CHAPTER 1
INTRODUCTION
CHAPTER 1

INTRODUCTION

1.1) A Review On Rheology

1.1.1) Definition

Rheology is a fundamental interdisciplinary science which is concerned with the study of the internal response of the real materials to stresses. Literally, rheology means the study of deformation and flow of matter as stated by Professor Bingham of Lafayette College, Easton, PA in 1929\cite{1}. A matter is said to be deformed when application of an appropriate force system alters the shape or size of the matter. A matter is said to flow if its degree of deformation changes continually with time. The scope of modern rheology however is much broader. Nowadays, this interdisciplinary field encompasses many different types of materials and applications, both in academia and industry. Rheology includes the phenomenon of irreversible flow as well as other cases of deformation which may or may not lead to a permanent change of the position of elements of the material. It occurs in a very broad intermediate range between the solid and fluid states. Colloidal materials, especially gels and pastes, commonly exhibit both solid-like (elastic) and liquid-like (viscous) behaviour.

The commercial importance of rheological studies is in industrial and municipal waste water treatment processes. Typically, the additives used for flocculation are high molecular weight cationic polyelectrolytes and the particles flocculated may range from clay particles to microorganisms\cite{2}. Recent advances in understanding the mechanism of particle flocculation have come from

Chapter 1
experimental studies of model colloidal systems flocculated by cationic watersoluble polymers or other additives as will be presented later in this thesis. Many other applications of polymeric flocculation can be found in the technological processes of mineral processing, separation of bacterial suspensions, sewage treatment, paper making, brewing, ceramics fabrication, pharmaceutical preparation, agrochemical formulation and food colloid stabilisation.

1.1.2) General Aspects of Rheology

Rheology can be used to characterise not only flow properties of a material, but also structural features. Flow properties, such as thickness and pourability contribute strongly to overall aesthetics and ease of commercial processing. Structural features refer to the strength of interparticle interactions when the material is at rest or not flowing. Insight on structural features helps to predict behaviour or stability of a material; thus rheology can be used to tune material’s mechanical properties rather than simply serve as a characterisation technique\(^3\).

Rheology is an excellent technique for determining the nature and degree of particle interactions while the surface chemistry of a colloidal suspension is being modified. (pH control, ionic strength control and the use of adsorbing chemical additives are the techniques usually employed to obtain the desired particle interactions and rheological properties of a colloidal suspension). Rheological properties such as viscosity and yield stress are good indicators of the
degree of flocculation in concentrated metal oxide suspensions such as zirconium dioxide, ZrO₂ and titanium dioxide, TiO₂.

1.1.3) Some Rheological Properties

A dispersion consist of two distinct phases with a surface or interface between them. Small particulates of droplets of one component are dispersed in a matrix of the other. Solid particulates suspended in a continuous phase comprise a suspension. A dispersion is uniform only on the macroscopic scale (in contrast, a solution of two phases is uniform on a molecular level). Suspensions can be dilute with no particle-particle interaction, sterically stabilised, flocculated when structure is fully formed, partially stable with some structure forming or sedimenting, (e.g., when 2-hydroxyethyl cellulose with molecular weight 15 000 is added as a chemical additive to the ZrO₂ suspensions). If the dimensions of the dispersed particle are 1-100nm[3] (10Å-1000Å), then the dispersion lies within the colloidal region.
1.1.3.1) Fundamental Rheological Variables

Fundamental rheological variables can be defined by reference to a sample confined between two parallel plates (Figure 1)

```
+-----------------+    F
|                  |
|   h             |
|                  |
| fluid velocity gradient |
+-----------------+    h
```

bottom plate stationary

Figure 1 : Parallel-plate depiction of shear rate

When a sample is placed between two parallel plates, one at rest and one moving at velocity \( v \), a velocity gradient or shear rate arises

The plates are separated by a distance, \( h \) that is small compared to the linear dimensions of the plates. When a force, \( F \) is applied parallel to the top plate while the bottom plate is held stationary, the portion of fluid in contact with the top plate moves at velocity, \( v \) while the portion of fluid in contact with the bottom plate does not move. Thus, there is a difference in the fluid’s velocity through its bulk, and the fluid experiences a velocity gradient. This velocity gradient is the shear rate, \( \dot{\gamma} \) (in \( \text{s}^{-1} \))

\[
\dot{\gamma} = \frac{v_{\text{top}} - v_{\text{bottom}}}{h} = \frac{v}{h}
\]  \hspace{1cm} (1)

Shear rate describes how quickly a fluid is made to flow. It is the materials intrinsic response to the applied stress.
The force acting on a sample that can cause flow is the shear stress, denoted by \( \sigma \). It is the force needed to keep the top plate moving at velocity, \( \nu \), divided by the area of the top plate.

\[
\sigma = \frac{\text{force}}{\text{area}} = \frac{F}{A}
\]  

(2)

1.1.3.2) Viscosity

Isaac Newton in “Principa” published in 1687 quoted that ‘the resistance which arises from the lack of slipperiness of the parts of the liquid, other things being equal, is proportional to the velocity with which the parts of the liquid are separated from one another’. The lack of slipperiness is what we now call ‘viscosity’[1]. Qualitatively, viscosity is the property of a material to resist deformation increasingly with increasing rate of deformation.

Quantitatively, a measure of this property is defined as the shear stress, \( \sigma \), divided by rate of shear, \( \dot{\gamma} \) in steady simple shear flow. Viscosity is often denoted as \( \eta \) with the unit Pa.s.

\[
\eta = \frac{\sigma}{\dot{\gamma}}
\]  

(3)
1.1.3.3) Yield stress

For some fluids, the shear rate remains at zero until a threshold shear stress is reached. This is termed as yield stress, $\tau_y$ and has the same unit as the shear stress, i.e. Pa. In other word, yield stress is the stress corresponding to the transition from elastic to plastic deformation. Beyond the yield stress, flow begins\(^1\). From the experimental point of view, yield stress can be regarded as a measure of the strength of the interaction in a colloidal system. The more attractive the interaction among the particles, the more viscous is the colloidal system and hence, higher the yield stress. The yield stress of real materials can be significantly affected by such variables as shear rate, temperature, pressure and time of shearing. These are important and therefore need to be measured. In this project, the effects of pH on the yield stress and viscosity of metal oxide suspensions with several type of additives have been investigated. As will be reported in this thesis the pH and the concentration of additives are variables that have large effects on the rheological properties of metal oxide suspensions.
1.2 Newtonian & non-Newtonian Behaviour

1.2.1) Description of Newtonian & non-Newtonian Behaviour

A model fluid characterised by a constant value for the quotient of the shear stress divided by the rate of shear in a simple shear flow and with zero normal stress differences are called a Newtonian fluid. In other word, Newtonian fluid is a fluid whose rheological behaviour is described by Newton’s Law of Viscosity\(^{[4]}\).

