tbody>
</table>

Table A.1: Experimentally measured surface tension data.
Appendix B

B.1 Contact angle measurements

The following section contains the experimentally measured values of contact angle, θ, using the Kruss Processor Tensiometer. The measurements were carried out using silanised and unsilanised glass microscope cover slides and the appropriate bridging liquid. Chapter 3 contains a full explanation of contact angle theory and Chapter 6 a full explanation of the experimental apparatus and method. To obtain the values the following equation is used by the computer software,

\[ F = p \gamma_{lw} \cos \theta \]  

where;
- \( F \) is the force on the balance
- \( p \) is the perimeter of the glass slide
- \( \gamma_{lw} \) is the surface tension (measurements in Appendix A).

The value of the both the advancing and receding contact angle was measured.
### Table B.1: Measured contact angle for glass - dodecane.

<table>
<thead>
<tr>
<th></th>
<th>Measured contact angle (degrees)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature 21.6 °C</td>
<td></td>
</tr>
<tr>
<td>Unsilanised coverslip</td>
<td>Advancing 0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Receding 0</td>
<td>0</td>
</tr>
<tr>
<td>Silanised coverslip</td>
<td>Advancing 16.6</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>Receding 10.2</td>
<td>12.5</td>
</tr>
</tbody>
</table>

### Table B.2: Measured contact angle for glass - reverse osmosis water.

<table>
<thead>
<tr>
<th></th>
<th>Measured contact angle (degrees)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature - 25.0°C</td>
<td></td>
</tr>
<tr>
<td>Unsilanised coverslip</td>
<td>Advancing 94.8</td>
<td>91.2</td>
</tr>
<tr>
<td></td>
<td>Receding 74.6</td>
<td>77.4</td>
</tr>
<tr>
<td>Silanised coverslip</td>
<td>Advancing 53.7</td>
<td>54.1</td>
</tr>
<tr>
<td></td>
<td>Receding 26.4</td>
<td>27.2</td>
</tr>
</tbody>
</table>

### Table B.3: Measured contact angle for glass - 50 / 50 water / glycerol mix.

<table>
<thead>
<tr>
<th></th>
<th>Measured contact angle (degrees)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature 25.9°C</td>
<td></td>
</tr>
<tr>
<td>Unsilanised coverslip</td>
<td>Advancing 61.4</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td>Receding 41.4</td>
<td>40.8</td>
</tr>
<tr>
<td>Silanised coverslip</td>
<td>Advancing 98.0</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>Receding 74.9</td>
<td>77.9</td>
</tr>
<tr>
<td>Unsilanised coverslip</td>
<td>Temperature 26.6°C</td>
<td>Average</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------------------</td>
<td>---------</td>
</tr>
<tr>
<td><strong>Advancing</strong></td>
<td>75.8</td>
<td>75.1</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>25.3</td>
<td>25.3</td>
</tr>
<tr>
<td>Silanised coverslip</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Advancing</strong></td>
<td>91.4</td>
<td>91.0</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>89.6</td>
<td>89.7</td>
</tr>
</tbody>
</table>

Table B.4: Measured contact angle for glass - glycerol.

<table>
<thead>
<tr>
<th>Unsilanised coverslip</th>
<th>Temperature - 24.2°C</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advancing</strong></td>
<td>21.5</td>
<td>20.1</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>17.6</td>
<td>18.6</td>
</tr>
<tr>
<td>Silanised coverslip</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Advancing</strong></td>
<td>18.0</td>
<td>17.8</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>15.2</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Table B.5: Measured contact angle for glass - 200/5cS silicone fluid.

<table>
<thead>
<tr>
<th>Unsilanised coverslip</th>
<th>Temperature - 23.6°C</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advancing</strong></td>
<td>17.2</td>
<td>17.4</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>15.3</td>
<td>16.1</td>
</tr>
<tr>
<td>Silanised coverslip</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Advancing</strong></td>
<td>18.8</td>
<td>19.0</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>17.9</td>
<td>17.9</td>
</tr>
</tbody>
</table>

Table B.6: Measured contact angle for glass - 200/50cS silicone fluid.
### Measured contact angle (degrees)

<table>
<thead>
<tr>
<th></th>
<th>Unsilanised coverslip</th>
<th>Temperature - 24.4°C</th>
<th>Silanised coverslip</th>
<th>Temperature - 23.9°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advancing</strong></td>
<td>21.7</td>
<td>18.8</td>
<td>24</td>
<td>24.9</td>
</tr>
<tr>
<td><strong>Receding</strong></td>
<td>16.9</td>
<td>16.0</td>
<td>15.4</td>
<td>17.7</td>
</tr>
</tbody>
</table>

*Table B.7: Measured contact angle for glass - 200/200cS silicone fluid.*
Appendix C

C.1 Pipette force constant calculation

To measure the pipette force constant the pipette is mounted in the static pipette micromanipulator (figure C.1). The particle on the end of the pipette is then brought into focus and the value on the microscope’s fine focus micrometer noted.

A series of weights are hung over the 90° bend in the flexible micropipette (figure C.2) and the resulting displacement measured (by bringing the particle back into focus and noting the new micrometer reading). The weights are small lengths of nichrome wire bent into horseshoe shapes. Their mass was measured to the nearest one thousandth of a gram using a balance. Their addition and removal is facilitated using long nosed tweezers.
APPENDIX C. PIPETTE FORCE CONSTANT CALCULATION

Figure C.1: Flexible micropipette mounted in micromanipulator.

Figure C.2: Weight hung on flexible micropipette.

For each weight the reading is repeated three times and an average taken. A force displacement table is then produced (Table C.1). The force constant for each weight is calculated and an average value taken. The data can also be represented on a graph to show the linear nature of the force displacement for glass micropipettes (figure C.3).
### Table C.1: Force - displacement data for glass micropipette.

<table>
<thead>
<tr>
<th>Force applied (microNewtons)</th>
<th>Distance moved (micrometers)</th>
<th>Force constant (microNewtons / micrometer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>32.34</td>
<td>50</td>
<td>0.647</td>
</tr>
<tr>
<td>35.28</td>
<td>55</td>
<td>0.641</td>
</tr>
<tr>
<td>45.05</td>
<td>65</td>
<td>0.693</td>
</tr>
<tr>
<td>50.96</td>
<td>77</td>
<td>0.662</td>
</tr>
<tr>
<td>52.92</td>
<td>83</td>
<td>0.638</td>
</tr>
<tr>
<td>59.78</td>
<td>94</td>
<td>0.636</td>
</tr>
<tr>
<td>69.58</td>
<td>107</td>
<td>0.650</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td><strong>0.652</strong></td>
</tr>
</tbody>
</table>

![Pipette force displacement curve](image)

**Figure C.3:** Force - displacement curve for glass micropipette.
Appendix D

D.1 Control Electronics

The electronic equipment (figure D.1), which controls the linear variable differential transformers (LVDT) and the piezoelectric crystals (PEC) on the adapted stage and provides the interface for the A/D board in the computer, was designed and built by Roger Murphy of the Department of Physics at the University of Bristol. It consists of a driven channel and a follower channel.

The driven channel drives a Physic Instrumente (PI) P810.30 (30μm expansion) PEC, its expansion monitored by a PI E115.21 (±0.5mm) LVDT. A single channel control module PI E810.10, which provides LVDT conditioning, error control amplification, HV (high voltage) drive amplification and a DC/DC converter, is used to control the driven channel. It is due to the non linearity and hysteresis associated with PECs that such a control system is required.
Local control of this driven channel is provided by means of a front panel potentiometer. Alternatively, signal control may be exerted via either the BNC socket on the front panel or via the multiway signal I/O (input/output) 'D' connector on the rear panel. A ±5V signal level change causes full expansion and contraction of the PEC. Note that all input and output signals have alternative access via the 15 way 'D' socket on the rear panel. Pin allocation is shown in Table D.1. These are linked to the A/D board in the computer.

Figure D.2: Schematic of front panel of control electronics
Table D.1: Pin allocation for 15 way 'D' socket on rear of control electronics.

<table>
<thead>
<tr>
<th>PIN</th>
<th>SIGNAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RO MON 1 (reflecto-optical monitor)</td>
</tr>
<tr>
<td>2</td>
<td>RO MON 2 (reflecto-optical monitor)</td>
</tr>
<tr>
<td>3</td>
<td>RO EXTERNAL INPUT</td>
</tr>
<tr>
<td>4</td>
<td>LVDT SENSE FOLLOWER CHANNEL</td>
</tr>
<tr>
<td>5</td>
<td>V_{OUT}/100 FOLLOWER CHANNEL</td>
</tr>
<tr>
<td>6</td>
<td>LVDT SENSE DRIVEN CHANNEL</td>
</tr>
<tr>
<td>7</td>
<td>V_{OUT}/100 DRIVEN CHANNEL</td>
</tr>
<tr>
<td>8</td>
<td>V_{IN} DRIVEN CHANNEL</td>
</tr>
<tr>
<td>9</td>
<td>GROUND</td>
</tr>
<tr>
<td>10</td>
<td>GROUND</td>
</tr>
<tr>
<td>11</td>
<td>GROUND</td>
</tr>
<tr>
<td>12</td>
<td>GROUND</td>
</tr>
<tr>
<td>13</td>
<td>GROUND</td>
</tr>
<tr>
<td>14</td>
<td>GROUND</td>
</tr>
<tr>
<td>15</td>
<td>GROUND</td>
</tr>
</tbody>
</table>

The movement of a pipette attached to the driven assembly can be measured by attaching a small mirror at the point of interest, in this case at the bend. The follower channel can then be set up to follow the movement of the edge of the mirror. A schematic of the overall control circuit configuration is shown in figure D.3. To control the follower a reflecto-optic (RO) sensor is used to linearly detect the position of the edge of the mirror in its field. This signal is used to drive the RO amplifier.

The amplifier output provides the input to the drive amplifier on a second single channel control module E810.10. The follower drives a PI P810.10 (15μm expansion) piezo electric crystal and the position is measured by a PI E115.21 LVDT.
Figure D.3: Circuit diagram of control electronics.
The equipment is 240V ac mains powered via a fused IEC mains socket on the rear panel together with a power on switch. Internally the equipment is provided with a modular power supply type HSU 100-32, manufactured by Contact Lambda providing 12V @ 5amps and -12V @ 0.5 amps.

PI Operating manual PZ54E describes the set up and operation of the E810.10 module. All jumper links are placed for standard settings.

**D.1.2 Equipment set-up**

![Diagram of electronically controlled stage parts](image)

**Figure D.4: Schematic of electronically controlled stage parts.**

Figure D.4 is a schematic of the electronically controlled mechanical assembly on the microscope stage as viewed from above. The driven movement of both the driven PEC and the follower PEC is in a left and right horizontal plane. Movement in other directions is achieved by manual manipulation of the micrometers. The cylindrical body of the RO sensor has its major axis perpendicular to the horizontal and optically senses objects 4.5mm above its face. Therefore the mirror, on the right angled bend of the micropipette must lie horizontally.
Often the set-up depends on the experiment to be carried out. However, in most cases it is necessary for the movement of the follower to be located about at the centre point of the driven movement. i.e.,

Driven channel’s range (30\(\mu\)m) \[\text{P810.30}\]

\[\text{P810.10}\]

This allows non-invasive control over the whole range of the follower.