According to Newton’s law of viscosity, the diagram relating shear stress, \(\sigma\) and shear rate, \(\dot{\gamma}\) of a Newtonian fluid is a straight line through the origin and named as flow-curve of Newtonian fluid. The slope of this line is equal to the viscosity, \(\eta\) of the fluid. Thus, the viscosity does not change with the shear rate.

\[
\begin{align*}
\text{Slope} &= \text{viscosity of the fluid} \\
\sigma &\quad \downarrow \\
\dot{\gamma} &\quad \uparrow
\end{align*}
\]

*Figure 2: Flow curve of a Newtonian fluid*
Newtonian behaviour in experiments conducted at constant temperature and pressure has the following characteristics\(^1\):

i) The only stress generated in simple shear flow is the shear stress \(\sigma\), the two normal stress differences being zero.

ii) The viscosity does not vary with the shear rate.

iii) The viscosity is constant with respect to the time of shearing and the stress in the liquid falls to zero immediately the shearing is stopped. In any subsequent shearing, however long the period of resting between measurements, the viscosity is as previously measured.

iv) The viscosity measured in different types of deformation are always in simple proportion to one another, for example, the viscosity measured in uniaxial extensional flow is always three times the value measured in simple shear flow.

A fluid showing any deviation from the above behaviour is non-Newtonian fluid. In other words, all those fluids for which the flow curve \(\sigma = f(\dot{\gamma})\) is not linear through the origin at a given temperature and pressure are said to be non-Newtonian.

Figure 3 show some simple examples of flow curves which exhibit non-Newtonian behaviour\(^4\). The obvious preliminary classification of these curves distinguishes those lines which pass through the origin from those which have an intercept on the shear stress axis. The first category describes fluids without the yield stress and the second describes fluids which exhibit a yield stress.

\(\text{Chapter 1}\)
Figure 3: Flow curves of fluids without yield stress and with yield stress

The viscous properties of fluid without a yield stress are described by curves of type (a) – (c)

- curve (a) is the familiar flow curve of a Newtonian fluid, for which there is a direct proportionality between the shear stress and the shear rate.
- curve (b) characterises fluids for which the shear stress decreases with the increase in the shear rate. Such fluids are called shear-thinning fluids, also described as pseudo-plastic fluids.
- curve (c) characterises fluids for which the shear stress increases with the increase in the shear rate. Such fluids are called the shear-thickening fluids, also described as dilatant.
The viscous properties of fluids with a yield stress which is sometimes referred to as viscoplastic fluids are described by curves $\eta - \gamma$.

For shear-thinning materials, the general shape of the curve representing the variation of viscosity with shear rate is shown in the following Figure$^1$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4}
\caption{Viscosity versus shear rate for a shear-thinning fluid}
\end{figure}

The curve indicates that in the limit of very low shear rates and in the limit of high shear rates, the viscosity is constant at the upper and lower viscosity regions respectively. The higher constant viscosity value is called the 'zero shear viscosity'.

The corresponding graph of shear stress against shear rate is shown below.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5}
\caption{Shear stress versus shear rate for a shear-thinning fluid. In the middle of the graph, the stress changes very slowly with increasing shear rate. The dotted line represents ideal yield stress (or Bingham plastic) behaviour.}
\end{figure}
By definition, Bingham plastics will not flow until a critical yield stress, \( \tau_y \) is exceeded. The viscosity is infinite at zero shear rate and there is no question of ‘zero shear stress’ in this case.

1.2.2) **Description of non-Newtonian fluid behaviour in shear**

Non-Newtonian fluids are usually considered to be those for which the relation connecting shear stress and shear rate is not linear, that is, the viscosity of a non-Newtonian fluid is not constant at a given temperature and pressure but depends on the rate of shear or, more generally on the previous kinematic history of the fluid\(^5\). It is well known that liquids with complex structure such as macromolecular solutions and melts, soap solutions and suspensions behave in unexpected ways and are not described by the equation for Newtonian liquids. Some of the non-Newtonian rheological effects which have been observed are:

1.2.2.1) **Shear-rate-dependent viscosity**

Most of these fluids display ‘shear-thinning’, that is, the viscosity decreases with increasing shear rate.

1.2.2.2) **Normal-stress effects in steady shear flows**

These fluids usually exhibit a number of second-order effects associated with inequality of normal stresses in steady shear flow and related simple flows. This include the Weissenberg effect\(^5\), in which macromolecular fluid climbs up a
rotating rod, the reversal of direction of the secondary-flow pattern when a disc rotates liquid in a beaker, and the slight bulging of the surface of a liquid as it flows down.

1.2.3) **Classification of non-Newtonian fluids**

Non-Newtonian fluids may be classified into three broad types\(^5\):

1.2.3.1) **Time-independent non-Newtonian fluids**

These are the fluids for which the rate of shear at any point is some function of the shear stress at that point and depends on nothing else. Fluids of this type can be described by the following rheological equation

\[
\frac{du}{dy} = \dot{\gamma} = f(\sigma)
\]  

(4)

where the only velocity component \(u\) is in the x-direction and all velocity variation is in the y-direction. This equation implies that the shear rate \((\dot{\gamma})\) at any point in the fluid is a function of the shear stress \((\sigma)\) at that point. These fluids may conveniently be subdivided into three distinct types depending on the nature of the function in the equation above:
Bingham plastics

\[ \sigma \]

\[ \tau_y \]

\[ \gamma / s^{-1} \]

Figure 6: Shear stress (\(\sigma\)) versus shear rate (\(\dot{\gamma}\)) for Bingham body;

\(\tau_y\) is the yield stress, the tangent of the slope, \(\beta\) gives the incremental viscosity and the dashed line show Newtonian behaviour

Bingham plastics are characterised by a flow curve which is a straight line having an intercept, \(\tau_y\) on the shear stress axis. The yield stress, \(\tau_y\) is the magnitude of the stress which must be exceeded before flow starts.
**Pseudo-plastic fluid**

![Graph showing shear stress (σ) versus shear rate (γ) for pseudo-plastic or shear-thinning fluid](image)

*Figure 7: Shear stress (σ) versus shear rate (γ) for pseudo-plastic or shear-thinning fluid*

Pseudo-plastic (or shear-thinning) fluids show no yield stress value and the typical flow curve for these materials indicates that the ratio of shear stress to the rate of shear, which is termed the viscosity, falls progressively with shear rate and the curve becomes linear only at very high rates of shear. This limiting slope is known as the viscosity at infinite shear rate and is designated $\eta_{\infty}$. Returning to the parallel plate example[^1], if the top plate is made to move at an increasing velocity or shear rate, the force required to maintain the velocity ramp decreases. This is because the structure breaks down by shearing forces over the course of the experiment so that at the high shear rate a dispersion of only individual particles remains.