**D.1.3 Driven channel set-up**

To set up the driven channel the control unit must first be switched off before the leads are connected. The control unit can then be switched back on again. At all times, it is important to note that output voltages of up to 120V occur on the central pin of the connectors to the PECs on the front panel of the equipment. The mode of operation is then switched to open loop (switch on front panel), and the potentiometers set to 5.0 (if travel is required only in one direction they are set 15% away from limit of the potentiometer) and no input signal is applied to the BNC socket. With the LVDT in an uncompressed condition, the voltage on the driven sensor test point is monitored, and the LVDT is then slowly compressed. Figure D.5 shows the output voltage characteristics of a LVDT with compression, and the set-up point is indicated (here further compression results in an increase in the output of the LVDT above 5 volts and vice-versa). Compression can be achieved either with the LVDT grub screw (mounted against the LVDT on the micromanipulator assembly) or by the RH micrometer of the micromanipulator. The sensed voltage is adjusted to +5.0\(\pm\)0.05V (point shown on figure D.4). The LVDT electronics are set up so that full PEC expansion results approximately in a 10 volt change from the LVDT sense output. The mode of operation is then switched to closed loop (CL), if the set-up is correct the sensed voltage should remain at +5.0\(\pm\)0.5V.
The driven channel is now set up to follow an input signal, provided that it is within the range ±5.0V and frequency <10Hz. From this point no alterations of the grub screw or the RH micrometer are required. The LH micrometer is used to move the whole driven assemble without altering the set-up conditions.

![Diagram of LVDT voltage output characteristics](image)

Figure D.5: Voltage output characteristics of a LVDT.

### D.1.4 Follower channel set-up

First set the driven channel to CL and 5.0 on the potentiometers and have no input signal (section D.4). The three front panel switches (on the RO amplifier board) are then set to OL, FIX and INT. The RO sensor is positioned for total reflection from the mirror with a separation of approximately 4.5mm for gas (air) phase work and 6.0mm for liquid (water) phase work. The output of MON 1 is monitored and by vertical adjustment of the RO sensor, the most negative signal in the range 0 to -5V is sought (if the mirror is too good the sensor becomes over sensitive). The RO device is then moved to the edge of the mirror (either by moving the driven or the follower assemblies) until the voltage at MON 2 is 0.0 ±0.05V. The lightspot from the RO sensor is now on the RH edge of the mirror.
The FIX setting demands a 50% open loop expansion (alternative starting positions are possible by selecting ADJ and using the potentiometers). The mode of operation is now switched to closed loop (CL), if correctly set up the PEC stays at 50% expansion. The uncompressed follower LVDT, should now be compressed (as with the driven channel) until the set up point is reached and measures 5.0±0.05V.

An ac or dc variation of the driven channel should now result in a corresponding change in the follower channel, subject to compatibility with its smaller range.

D.1.5 Adjustments and calibration

The driven and follower side have different internal amplifications. Thus this has to be allowed for in their voltage change against distance moved calibration (figure F.1).

The switch positions work as follows. When the fix/adj. switch is on ‘fix’, the int/ext switch is inoperative. With the fix/adj switch on ‘fix’, the electronics are set so that when the LVDT and PEC are set up in the open loop state, the PEC is half-way through its total travel (i.e. at 50% expansion). Closing the loop should introduce only a small error demand, so that it is stable.

If set up at one end of the PECs travel is required, the fix/adj. switch is set to ‘adj’. The voltage output to the PEC can then be adjusted. With the int/ext switch on ‘int’, the potentiometer on the front will adjust the position. With the int/ext switch on ‘ext’, the potentiometer is inoperative. Instead, an external voltage (e.g. from a computer output) can be used to control the position.
Appendix E

E.1 Code for Data Acquisition

To convert the analogue voltage values of the LVDTs to digital values capable of being logged, an IBM PC compatible Advantech PCL-818HD data acquisition card is fitted to the computer. It incorporates 12-bit A/D conversion with a ±10 volt input range, D/A conversion with an output range of 0 to 10 volts and a timer / counter with a maximum time base of 100MHz.

To control the functions of the data acquisition card, it was necessary to write a computer program. This program was written in the computer language C and is given in the following pages. The program works with a software driver (supplied by Advantech), which allows all the user defined options to be specified in a common parameter table.

The code was written and compiled using a Borland Turbo C environment. Where possible ANSI C code was used. A full explanation of the programming of the board can be found in the Advantech PCL-818HD user’s manual.
APPENDIX E. CODE FOR DATA ACQUISITION

#include <stdio.h>
#include <conio.h>
#include <stdlib.h>
#include <dos.h>
#include <time.h>
#include <bios.h>

/* key definition */
#define UPARR 0x4800
#define DNARR 0x5000
#define ESC 0x1b
#define F1 0x3b00

extern pcl818HD(int, unsigned int *);
FILE *results;
unsigned int param[60]; /* Parameter array */
unsigned int AD_data[100]; /* Buffer for A/D data */
unsigned int DA_data[100]; /* Buffer for D/A data */
void board_error(void); /* board_error function prototype */

/* Pointer to get the segment and offset of arrays */
unsigned int far * dataAD;
unsigned int far * dataDA;
int main()
{
    int exitloop=0;
    int record_LVDTs=0;
    int readkey;

    float output; /* Output of D/A (corresponds to voltage) */
    float out_volt; /* Holds data during conversion to a voltage value */
    float Follower; /* */
    float Driven; /* */
    float Follower_Vout; /* Holds data during conversion to a voltage value */
    float Driven_Vout; /* */
    float RO_Mon1; /* */
    float RO_Mon2; /* */

    /* local time code */

    time_t timer;
    struct tm *tblock;

    /* print top of screen */

    clrscr();
    printf("\\n\\n*********************************************************
                **********\\n\nRobert's GREAT CHANNEL MONITORING AND DRIVING
PROGRAM *")
    printf("\\n\\nPress ESC key to exit program");
APPENDIX E. CODE FOR DATA ACQUISTION

```c
printf("\n\n Results file called RESULTS.CSV load in Excel\n");

/* ask for and set initial voltage output */

printf("\n\n Please input required output voltage\n");
printf("\n Range 0 - 10 volts\n");
printf("\n :\n");
scanf("%f", &out_volt); /* Get initial out voltage */
output = out_volt * 409.6; /* Convert to 12bit number */
gotoxy(14,13);
printf("\n\n\n");
printf("\n\n\n");

/* PARAMETER TABLE */

param[0] = 0; /* Board no. for this parameter table. 0: 1st board */
param[1] = 0x320; /* Card base I/O address */
                        /* This is set on the card by switch SW1 */

/* Trigger pacer rate = (card base frequency) / (C1 * C2) */
/* = base freq. / (param[5] * param[6]) */
param[5] = 1000; /* Pacer divider constant C1 */
param[6] = 100; /* Pacer divider constant C2 */
param[7] = 0; /* Trigger mode, 0: pacer trigger */

dataAD = AD_data; /* Get the address of the A/D data buffer */
param[10] = FP_OFF(dataAD); /* Offset of A/D data buffer A */
param[11] = FP_SEG(dataAD); /* Segment of buffer A */
param[12] = 0; /* Offset of A/D data buffer B. If B not used, set to 0 */
param[13] = 0; /* Segment of A/D data buffer B. If B not used, set to 0 */
```
APPENDIX E. CODE FOR DATA ACQUISITION

param[14] = 6; /* Number of A/D conversions */
param[15] = 0x0; /* A/D conversion start channel */
    /* Follower piezo is measured on channel 0 */
param[16] = 0x5; /* A/D conversion stop channel */
    /* Driven side piezo is measured on channel 1 */
param[17] = 8; /* Overall gain. 8: +/- 10V */
    /* See appendix C: page 117 for details */

/* D/A param[] definitions */

dataDA = DA_data; /* Get the address of the D/A data buffer */
param[20] = FP_OFF(dataDA); /* Offset of D/A data output buffer A */
param[21] = FP_SEG(dataDA); /* Segment of D/A output data buffer A */
param[22] = 0; /* Offset of D/A data buffer B. If B not used, set to 0 */
param[23] = 0; /* Segment of D/A data buffer B. If B not used, set to 0 */
param[24] = 1; /* D/A conversion number */
param[25] = 0; /* D/A conversion start channel */
param[26] = 0; /* D/A conversion stop channel */

/* param[45] holds the return error code, 0 if no error */
/* Appendix A of PCL-818HD User's Manual has full list or error codes */

/* ACQUIRE DATA */

pcl818HD(3, param); /* Initialise driver */
    if (param[45] != 0) {board_error();}

pcl818HD(12, param); /* D/A initialisation */
    if (param[45] != 0) {board_error();}

dataDA[0] = output;
/* D/A conversion */

pcl818HD(13, param); /* D/A conversion */

/* Return any param[45] error code */
/* A param[45] value of 2 means the driver has not been loaded */
/* The PCL-818HD.EXE program loads the driver as a TSR program (P.3 of manual) */

pcl818HD(100, param); /* Initialise card A/D */

if (param[45] != 0) {board_error();} /* check for errors */

results = fopen("RESULTS.CSV", "w");

/* PROGRAM LOOP */

while(exitloop==0) /* loops (ie takes readings) until escape key is pressed */
{
    pcl818HD(101, param); /* A/D conv. with S/W data transfer */
    if (param[45] != 0) {board_error();} /* check for errors */

/* DISPLAY ACQUIRED DATA FROM BUFFER */

    /* The top four bits of each A/D data element hold the channel no.
        We mask off the top four bits from the 16 bit data then convert it
to a voltage according to the gain and in/out range */

    Follower = AD_data[0] & 0xFFF;
    Follower = ( (10 - (-10)) * Follower / 4096) + (-10);

    Driven = AD_data[1] & 0xFFF;
    Driven = ( (10 - (-10)) * Driven / 4096) + (-10);
Follower_Vout = AD_data[2] & 0xFFF;
Follower_Vout = ( (10 - (-10)) * Follower_Vout / 4096) + (-10);

Driven_Vout = AD_data[3] & 0xFFF;
Driven_Vout = ( (10 - (-10)) * Driven_Vout / 4096) + (-10);

RO_Mon1 = AD_data[4] & 0xFFF;
RO_Mon1 = ( (10 - (-10)) * RO_Mon1 / 4096) + (-10);

RO_Mon2 = AD_data[5] & 0xFFF;
RO_Mon2 = ( (10 - (-10)) * RO_Mon2 / 4096) + (-10);

/*
(10 - (-10)) : A/D input range (-10V to 10V)
4096 : Full scale for 12-bit A/D data
Follower & Driven : A/D input data
(-10) : A/D input range (-10V)
*/

out_volt = output / 409.6;  /* convert 12bit number to voltage */

/* Time code */
timer = time(NULL);          /* Gets the time of day */
tblock = localtime(&timer);   /* Converts date/time to a structure */

/* Print out the data */
gotoxy(17,11);
if (record_LVDTs==0)
printf(" Press F1 to start recording LVDT outputs");
else
printf(" RECORDING OUTPUTS TO FILE 
");

gotoxy(24,13);
printf("%s", asctime(tblock));

gotoxy(17,15);
printf("Channel 0: Follower LVDT = %1.3f Volts ", Follower);
gotoxy(17,16);
printf("Channel 1: Driven LVDT = %1.3f Volts ", Driven);

if (record_LVDTs==1)
fprintf(results," %1.3f, %1.3f, %s", Follower, Driven, asctime(tblock));

gotoxy(17,18);
printf("Channel 2: Follower Vout/100 = %1.3f Volts ", Follower_Vout);
gotoxy(17,19);
printf("Channel 3: Driven Vout/100 = %1.3f Volts ", Driven_Vout);

gotoxy(17,20);
printf("Channel 4: RO Amplifier Mon1 = %1.3f Volts ", RO_Mon1);
gotoxy(17,21);
printf("Channel 5: RO Amplifier Mon2 = %1.3f Volts ", RO_Mon2);

gotoxy(22,23);
printf("Output voltage = %1.3f Volts ", outvolt);
gotoxy(22,24);
printf("Output number = %1.1 f ", output);

if (bioskey(l)==0) continue;

readkey=bioskey(0);
switch(readkey){

case UPARR:
    if (output>=4088) {output=4096; break;}
    else
        output = output + 8;
    dataDA[0] = output;
    pcl818HD(13, param); /* D/A conversion */
    break;

case DNARR:
    if (output<=8) {output=0; break;}
    else
        output = output - 8;
    dataDA[0] = output;
    pcl818HD(13, param); /* D/A conversion */
    break;

case F1:
    record_LVDTs=1;
    break;

case ESC:
    exitloop=1;
    break;

default:
    break;
}
}

fclose(results);
return 0;
}

/* BOARD ERROR FUNCTION */

void board_error(void)
{
    printf("\nDriver initialisation failed!\n");
    if (param[45] == 2) {
        printf("\nDriver not installed\nRun the PCL818HD.EXE program.\n");
    }
    printf("\nParam[45]=%d See Appendix A page 98\n", param[45]);

    while(!kbhit()) {delay(10);} /* waits until a key is pressed */

    exit(1);
}
Appendix F

F.1 Processing of computer data

The computer program (appendix E) acquires LVDT voltage information from the A/D board at a rate of ten readings per second. This information is stored along with time information in a CSV (comma separated variable) file. The software package Microsoft Excel can then be used to open and process the data.