*Chapter 1*
Dilatant fluids

![Graph showing shear stress (\(\sigma\)) versus shear rate (\(\dot{\gamma}\)) for dilatant or shear-thickening fluid.]

Figure 8: Shear stress (\(\sigma\)) versus shear rate (\(\dot{\gamma}\)) for dilatant or shear-thickening fluid

Dilatant fluids are similar to pseudo-plastic in that they show no yield stress but the viscosity for these materials increases with increasing rates of shear. This behaviour was originally discussed in connection with concentrated suspensions of solids by Osborne Reynolds (1885)[6]. He suggested that when these concentrated suspensions are at rest, the 'voidage' (volume) is at a minimum and the liquid is only sufficient to fill the voids. When these materials are sheared at low rates, the liquid lubricates the motion of one particle past another and the stresses are consequently small. At higher rates of shear, the dense packing of the particles is broken up and the material expands or 'dilates' slightly and the voidage (volume) increases. There is now insufficient liquid in the new structure to lubricate the flow of the particles past each other and the applied stresses have

Chapter 1
to be much greater. The formation of this structure causes the viscosity to increase rapidly with increasing rate of shear. An example\(^3\) of dilatency is a sand water suspension at the ocean shore. If a foot is placed gently on wet sand, it sinks but sudden pressure causes the sand to become rigid. The grains of sand, originally close-packed, are disturbed, the water is pushed from the interstices between sand particles, and the sand appears to become dry. The volume occupied by the sand increases. This increase is called dilatency. However, not all concentrated suspensions which are sheared are associated with a volume increase. Such suspensions are called shear-thickening fluids. Therefore dilatency is not synonymous with shear-thickening, but both phenomena increase the viscosity of the suspension with the increase of shear rate. Shear-thickening behaviour is dependent on particle shape, size and volume fraction, nature and strength of association to neighbouring particles, continuous-phase viscosity and experimental parameters characterising this behaviour (parameters include the type, rate and duration of the applied shear deformation)

Generally, non-Newtonian behaviour whether shear-thinning or shear-thickening, follows the power law model\(^7\).

\[ \eta = K\dot{\gamma}^{n-1} \]  \hspace{1cm} (5)

where \(n=1\) for Newtonian fluids; \(n<1\) for shear-thinning fluids; and \(n>1\) for shear-thickening fluids. Therefore a low exponent value implies a very shear-thinning fluid.
1.2.3.2) Time-dependent non-Newtonian fluids

These fluids may be subdivided into two classes, according to whether the shear stress decreases or increases with time when the fluid is sheared at a constant rate as follows[^5]:

*Thixotropic fluids* - breakdown of structure by shear

Thixotropic materials are those whose consistency depends on the duration of shear as well as on the rate of shear. If a thixotropic material is sheared at a constant rate after a period of rest, the structure will be progressively broken down and viscosity will decrease with time. The rate of breakdown of structure during shearing at a given rate will depend on the number of structural linkages available for breaking and must therefore decrease with time. An example[^3] for thixotropic behaviour is demonstrated in Silly Putty (polydimethylsiloxane). Silly Putty is very viscous, but will eventually level out when placed in a container after a sufficient time. Pulled slowly, it extends like chewing gum. However, a ball of it bounces when dropped on the floor. Struck sharply with a hammer, it shatters like glass. Thus, in a slow flow process occurring over a long time, the putty behaves like a liquid because it levels within its container. However, under the severe and sudden deformation of being struck, it breaks like a solid. The example shows that the viscosity decreases as the length of time at a constant shear rate increases. Thixotropy may result from the formation of isolated large flocs or from a single flocculated structure throughout an entire dispersion.
Rheoplectic fluids - formation of structure by shear

In this case, a gradual formation of structure by shear occurs. There is often a critical amount of shear beyond which reformation of structure is not induced and breakdown occurs. This behaviour was observed with dilute aqueous solutions of vanadium pentoxide and bentonite. There are other materials, however in which structure only forms under shear and gradually disintegrates when at rest. This is usually termed 'rheopexy'. Even so, this behaviour is only noted at moderate rates of shear, for if shearing is rapid the structure does not form. A suspension of ammonium oleate behaves in this way when it flows through a capillary tube. At a moderate pressure difference the flow is rapid at first and then decreases as the structure builds up. At a high pressure difference the flow is always rapid and does not fall off because the structure does not build up at high rates of shear.

1.2.3.3) Viscoelastic materials

In the classical linearised theory of elasticity, the stress in a sheared body is proportional to the amount of shear. In a Newtonian fluid the shearing stress is proportional to the rate of shear. In most materials, if a very wide range of stress is applied over a very wide range of time, effects of both elasticity and viscosity are noticeable, and the materials are called viscoelastic materials. Viscoelasticity is a property of systems with at least a fairly well developed internal structure. This structure arises from polymer-polymer, polymer-particle or particle-particle interactions and is present in concentrated polymer, colloidal and micellar systems. Viscoelastic behaviour (as all rheological behaviour) depends on the
time scales of the applied stresses and experimental detection. A theoretical representation of viscoelasticity is the Maxwell model\textsuperscript{[3]}.

\begin{center}
\begin{tikzpicture}
  \node[draw,inner sep=0.5cm] (left) {\textbf{Elastic Element:}};
  \node[draw,inner sep=0.5cm] (right) {\textbf{Viscoelastic Element:}};
  \node[draw,inner sep=0.5cm] (left2) {\textbf{Spring}};
  \node[draw,inner sep=0.5cm] (right2) {\textbf{Maxwell Element}};
  \node[draw,inner sep=0.5cm] (left3) {\textbf{Elasticity: $G$}};
  \node[draw,inner sep=0.5cm] (right3) {\textbf{Characterized by}};
  \node[draw,inner sep=0.5cm] (left4) {\textbf{Viscous Element:}};
  \node[draw,inner sep=0.5cm] (right4) {\textbf{a Modulus $G$}};
  \node[draw,inner sep=0.5cm] (left5) {\textbf{Dashpot}};
  \node[draw,inner sep=0.5cm] (right5) {\textbf{a Relaxation Time $\tau$}};
  \node[draw,inner sep=0.5cm] (left6) {\textbf{Viscosity: $\eta$}};
  \node[draw,inner sep=0.5cm] (right6) {\textbf{$\tau = \eta / G$}};

\end{tikzpicture}
\end{center}

\textit{Figure 9: Maxwell model for viscoelasticity}

The elastic response is represented by a spring with elasticity, $G$, and the viscous response is shown by dashpot, $\eta$. The spring and dashpot combine in series to form a Maxwell element characterised by a relaxation time, $\tau$ where $\tau$ is the ratio of the viscous component to the elastic component ($\eta/G$) and represents a molecule’s rate of motion.