Initially the comma separated variable file contains information as shown in table F.1.

<table>
<thead>
<tr>
<th>Follower LVDT voltage</th>
<th>Driven LVDT voltage</th>
<th>Time</th>
</tr>
</thead>
</table>

Table F.1: Sample of raw computer acquired data.
F.1.2 Force and particle separation calculations

To convert the voltage data into particle separation and force exerted on the flexible pipette requires a few simple calculations (see table F.2). Initially it is necessary to calculate the change in voltage output of the LVDTs (columns 4 and 5). This is done by taking a value for the outputs of the LVDTs at zero separation and zero force (in this case 9.512 volts for the follower and 8.091 volts for the driven) and subtracting these values from the acquired readings.

The calibration of change of voltage with distance moved for the LVDTs (set by the electronics) is then used to calculate the movement of the LVDTs in microns. In this case the value in column 4 is multiplied by (-)1.69 to give column 6 and the value in column 5 by (-)3.15 to give column 7.

The distance moved by the follower gives the separation distance between the particles (column 6).

The distance moved by the follower (column 6) subtracted from the distance moved by the driven LVDT (column 7) gives the amount of bend in the pipette in microns (column 8). This value can then be multiplied by the pipette force constant (in this case 0.346μN/μm) to give the force exerted on the flexible pipette (column 9).

F.1.3 Calibration check for the electronics

For every experiment it was possible to check the calibration and the workings of the LVDTs. To do this the driven side particle was driven throughout the range of the LVDT with no liquid bridge present. It would therefore be expected that there should be no force detected for all separations. Figure F.1 shows a plot of such data. The small errors observed are considered to be due to vibrations due to the movement of air around the stage, rounding errors of both the hardware and software and slight inaccuracies in the calibrations of the LVDTs.
It can be calculated that the maximum error in measurement of 0.5\( \mu \)m on a 15\( \mu \)m bend corresponds to an error of 3.33\%, or for any given separation 0.5\( \mu \)m multiplied by the pipette force constant (in this case 0.5\( \mu \)m x 0.346\( \mu \)N/\( \mu \)m = 0.176\( \mu \)N).

<table>
<thead>
<tr>
<th>Follower Volts</th>
<th>Driven Volts</th>
<th>Time</th>
<th>( \Delta ) Follower Volts</th>
<th>( \Delta ) Driven Volts</th>
<th>Follower move (( \mu )m)</th>
<th>Driven move (( \mu )m)</th>
<th>Bend (( \mu )m)</th>
<th>Measured force (( \mu )N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Initial readings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.512</td>
<td>8.091</td>
<td>15:14:59</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>9.502</td>
<td>8.096</td>
<td>15:14:59</td>
<td>-0.010</td>
<td>0.005</td>
<td>0.017</td>
<td>-0.016</td>
<td>-0.033</td>
<td>-0.011</td>
</tr>
<tr>
<td>9.512</td>
<td>8.101</td>
<td>15:14:59</td>
<td>0.000</td>
<td>0.010</td>
<td>0.000</td>
<td>-0.032</td>
<td>-0.032</td>
<td>-0.011</td>
</tr>
<tr>
<td>9.517</td>
<td>8.105</td>
<td>15:14:59</td>
<td>0.005</td>
<td>0.014</td>
<td>-0.008</td>
<td>-0.044</td>
<td>-0.036</td>
<td>-0.012</td>
</tr>
<tr>
<td>Maximum force readings</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.165</td>
<td>6.138</td>
<td>15:15:30</td>
<td>-0.347</td>
<td>-1.953</td>
<td>0.586</td>
<td>6.152</td>
<td>5.566</td>
<td>1.926</td>
</tr>
<tr>
<td>9.146</td>
<td>6.113</td>
<td>15:15:30</td>
<td>-0.366</td>
<td>-1.978</td>
<td>0.619</td>
<td>6.231</td>
<td>5.612</td>
<td>1.942</td>
</tr>
<tr>
<td>9.102</td>
<td>6.089</td>
<td>15:15:30</td>
<td>-0.410</td>
<td>-2.002</td>
<td>0.693</td>
<td>6.306</td>
<td>5.613</td>
<td>1.942</td>
</tr>
<tr>
<td>9.087</td>
<td>6.099</td>
<td>15:15:30</td>
<td>-0.425</td>
<td>-1.992</td>
<td>0.718</td>
<td>6.275</td>
<td>5.557</td>
<td>1.923</td>
</tr>
<tr>
<td>9.053</td>
<td>6.060</td>
<td>15:15:30</td>
<td>-0.459</td>
<td>-2.031</td>
<td>0.776</td>
<td>6.398</td>
<td>5.622</td>
<td>1.945</td>
</tr>
<tr>
<td>9.033</td>
<td>6.074</td>
<td>15:15:31</td>
<td>-0.479</td>
<td>-2.017</td>
<td>0.810</td>
<td>6.354</td>
<td>5.544</td>
<td>1.918</td>
</tr>
<tr>
<td>8.906</td>
<td>6.050</td>
<td>15:15:31</td>
<td>-0.606</td>
<td>-2.041</td>
<td>1.024</td>
<td>6.429</td>
<td>5.405</td>
<td>1.870</td>
</tr>
<tr>
<td>Readings for separation of approximately 7 ( \mu )m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Readings for rupture separation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.059</td>
<td>2.275</td>
<td>15:17:02</td>
<td>-9.571</td>
<td>-5.816</td>
<td>16.175</td>
<td>18.320</td>
<td>2.145</td>
<td>0.742</td>
</tr>
<tr>
<td>-0.059</td>
<td>2.280</td>
<td>15:17:03</td>
<td>-9.571</td>
<td>-5.811</td>
<td>16.175</td>
<td>18.305</td>
<td>2.130</td>
<td>0.737</td>
</tr>
<tr>
<td>-0.068</td>
<td>2.280</td>
<td>15:17:03</td>
<td>-9.580</td>
<td>-5.811</td>
<td>16.190</td>
<td>18.305</td>
<td>2.114</td>
<td>0.732</td>
</tr>
<tr>
<td>-0.068</td>
<td>2.280</td>
<td>15:17:03</td>
<td>-9.580</td>
<td>-5.811</td>
<td>16.190</td>
<td>18.305</td>
<td>2.114</td>
<td>0.732</td>
</tr>
</tbody>
</table>

Table F.2: Sample of processed raw data for force versus separation curves.
Figure F.1: Variation of measured bend of micropipette with separation for zero force case.
Appendix G

G.1 Publications, Conferences and Presentations

G.1.1 Refereed Journals


G.1.2 Conference Proceedings


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**G.1.3 Seminars**


**G.1.4 EPSRC Soft Solids Research Events (Poster Presentations)**

Imperial College, 11th April 1995
University of Birmingham, 17-18th April 1996
University of Loughborough, 15th April 1997

**G.1.5 Company Internal Report**


**G.1.6 Copy of sample publication**

The following 6 pages show a reproduction of a paper written half way through the project published in Particle and Particle Systems Characterization.
Particle & Particle Systems
Characterization
Measurement and Description of Particle Properties and Behavior in Powders and Other Disperse Systems
Modelling of Binder-Induced Agglomeration

Robert J. Fairbrother, Stefaan J. R. Simons*

(Received: 10 April 1997; resubmitted: 3 August 1997)

Abstract

From the analysis of pendular liquid bridge forces between spherical particles, a model has been developed to predict bridge rupture energies. Whilst this model has been shown to predict the correct trends in certain stages of agglomeration, it is limited by the assumptions of zero contact angle, toroidal bridge geometry, spherical particles and quasi-static rupture. The work described here is aimed at extending the model to more generally applicable conditions using direct measurement of bridge rupture energies between particles down to 3 μm in diameter under different physiochemical conditions. Initial results show that the spreading coefficient of the binder to the particle has a marked effect on the dynamic behaviour of the bridge itself and its subsequent geometry at equilibrium, i.e. for non-zero contact angles theoretical equations tend to over-predict the force of adhesion, whilst for zero contact angles the force of adhesion agrees with that predicted using the Laplace equations for constant curvature. On the other hand, the corrected expression for maximum separation distance shows good agreement with experimental results.

1 Introduction

An understanding of the capillary adhesion forces and the interfacial geometries between particles in dispersions with immiscible fluid phases is of importance in operations such as flotation, coating, flocculation and granulation. In the latter example, particles can be encouraged to come together by the addition of a liquid for which they have a greater affinity than the surrounding fluid medium. By agitating the liquid in some way, the particles collide and a liquid bridge is formed between them. Thus an agglomerate nuclei results, from which further growth may or may not occur, depending on the process conditions. To model "wet" agglomeration processes satisfactorily, it is necessary to predict the behaviour of colliding binder coated primary particles. The relative magnitude of their kinetic energy against the retarding force of any liquid bridge formed will determine whether the particles rebound off each other or become attached via the bridge. Currently there remains a gap between the work which has been carried out on the macroscopic mechanisms and modelling of agglomeration processes and the microscopic particle-particle and particle-fluid interactions.

2 Theory

Consider a pendular liquid bridge formed between two particles and providing an adhesive force (Figures 1 and 2). For small (< 1 mm diameter) static particles the force can be considered to be a combination of the surface tension of the liquid (γ) and the hydrostatic suction (capillary pressure), generated by the curvature of the liquid meniscus at the fluid-liquid interface. If these forces are considered to act at the neck of the bridge the following equations can be derived [1]:

\[ F_{\text{pend}} = F_\gamma + F_\phi = 2\pi \gamma r + \pi (r_2)^2 \Delta P. \]  

(1)

For situations where the meniscus conforms to a surface of constant mean curvature, \( \Delta P \) can be calculated from the Laplace-Young equation,

\[ \Delta P = \gamma \left( \frac{1}{r_1} - \frac{1}{r_2} \right). \]  

(2)

Combining Eqs. (1) and (2) gives,

\[ F_{\text{pend}} = \pi \gamma r_1 r_2 (r_2 + r_1). \]  

(3)

The above is known as the "gorge" method for theoretically deriving the force equations. Alternatively the equations may be evaluated at the surface of the particles. This is known as the boundary method [2] and leads to the expression,

\[ F_{\text{pend}} = 2\pi \gamma R \sin \beta \sin(\beta + \theta) + \pi R^2 \Delta P \sin^2 \beta \]  

(4)

where \( \Delta P \) is again calculated from the Laplace-Young equation.
The volume of the bridge is calculated by integrating the equation of the meniscus line $C_1C_2$ around the $x$-axis and subtracting the volumes of the segments of the spheres [3]. This is a relatively trivial task when the bridge adopts the geometry of a toroid (the usual theoretical assumption) but becomes significantly more challenging for non-constant curvature meniscus geometries. In many experimentally observed systems the shape of the meniscus changes with varying separation distance and hysteresis effects also seem to play a part.

### 3 Experimental Procedure

As there is a lack of published data for the forces between particles attached by liquid bridges at varying separation distances, especially particles below 10 $\mu$m in diameter, a microscopic approach has been adopted here. Thus the experimental equipment consists of an optical microscope, which allows either transmitted or reflected illumination to be used, and has a theoretical maximum resolution of 0.45 $\mu$m (Figure 3).