\textit{Chapter 1}
1.3) **A review on colloidal systems**

1.3.1) **Background**

The Greek found that they needed only two fundamental forces to account for all natural phenomena. One was 'Love' and the other was 'Hate'\[8\]. The first brought things together while the second caused them to part (in modern science, the former is addressed as attractive forces and latter as the repulsive forces). The Love and Hate idea that was first proposed by Empedocles around 450 B.C, was much improved by Aristotle, and formed the basis of chemical theory for 2000 years. The ancients appear to have been particularly inspired by certain mysterious forces, or influences, that sometimes appeared between various forms of matter (forces that we would now label as magnetic or electrostatic). They were intrigued by the 'action-at-a-distance' property displayed by these forces, as well as by gravitational forces, and were moved to reflect upon their virtues. What they lacked in concrete experimental facts they more than made up for by the abundant resources of their imagination. Thus, magnetic forces could cure diseases, though they could also cause melancholy and thievery. Magnets could be used to find gold, and they were effective as love portions and for testing the chastity of women. Electric phenomena were endowed with attributes no less spectacular, manifesting themselves as visible sparks in addition to a miscellany of attractive or repulsive influences that appeared when different bodies were rubbed together. All these wondrous practices, and much else were enjoyed by our forebears until well into the seventeenth century.

*Chapter 1*
In the seventeenth century, Newton considered how the forces between molecules could be linked to the physical properties of matter, and later a number of eighteenth century researchers investigated the phenomenon of capillary rise of liquids in glass tubes. In 1808, Clairaut[8] suggested that capillarity could be explained if the attraction between the liquids and glass molecules was different from the attraction of the liquid molecules for themselves. It was also noticed that the height of rise of a liquid column does not depend on the capillary wall thickness, which led to the conclusion that these forces must be of very short range. During the nineteenth century, it was believed that one simple universal force law would eventually be found to account for all intermolecular attractions. Only with the elucidation of the electronic structure of atoms and molecules and the development of the quantum theory in the 1920’s was it possible to understand that the origin of intermolecular forces are essentially electrostatic in origin. Thus, for two charges, the familiar inverse-square Coulomb force exists, while for moving charges, electromagnetic forces exist, and for the complex fluctuating charge distributions occurring in and around atoms, the various interatomic and intermolecular bonding forces are operating. This seems marvellously simple. Unfortunately exact solutions are not easy to come by. For this reason, it has been found useful to classify intermolecular interactions into a number of seemingly different categories even though they all have the same fundamental origin. Thus, such commonly encountered terms as ionic bonds, metallic bonds, Van der Waals forces, hydrophobic interaction, hydrogen bonding and solvation forces are a result

Chapter 1
of this classification, often accompanied by further divisions into strong and weak interactions and short-range and long-range forces.

When a volume fraction grows large, particles increasingly enter the neighbourhood of other particles. The resulting disturbance of the flow increases the viscosity. At relatively small concentrations only binary interactions are likely to occur. With increasing concentration, more than two particles can interact simultaneously. This causes the viscosity to grow at an increasing rate with concentration. Different kinds of forces are active in particle interactions. Depending on their magnitude, the microstructure and the rheology of the suspension can vary widely. A suspension with 1 vol% of dispersed phase can be a fluid with approximately the viscosity of water, or it can respond as a solid, depending on the relative value of the various interaction forces. Some of the factors that vary the interaction forces in the suspension are the concentration of the dispersed phase, type of additive added, pH and the ionic strength of the suspension.

1.3.2) Stability of a colloidal dispersion

This work describes the various colloidal forces and their effects on the yield stress and viscosity of aqueous oxides suspensions. The ability to control these rheological properties is extremely important for the optimal processing of industrial dispersions. Many of the non-solid systems of industrial interests are essentially dispersions of solid particles in fluid media or of liquid droplets in fluid media. The former are called dispersions and the latter emulsions[9]. In the
stationary state, the particles or droplets may come together and form a network structure which exhibits viscoelastic behaviour at low shear stress. With increasing shear the inter-linked structure gradually breaks down until eventually, at sufficiently high shear, these systems flow like viscous liquids. Both low and high shear studies are of interest, the former probably in relation to production quality control, and the latter to practical usage conditions. The magnitude of the yield stress and viscosity is determined by the nature and strength of the colloidal forces. These colloidal forces have a profound effect on the rheological properties of dispersions, particularly yield stress and viscosity.

The surface charge of a dispersed particle may be spontaneously acquired by surface ionization (resulting from dissociation) or by preferential adsorption of cations or anions leaving their counter ions in solution. Examples of the first mechanism are the pH dependence of the charge on mineral oxides (for instance zirconium dioxide and titanium dioxide) in water, which become positively charged at low pH, negatively charged at high pH, and neutral at an intermediate pH.

Three kinds of forces coexist to various degrees in flowing suspension. First, there are those of colloidal origin that arise from interactions between the particles. These are controlled by properties of the fluid such as polarisability, but not by viscosity. These forces can result in an overall repulsion or attraction between the particles. The former can arise, for instance, from like electrostatic charges or from entropic repulsion of polymers. The latter can arise from the ever-present London - Van der Waals attraction between the particles, or from

Chapter I
electrostatic attraction between unlike charges on different parts of the particle. If the net of all of forces is an attraction, the particles flocculate, whilst overall repulsion means that they remain separate (i.e. dispersed or deflocculated).

Secondly, the ever-present Brownian (thermal) randomising force must also be considered. For particles of all shapes, this constant randomisation influences the form of the radial distribution function, whereas for non-spherical particles, spatial orientation is also being randomised. The Brownian force is of course strongly size-dependent, so that below a particle size of 1μm it has a big influence. This force ensures that the particles are in constant movement and any description of the spatial distribution of the particles is a time average.

Thirdly, the viscous forces acting on the particles are taken into account. The viscous forces are proportional to the local velocity difference between the particle and the surrounding fluid.

Clearly, the rheology measured macroscopically is strongly dependent on these microstructural considerations. For instance, the presence of isolated particles means deviation of the fluid flow lines and hence an increased viscosity. At higher concentrations, more resistance arises because particles have to move out of each other’s way. When particles form flocculated structures, even more resistance is encountered because the flocs, by enclosing and thus immobilising some of the continuous phase, have the effect of increasing the apparent phase volume, thus again giving a higher than expected viscosity.

Obviously, the stability of the dispersion and its rheological properties are both very important for the study of colloidal particles. Both of these properties
are controlled by the forces acting between colliding particles and these interactions are sensitive to the presence on the solid surface of adsorbed layers of surfactants or polymers.

A suspension is said to be ‘stable’ when it is dispersed and ‘unstable’ when it is aggregated. The ability of particles to remain stable (dispersed) in a suspension is dependent on the balance of attractive and repulsive forces. The attractive forces consist of Van der Waals, hydrophobic, bridging, depletion and charged patch interactions. The repulsive forces are typically electrostatic, steric and hydration.

For a suspension without any additive, the dominant interaction forces are the attractive Van der Waals and the repulsive electrostatic forces as described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Nevertheless, a combination of more than these two fundamental forces is possible in the presence of an additive. Eventually, the net force will determine the physical conditions of the suspension, i.e. either dispersed or aggregated. Overall repulsion between the particles of a suspension is created if the particles carry electrostatic charges of the same sign. The particles then take up positions as far from one another as possible. For flow to occur, particles have to be forced out of their equilibrium positions and induced to move against the electric fields of neighbouring particles into nearby vacancies in the imperfect lattice. Repulsion can also arise from adsorbed additives onto particle surfaces.

In many products and processes, it is important to obtain significantly stable, uniform dispersions of finely divided solids. Dispersed phase should be extremely finely divided (1-100nm), so that it has a very large specific surface
area. Therefore the properties of the surfaces are much more important than the bulk characteristics of the particles. Consequently the total rheological behaviour of the bulk fluids can be changed simply by the surface modification of the particles. When a preformed, finely divided solid is immersed in a liquid, it often does not form a stable dispersion. Many of the particles remain attached (aggregated) in the form of clumps, and those particles that do disperse in the liquid very often clump together again to form larger aggregates that settle out of the suspension. Therefore the presence of cationic or anionic additives in the system is very important to keep the suspension stable. However, the additives alone cannot keep the system stable. The forces between particles in these suspensions together with the particle size and shape and the volume of the dispersed phase, play the vital roles in determining the properties of the suspensions. Therefore it is important to review these forces between particles before discussing the results obtained.
1.4) A Review on Interparticle Forces

1.4.1) Electrostatic and Van der Waals Forces

*Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory*[^10]

The electrostatic and Van der Waals interparticle forces are described in the well-established theory of the stability of lyophobic dispersions (colloidal dispersions of particles that are not surrounded by solvent layers). This theory was developed independently by Derjaguin and Landau (1941)[^11] and Verwey and Overbeek (1948)[^12], and therefore called the DLVO theory. This theory assumes a balance between repulsive and attractive potential energies of interaction of the dispersed particles. The electrostatic forces arise from the presence of surface charges on a particle. In aqueous media, particles can be electrically charged. As a result, the ions in the water that have opposite charge to that of the particle charge (the counter ions) will be drawn toward the particle. Immediately near the surface, a monolayer composed of such ions develops, forming a narrow double layer with the particle surface (the Stern layer). Outside this layer the concentration of counter ions gradually decreases toward the bulk concentration in the water; these counter ions make up the electrical double layer, as shown schematically in the Figure 10 below

[^12]: [Verwey and Overbeek](https://en.wikipedia.org/wiki/Julius_Verwey)
Figure 10: Distribution of ions around a charged particle (dashed line separates Stern layer from the diffused double layer)

Repulsive interactions are due either to the similarly charged electrical double layers surrounding the particles or to the particle-solvent interactions. Attractive interactions are mainly due to the Van der Waals force between the particles. To disperse the particles, the repulsive interactions must overcome the attractive interactions; to aggregate the particles, the attractive interactions must be dominant. The total potential energy of interaction\(^{[13]}\), \(V\) is the sum of the potential energy of attraction, \(V_A\) and that of repulsion, \(V_R\)

\[ V = V_A + V_R \]  

(6)

The potential energy of attraction in a vacuum for similar spherical particles of radius \(a\) whose centres are separated by a distance \(R\) is given by the expression (Hamaker, 1937)\(^{[10]}\)
\[ V_A = -\frac{Aa}{12H} \]  

(7)

where \( A \) is the Hamaker constant and \( H (=R-2a) \) is the nearest distance between the surfaces of the particles. The attractive potential energy is always negative because its value at infinity is zero and decreases as the particles approach each other.

The potential energy of repulsion \( V_R \) depends on the size and shape of the dispersed particles, the distance between them, their surface potential \( \Phi_0 \), dielectric constant \( \varepsilon_r \), of the dispersing liquid, and the effective thickness of the electrical double layer \( \left( \frac{1}{\kappa} \right)^{10} \), where

\[
\frac{1}{\kappa} = \left( \frac{\varepsilon_r \varepsilon_0 RT}{4\pi F^2 \sum_i c_i z_i^2} \right)^{1/2} \tag{8}
\]

when \( R = \) Boltzmann constant

\( F = \) Faraday constant

For two spherical particles of radius \( a \), when \( a \left( \frac{1}{\kappa} \right)^{10} (= \kappa a) << 1 \), i.e., small particles and relatively thick electrical double-layer,

\[
V_R = \frac{\varepsilon_r a^2 \Phi_0^2}{R} e^{-\kappa a} \tag{9}
\]

when \( \kappa a >> 1 \), i.e., large particles and relatively thin electrical double layer

\[
V_R = \frac{\varepsilon_r a \Phi_0^2}{2} \ln\left(1 + e^{-\kappa a} \right) \tag{10}
\]
\[ V_R = \frac{\varepsilon \alpha \varphi_0^2}{2} \ln(1 + e^{-\alpha H}) \] (10)

The potential energy of repulsion is always positive, since its value at infinity is zero and increases as the particles approach each other.

Figure 11: Total interaction energy curves (obtained by summation of attraction and repulsion curves) for two repulsion curves of different heights [(1) and (2)].
From Figure 11, the particles tend to aggregate at those distances where the attractive energy is greater than the repulsive energy and the total energy, $V$, becomes negative.

When $\kappa a >> 1$, the curve for total energy, $V$ (Figure below) shows a secondary minimum (S) at a relatively large distance of separation between the particles in addition to the primary minimum (P).

![Graph showing potential energy of interaction as a function of distance of particle separation for $\kappa a >> 1$.](image)

**Figure 12**: Potential energy of interaction as a function of distance of particle separation for $\kappa a >> 1$

Particles may therefore aggregate at a relatively large distance between the particles. This type of aggregation is sometimes called flocculation, to distinguish it from aggregation in the primary minimum which is termed coagulation. Since the depth of the secondary minimum is rather shallow, flocculation of this type is easily reversible and the particles can be freed by agitation.

An addition of indifferent electrolyte to the dispersion medium will compress the electrical double layer (i.e. will increase $\kappa$) and the energy barrier for coagulation ($V_{\text{max}}$) will decrease and may even disappear, consistent with the known coagulation of lyophobic colloidal dispersions by electrolyte.