![Schematic representation of equipment layout. The equipment consists of an optical microscope fitted with an adapted stage which allows the measurement of liquid bridge forces.](image)

Initially a straight micropipette is clamped onto the static pipette micromanipulator with the particle being placed under the objective lens of the microscope. Fine adjustment in all three dimensions is achieved using the individual plane micrometers. The second particle, attached to a pre-calibrated flexible micropipette, is then placed under the objective in contact with the first particle. Again, fine adjustment can be made using the micrometers. This micromanipulator also incorporates a 45 $\mu$m expansion piezo-electric crystal, which allows the pipette to be driven remotely. Because piezo-electric crystals exhibit non-linear expansion and hysteresis with respect to applied voltage, a Linear Variable Differential Transducer (LVDT) is fitted to monitor the piezo’s expansion. To form the bridge, binding liquid is fed through a third micropipette onto the particles. To achieve a constant, bubble free, flow of binding liquid, the micropipette is pre-loaded with the liquid before mounting. When a suitable bridge has been formed the particles are separated by applying a signal causing the piezo to expand. The force of the liquid bridge causes the flexible pipette to bend, with the bend being proportional to the force. To calculate the bending moment, the fourth follower micromanipulator monitors the tip of the pipette via a mirror. To control the follower a reflecto-optic (RO) sensor is used to linearly detect the position of the edge of the mirror in its field. The RO sensor (developed for reading bar codes on shop goods) works by transmitting a beam of light and measuring how much is reflected back. The output from the sensor, when focused on the edge of the mirror, is 0 volts; movement onto the mirror causes an increase in the output and movement away a decrease. To keep the sensor focused on the edge of the mirror, control electronics are used to drive a second 30 $\mu$m expansion piezo crystal. The expansion is measured by a LVDT. The difference between the output of the two LVDTs is used to calculate the bending moment and thus the force. The separation of particles and monitoring of the LVDTs is computer controlled via an analogue to digital interface.
4 Modelling

The behaviour of "wet" agglomerating systems has been subject to numerous investigations, for example a large body of work has focused on granulation, in particular granular strength and granular growth mechanisms. However, developing the theories of inter-particle forces between pairs of spheres to multi-body agglomerates is no trivial task. It is desirable to determine which parameters, such as binder viscosity, binder surface tension, contact angle, degree of agitation etc., should be used as predictive criteria for successful agglomeration. Currently, the mechanisms of agglomeration in relation to these parameters are still poorly understood and manipulation of process conditions to optimise agglomeration is still largely empirical and system-specific.

To successfully model "wet" agglomeration processes, it is important to be able to predict the initial agglomeration behaviour, i.e., whether collisions between binder coated particles will give rise to rebound or capture. The relative magnitude of their kinetic energy against the retarding force of any liquid bridge formed will determine whether the particles rebound off each other or become attached via the bridge.

Ennis et al. [4] investigated the forces involved in the collision between two spherical particles, surface-wet with a layer of binder, in an attempt to develop the fundamental understanding of granule growth. Both capillary and viscous dissipation mechanisms were considered. However, it was shown that the latter effectively dominated the surface tension effects provided the binder was well dispersed and sufficiently viscous. By considering the energy dissipation in a dynamic pendular bridge, expressions were developed for the minimum velocity required for the particles to rebound.

A viscous Stokes number for two equal spheres colliding was defined and it was stated for rebound to occur this Stokes number must exceed a critical value. In order to relate their model to granulation processes, Ennis et al. [4] assumed granules to be non-porous, surface-wet, solid spheres with elastic, or near elastic, behaviour on collision. In reality, granules will either plastically deform on impact, fracture or break-up, leading to growth by either coalescence or crushing and layering. In certain conditions, granules will also be surface-dry. Nevertheless, the approach represents a significant step in focusing on the governing parameters in agglomerate formation in the presence of liquid binders.

4.1 The Rupture Energy Model

Simons et al. [5] took a different approach to Ennis in developing a model to provide an approximate value of the rupture energy of pendular liquid bridges, in order to predict whether initial contact between single "wet" particles results in rebound or capture. They stated that the viscous forces do not always dominate and considered the rupture energy of a liquid bridge to be the integral of the quasi-static capillary forces with respect to separation distance, between the limits of zero (particles in contact) and the critical separation distance (rupture). However, to calculate this would be an arduous process since a non-trivial integral is obtained as a constant bridge volume requires that the half-filling angle, \( \beta \), varies with separation distance. Thus a simple expression for the energy required to rupture a pendular liquid bridge was derived. They showed that agglomerate (or granule) strength is a monotonic function of the bridge rupture energy and proposed the following relationship from which rupture energies can be predicted,

\[
W^* = k V_b^{0.5}
\]

where \( W^* \) is the dimensionless rupture energy \( (W^* = W/\gamma R^2) \), \( V_b^* \) is the dimensionless bridge volume \( (V_b^* = V_b/R^3) \) and \( k \) is a constant equal to 1.8.

The model only considers equi-sized spheres wet with a binder giving a zero contact angle in a static situation. It also assumes \( \beta \) is independent of separation distance. Viscous effects are not considered, which means the model is not applicable to higher states of liquid saturation (funicular and capillary states) where the liquid-air interfacial area is reduced and viscous dissipation mechanisms dominate [6]. Nevertheless, such an approach has important implications in the modelling of processes where agglomerates of particles held together by pendular bridges exist. For instance, in a similar argument to that put forward by Ennis et al. [4], the particle kinetic energy can be related to the rupture energy of the liquid bridge formed between two colliding, surface wet particles, to predict rebound or capture. This approach has been shown to correlate well with the defluidisation velocity of surface wet particles in fluidised beds [7]. Currently work is being carried out to both verify and extend the model to include non-zero contact angles, unequal sized particles and consider dynamic surface tensions. The latter may be significant in commercial separation processes which are often dynamic in nature. Here the time effects associated with the addition of surfactants can be crucial in deciding trends which may be very different from those observed at equilibrium. In solid/liquid/liquid systems, for example, the transport of surfactant molecules to the respective surfaces may be hindered if one of the liquids is highly viscous or if there is a limited solubility of the surfactant in either liquid.