*Chapter 1*
1.4.2) Steric Forces

The types of electrostatic effects mentioned above are at a maximum in polar media. Dispersions of solids in liquids can be stabilised by steric barriers, and in the absence or presence of electrical barriers\textsuperscript{[4]}. Such barriers can be produced when portions (lyophilic chains) of molecules are adsorbed or chemically grafted onto the surfaces of the solid particles, extend into the liquid phase and interact with each other. Being soluble in the continuous phase, they will significantly increase the effective radius of the particle (Figure 13).

![Figure 13: Particles sterically stabilized by polymer coating](image)

The interactions of the extended lyophilic chains with the liquid phase can produce two effects:

1.4.2.1) A mixing effect

The mixing effect is due to the solvent-chain interactions and the high concentration of chains in the region of overlap. This effect becomes significant
when adjacent particles approach each other to slightly less than twice the thickness of the adsorbed layer on the particles (i.e., there is an interpenetration of the adsorbed molecules layers upon approach of particles without compression). When the solvent-chain interaction is stronger than the chain-chain interaction, then the free energy of the system is increased when the regions containing the extended portions of the adsorbed molecules overlap, and an energy barrier to closer approach is produced, resulting in repulsion force. When the chain-chain interaction is greater than the solvent-chain interaction, the free energy is decreased when the regions overlap, and attraction, rather than repulsion occurs.

1.4.2.2) An entropic effect

The entropic effect is due to restriction of the motion of the chains extending into the liquid phase when adjacent particles approach each other closely (i.e., there is a compression of adsorbed molecules when adjacent particles approach each other but there is no interpenetration of adsorbed molecules from the two particles). This would lead to an unfavourable decrease in the configurational entropy of the adsorbed molecule and an increase in the overall free energy of interaction of the particles, thereby, resulting in repulsion. This effect becomes particularly important when the separation between particle surfaces becomes less than the thickness of the adsorbed layer.

Both effects increase with increase in the number of adsorbed chains per unit of surface area on the dispersed particles and with the length of the chains extending into the liquid phase. However, there is an optimum chain length for

Chapter 1
maximum stabilization, since the possibility of flocculation also increases with chain length. In cases where the nature of the liquid phase can be varied, steric stabilization is best when one group of the adsorbed molecule has only limited solubility in the liquid phase, thereby promoting its adsorption onto the solid to be dispersed, while the other (long) group has good compatibility or interaction with the liquid phase, assisting its extension into it.

When a polymer layer is present at the surface of the particles (either adsorbed or chemically grafted), a repulsion force can be created when the layers on two neighbouring particles overlap. This happens whenever the polymer molecules would rather become more compact than mix as the two layers are squeezed together (Figure 14)\textsuperscript{13}.

\textbf{Figure 14:}

\begin{itemize}
\item \textit{Interaction potential for polymerically stabilized suspension}
\item \textit{V}_D: attraction from dispersion force
\item \textit{V}_S: polymeric dispersion
\item \textit{V}_I: total interaction potential
\end{itemize}
If the molecules are dissolved and moving freely in the medium, they can favour flocculation rather than stabilisation.

In suspension rheology, the steric interaction potential, $V_{st}$ is commonly assumed to have the formula\(^{[13]}\)

$$V_{st} = \frac{K}{H^m}$$

(11)

where $K$ and $m$ are constants. The exponent $m$ takes a value ranging from 3 to 20. The value of $m$ depends upon the compressibility of the adsorbed layer. A large $m$ represents hard wall steric repulsion and small $m$ soft shell repulsion. A hard wall steric interaction is associated with an extremely large repulsive energy when the adsorbed layers are in contact. The steric energy drops to zero once contact is lost. A monolayer formed by strongly bound small molecules will make an ideal hard wall steric barrier. Layers formed by adsorbed polymers or other high molecular weight species form relatively soft steric barriers.

1.4.3) Hydration forces\(^{[14]}\)

Many of the interparticle forces, namely hydrophobic, steric and hydration forces, have been investigated using Surface Force Apparatus (SFA) measurements. With SFA the hydration forces have been classified as the short range interparticle force. Pashley\(^{[15]}\) reported a repulsive hydration force for interaction between mica sheets at separation less than 3nm in the presence of a relatively concentrated solution of metal ions such as $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Li}^+$, $\text{K}^+$ and $\text{Na}^+$ ions. This force decays exponentially with a decay length of about 1nm. With
the same surface dissociation model, but allowing $H^+$ to compete with the other cations for negative surface sites on the mica, it was shown that a strong repulsion occurs when the surfaces are predominantly covered by cations other than $H^+$. This shows that the cations that adsorb are hydrated, and it is the cations as they are brought together that gives rise to the repulsion, called a secondary hydration force.

1.4.4) \textbf{Bridging Forces}[^10]

Flocculation by bridging mechanism may occur in two ways:

\textit{Bridging by additive molecules with long functional groups}

A long additive molecule containing functional groups at various points in the molecule that can adsorb onto the sites on the surface of adjacent particles may attach itself to two or more dispersed particles, thereby binding them together in a loose arrangement (Figure 15)

\begin{center}
\includegraphics[width=0.5\textwidth]{Figure15.png}
\end{center}

\textit{Figure 15 : Schematic illustration of bridging flocculation by multi-charged polymer}
For this type of bridging to occur, the adsorption of the additive onto the surface of the adsorbed particles should be low, so as to provide ample sites for attachment of additive molecules extending from other particles (Kitchener, 1972)\(^{[16]}\). Thus, adsorbed additives that act as steric stabilizers when their particle surface coverage is high can act as flocculants when their surface coverage is low and surface sites for adsorption are available on adjacent particles. Bridging mechanism is usually applied in waste water treatment where high molecular weight additives are used as flocculants to remove suspended solids.

*Bridging by interaction of the extended portions of the additive molecules attached to different particles*

When additive molecules are adsorbed onto dispersed particles and the extended portions are capable of interacting with each other, bridging may occur by interaction of the extended portions attached to different particles. This type of bridging occurs when the surface coverage by the adsorbed molecules is so high that the sites for attachment by the previously described bridging mechanism is not applicable. This mechanism is usually applicable when long, polymeric surfactant molecules are used as additive. Also, these mechanism is prone to occur when the liquid phase is not a good solvent for the portion of the adsorbed molecules extending into it and is minimized when there is strong attractive interaction between those portions and the liquid phase. Therefore, it may also occur with the surfactants which contain one terminal hydrophobic group and one terminal hydrophilic group. When these typical surfactants adsorb onto the dispersed...
particle, the hydrophobic group orientates toward the liquid phase and when the
surface coverage becomes so high that the hydrophobic group will be forced to
extend into the aqueous phase. Under these conditions, hydrophobic groups from
two dispersed particles may come together to reduce their surface energies, thereby
bridging them together (Somasundaran, 1966)\textsuperscript{[17]}

In both the cases, the energy released upon bridging must be greater than the
energy required to desolvate the bridging groups.

1.4.5) Charged Patch Interaction

Gregory (1973, 1976)\textsuperscript{[18][19]} followed by Dickinson and Erikson (1991)\textsuperscript{[2]}
proposed the charged patch attraction model to account for the enhanced rate of
flocculation of their colloidal dispersions in the presence of a high molecular
weight polyelectrolyte. Charged patches are formed when a highly charged
polyelectrolyte is adsorbed onto an oppositely charged surface. The adsorbed
molecule charges need to exceed the underlying surface charges in the patch. At
rest, the interacting particles will tend to a state of minimum free or maximum
attractive energy. The particles will therefore align themselves in such a way that a
negative patch of one particle will be next to a positive patch of a second particle.

A quantitative charged patch interaction model was proposed by Miklavec
et. al (1994)\textsuperscript{[20]} as a possible explanation for the long range hydrophobic force, first
measured between two surfactant layers adsorbed on mica sheets in a surface force
apparatus (SFA) by Israelachivili and Pashley (1984)\textsuperscript{[21]}. The parameters that
have a strong influence on the interactions are ionic strength, patch potential, alignments, size and shape. The charged patch attraction predicted is only of the same magnitude as the Van der Waals.

In a recent work by Y.K. Leong [22] the existence of charged patch interaction in ZrO$_2$ dispersions with various concentrations of a strong polyelectrolyte, sodium salt of polystyrene sulphonic acid (NaPSS) was proposed. The negative patches formed by adsorbed NaPSS were believed to be attracted to the positive patches of the bare ZrO$_2$ surfaces at the closest point of interaction as shown in Figure 16.

Figure 16: A schematic diagram of charged patch interaction between two colloidal particles where the shaded-negative patches contain the adsorbed NaPSS and the unshaded-underlying surface are positively charged.

The strength of interaction is expected to depend upon surface coverage, patch size and its potential, ionic strength and patch alignment as suggested by Miklavec’s model except that there is a new inclusion of surface coverage influence[22]. At full surface coverage, the charged patch attraction is expected to diminish to zero as the coated particles are now fully negatively charged (i.e. there is no more bare particle surfaces).

Chapter 1
1.4.6) Hydrophobic force

The hydrophobic force, an attractive force of relatively long range and stronger than the Van der Waals forces, has been measured in SFA between hydrocarbon surfactants adsorbed on two cylindrical mica sheets arranged in a cross-configuration in an aqueous environment\cite{23}. Here, the surfactant is adsorbed with its head group next to the mica and its hydrocarbon tail exposed to form a hydrophobic surface. When two such surfaces are brought together in water, a strong attraction, significantly 10-100 times stronger than the Van der Waals force over most of its range is measured. This force has been called the hydrophobic attraction, because it is presumed to have similar origins to the hydrophobic attraction frequently used in explaining oil agglomeration, surfactant aggregation and many other phenomena.

Leong et. al. (1994)\cite{24} observed that the hydrophobic interaction increases the yield stress of ZrO₂ dispersions significantly in the presence of conventional additives, such as sodium dodecyl sulphate (SDS) and dodecylamine surfactants. The maximum yield stress (τ_{\text{ymax}}) increases rapidly with increasing surfactant concentration.

Hydrophobic force comprises two components: a short-range and a long-range force. The long-range component has a longer range than the Van der Waals forces. The origin of this force is not clearly understood. Nevertheless, a number of possible origins have been variously suggested. Israelachivili (1992)\cite{8} suggested that hydrophobic forces could be entropic in origin whereby the water molecules adjacent to a hydrophobic surface assume a different hydrogen bonding structure.
However, such structural change could not explain the long-range component extending over several hundreds nanometer. Later, in 1994, Miklavic\textsuperscript{[20]} suggested a possible interaction between heterogeneous surfaces, i.e., surfaces with non-uniform charge distribution or charged patches as mentioned earlier. Miklavic's model is sufficient to explain the long-range attraction but not in term of magnitude which should be much larger than Van der Waals. This attraction only becomes significant at very low ionic strengths and high patch surface potentials. Therefore it cannot explain the non-ionic strength dependence of the short-range component. Other proposals for the origin of the hydrophobic force includes the hydrodynamic effect by Ruckenstein. E, et. al (1991)\textsuperscript{[25]}. Thus, hydrophobic forces could probably be due to the combination of the two models by Israelachivili and Miklavic mentioned above. The entropic factor is likely to account for the short-range component and the charged patch attraction is the explanation for the long range component of hydrophobic forces.

1.4.7) \textbf{Depletion forces}\textsuperscript{[26]}

The theory of depletion flocculation between particles in a solution of non-adsorbing polymer was first proposed by Asakura and Oosawa (1954, 1958)\textsuperscript{[27],[28]}. However, the experimental evidence of depletion interaction was shown only in 1978 by Cowell et. al\textsuperscript{[29]} with latex particles sterically stabilised by grafted polymer manifesting a weak reversible flocculation upon the addition of a non-adsorbing polymer.
The phenomena of depletion flocculation occur when there is an osmotic pressure difference between the bulk solution and the pure solvent in between the particle gap when the spacing is less than the radius of gyration of the dissolved polymer. As a result, a 'depletion layer' develops at the interface where the segment concentration is lower than the bulk concentration. Overlap of the depletion layers of two approaching particles lead to expulsion of solvent from the overlap region into the bulk solution. In other words, the solvent molecules in the overlap region tend to reduce their chemical potential resulting in flocculation of the dispersion.

In good solvents, the polymer depleted regions between the particles can only be obtained by demixing polymer chains and solvent, a process that is thermodynamically unfavourable. Energy is needed to bring the particles to an appropriate interparticle gap. This gives rise to a repulsive potential energy between the particles that can be sufficient enough to bring about stability at higher concentrations of polymer than that required to induce flocculation. This occurrence is termed depletion stabilisation. Therefore, depletion stabilisation only occurs at polymer concentrations in excess of that required to cause the onset of depletion flocculation.
1.5) **Measurement Methods**

It is convenient to divide shear rheometers into two groups, i.e., *drag flows* in which shear is generated between a moving and a fixed solid surface, and *pressure-driven flows* in which shear is generated by a pressure difference over a closed channel\[^{13}\].

1.5.1) **Drag flows**

**Sliding plates**

One material is placed in between a large fixed plate and another moving at constant velocity to generate steady simple shear. If inertial and edge effects can be neglected, then the flow is homogeneous and the shear strain, shear rate and shear stress can be calculated from the equations of motion.