5 Results

5.1 Variation of Bridge Volume with Separation Distance

Initial results for a dodecane-silanised ballotini system have shown as separation distance increases the volume of the bridging liquid between the particles decreases. This change in volume is shown in Figure 5. It is assumed that the dodecane perfectly wets the silanised ballotini (i.e. has a contact angle of zero) and from the video footage of the rupture sequence, liquid can be seen to be moving over the particles and out of the bridge in the case of equal sized particles. It is interesting to note for the unequal sized particles liquid only appears to move over the smaller particle.

![Graph showing variation of bridge volume with separation distance](image)

Reconsideration of Eq. (1) allows the variation to be explained. The first term gives the force due to the surface tension and the second the hydrostatic suction pressure, generated by the curvature of the liquid meniscus. As separation distance is increased both \( r_1 \),
and $r_1$ decrease. This has the effect of causing the force generated by the surface tension to be reduced and the reduced hydrostatic pressure to decrease. The overall force generated by the liquid bridge thus decreases. In the case of perfect wetting a liquid layer exists all around the particle and onto the pipettes (which could be regarded as adjacent particles in a multi-particle agglomerate). This liquid acts as a reservoir of bridging liquid. Thus as the forces tending to pull liquid into the bridge decrease the balance between the cohesive and adhesive forces is maintained by the movement of bridging liquid around the particle of greatest curvature. At particle contact and small separations the liquid bridge seems to have the geometry of a toroid; however as the separation distance is increased the bridge takes on a different geometry in order that force equilibrium is maintained and, thus, the validity of the toroidal approach must be questioned. This movement of liquid is not observed for non-zero contact angle situations where the binding liquid does not surround the particles and the bridge ruptures to leave a discrete drop of liquid on each particle. However, as will be seen below, the geometry of such bridges can be very different from the outset to that of a toroid.

5.2 The Bridge Rupture Distance

The critical separation distance at which a liquid bridge ruptures has been subject to numerous theoretical investigations. Lian et al. [8] reviewed these and showed that for a liquid bridge between two particles at close separations there are two solutions of the Laplace-Young equation. As the separation distance is increased the two solutions converge until they become equal; for further increases in separation no solutions exist. By plotting dimensionless volume ($V_b^*$) against the dimensionless rupture distance ($a/a_{max}$) they proposed the following relationship,

$$ (a_1 + a_2)^* = (1 + 0.5\theta)^3 \sqrt{V_b^*} $$

where $\theta$ is the solid-liquid contact angle expressed in radians. This relationship was investigated here for three systems; a dodecane-silanised ballotini system, a pure glycerol-silanised ballotini system and a 50% water, 50% glycerol-unsilanised ballotini system. The solid-liquid contact angle was measured directly as shown in Figure 1. Figure 6 shows sample results for the three systems. For the dodecane-silanised ballotini system there is a degree of uncertainty associated with the measurement of the volume of the liquid bridge at rupture due to the movement of the bridging liquid around the particles and the non-toroidal geometry. However there is good agreement between experimental and predicted results for all cases.

Fig. 6: Comparison of experimentally measured and theoretically predicted rupture distances for three liquid bridge systems.

5.3 The Rupture Energy Model

Results have been obtained for the variation of the measured force with separation distance for both zero contact angle systems and non-zero contact angle systems. The variation of the measured force between two silanised ballotini particles (58.2 $\mu$m and 58.6 $\mu$m radii) wet with a 50% dodecane binding liquid is shown in Figure 7(a). The area beneath the curve represents the measured rupture energy of the liquid bridge. The measured force shows good agreement with that predicted by the gorge method. Comparison of the subsequent measured rupture energy with that predicted from the rupture energy model shows reasonable agreement with the value of the constant, $k$, being 2, compared with the published value [5] of 1.8.

For non-zero contact angle systems the measured force is lower than that predicted by both the gorge and the boundary force equations (Figure 7(b)). This is due to the non-toroidal nature of the liquid bridge. Figure 8(a) shows an image of a glycerol liquid bridge between two silanised glass ballotini particles (25.4 and 31.6 $\mu$m radii).

Fig. 7: (a) Variation of force with separation for two silanised ballotini (58.2 and 58.6 $\mu$m radii) wet with dodecane (zero contact angle), (b) Variation of force with separation for two unsilanised ballotini (28.9 and 22.72 $\mu$m radii) wet with 50% water/50% glycerol mix (34° contact angle).

Figure 8(b) shows liquid bridge geometry modelled using Witches of Agnesi curves, which more closely approximate the geometry of the liquid bridge for the non-zero contact angle systems. This provides a more accurate way of calculating the liquid bridge volume from the two-dimensional measurements obtained via the image analyser. Further work is now being carried out to rederive the force balance equations.
Fig. 8: (a) Image of glycerol liquid bridge between two silanised glass ballotini particles (25.4 and 31.6 µm radii). The figure is an example of the non-toroidal geometry adopted by liquid bridges in finite contact angle systems. (b) Liquid bridge geometry modelled using Witches of Agnesi curves.

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8 Symbols and Abbreviations

- $a$ separation distance between particles
- $a^*$ dimensionless separation distance ($a/R$)
- $F_s$ force due to the surface tension
- $F_{op}$ force due to the reduced hydrostatic pressure
- $F_{pend}$ total pendular force
- $k$ rupture energy model constant
- $R$ radius of particle
- $r_1, r_2$ principle radii of curvature of bridge
- $V_b$ volume of pendular liquid bridge
- $V_b^*$ dimensionless bridge volume ($V_b/R^3$)
- $W$ rupture energy of liquid bridge
- $W^*$ dimensionless rupture energy ($W^* = W/γR^2$)

Greek

- $β$ half-filling angle for liquid bridge
- $γ$ surface tension
- $θ$ contact angle

9 References