![Diagram of sliding plate rheometer](image)

*Figure 17: Schematic illustration of sliding plate rheometer*

However, at very short times or at high frequency oscillation inertial effects cannot be neglected, especially when testing low viscosity samples. It takes a finite time for the velocity profile to develop. A major problem with this geometry is edge effects. It is very difficult to keep the two plates parallel for large strains and also for large normal forces. The samples must be viscous enough not to run out.
Concentric Cylinder Rheometer

The first practical rotational rheometer was the concentric cylinder instrument of Maurice Couette (1890)\textsuperscript{[30]}. Couette utilized a rotating outer cup and an inner cylinder suspended by a torsion wire. The angular deflection of the wire was measured by a mirror and indicated the torque on the inner cylinder. Today, most commercial instruments utilize similar design concepts.

![Diagram of concentric cylinder rheometer](image)

Figure 18: Schematic diagram of higher shear rate concentric cylinder test fixtures. The tapered inner cylinder surfaces and universal joint allow operation at very narrow gaps. The outer gap is aligned to the tapered shaft and can be removed quickly from the rotating shaft and bath.

Working equations relating the shear stress, to torque measurements, the shear rate to angular velocity and normal stress coefficients to radial pressure difference are all installed in the computer memory which is connected to the instrument.

Chapter 1
Cone and Plate Rheometer

The cone and plate geometry for viscosity measurements was introduced by Mooney and Ewart (1934)\[31\].

![Diagram of Cone and Plate Rheometer]

**Figure 19 : Typical shearing geometry of cone and plate**

There are two important assumptions in deriving the cone and plate equations: that the free surface is spherical and the velocity field is maintained up to the edge. The edge effect can be neglected provided that the gap angle, \( \theta_0 \), is small. The shear rate is nearly the same everywhere in the liquid. The shear rate in the liquid is given by

\[
\dot{\gamma} = \frac{\Omega_1}{\theta_0} \quad (12)
\]

where \( \Omega_1 \) is the angular velocity of the rotating plate.

The shear stress (measured via the couple \( C \) on the cone) is given by

\[
\sigma = \frac{3C}{2\pi a^3} \quad (13)
\]

where \( a \) is the radius of the cone.

Since viscosity \( \eta = \frac{\sigma}{\dot{\gamma}} \)
Thus, the viscosity is given by

\[ \eta = \frac{3C \theta_0}{2 \pi a^3 \Omega_1} \]  \hspace{1cm} (14)

If the suspension under investigation has a low viscosity, high rotational speeds are often necessary to produce torque large enough to be measured accurately.

However, a more serious edge effect occurs with high viscosity samples, like polymer melts. At low shear rates, typically \( \gamma < 10 \text{s}^{-1} \), the sample appears to cut in at the mid plane and flow out at each of the solid surfaces, i.e., similar to sliding plates. Before it is even visible at the free surface, edge failure can be detected by a drop in the torque and normal force values. This defect severely limits the useful shear rate range or geometry with high viscosity samples.
Parallel Disks

Mooney (1934)\textsuperscript{[32]} has suggested the parallel disk geometry.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{parallel_disk.png}
\caption{Schematic illustration of a parallel plate rheometer}
\end{figure}

In many ways, the flow is similar to the cone and plate geometry. However, in contrast to the cone and plate, flow between parallel disks is nonhomogenous. With one disk stationary and the other rotating at $\Omega$, assuming no slip at these surfaces and neglecting inertial forces, the shear rate is given by,

$$\dot{\gamma} = \frac{\Omega}{h}$$  \hspace{1cm} (15)

where $h =$ the distance between the plates

\begin{itemize}
  \item \textit{Vane-in-cup}\textsuperscript{[13]} Applied angular motion
\end{itemize}

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{vaneFixture.png}
\caption{Schematic illustration of vane fixture}
\end{figure}

\textit{Chapter 1}
Vane fixture is designed for samples with a yield stress. It can be rotated with a close-fitting cylindrical cup. If the gap between the vane and the outer cup is small enough and in relative rotation, the test liquid enclosed in the gap experience an almost constant shear rate. Controlling the torque and measuring the angular motion at fixed shear rates is the method used to calculate the yield stress.

Specifically, if the radii of the outer cylinder and the vane are \( r_0 \) and \( r_1 \), respectively, and the angular velocity of the vane is \( \Omega_1 \) (the other being stationary) the shear rate is given by

\[
\dot{\gamma} = \frac{r_0 \Omega_1}{r_0 - r_1}
\]

If the couple on the cylinders is \( C \), the shear stress in the liquid is given by

\[
\sigma = \frac{C}{2\pi r_0^2 L}
\]

where \( L \) is the effective immersed length of the liquid being sheared.

Large particles present a less severe problem than they do for a narrow gap Couette device, but, most significantly, for strongly shear thinning fluids, the fluid within the vanes moves as a solid plug. This helps to prevent wall slip. For less shear thinning fluids, there will be secondary flow between the vanes, and the geometry will not give correct viscosity shear data.
1.5.2) Pressure-driven flows

*Capillary Rheometer*\(^1\)\(^3\)

Capillary rheometer was the first rheometer, and remains the most common method for measuring viscosity.

![Image of capillary rheometer diagram]

*Figure 22: Schematic of capillary rheometer*

To generate pressure on the test fluid in a reservoir, gravity, compressed gas or a piston is used. A capillary tube of radius, \(R\) and length, \(L\) is connected to the bottom of the reservoir. Pressure drop and flow rate through this tube are used to determine viscosity.

Using this method, error in shear rate occurs when there is wall slip, especially for concentrated dispersions. For dispersions, because of the inpenetrability of the wall, the layer of particles next to a rheometer wall is typically more dilute than in the bulk dispersion. During flow, the shear rate gradient causes particles to migrate away from the wall. This shear induced migration is greater for small capillaries and higher shear rates. Therefore, the
thin, dilute layer near the wall will have a much lower viscosity and will act as if the bulk fluid were slipping along the wall.

**Slit rheometer**[13]

Capillary rheometer is modified to force liquid through a thin rectangular channel or slit.

![Figure 23: Schematic of slit rheometer with flush-mounted pressure transducers](image)

The major advantage of the slit rheometer is the direct measurement of the pressure gradient. This is possible because pressure transducers can be mounted on the wide flat sides of the slit geometry. Even if pressure holes are used, they are easier to construct and will not disturb the flow as much as in a small diameter capillary. The difficulty to clean is a disadvantage for slit rheometer.
Axial annular flow between parallel plates\textsuperscript{[13]}

Pressure-driven axial flow through a narrow annulus is essentially similar to flow through a slit, but without the side walls. The lack of side walls may be helpful for studying slip phenomena and for reducing residence time distribution.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{annulus.png}
\caption{Schematic of axial annular flow die with wall pressure difference measurement}
\end{figure}

However, the disadvantages of this geometry are the difficulties in construction and cleaning.
1.6) Previous Studies on ZrO$_2$ and TiO$_2$

The rheological properties of ZrO$_2$-suspension (a ceramic material) in aqueous additive solutions have been studied extensively by Y.K.Leong et. al since 1991 till now$^{[22]-[24],[26],[33]-[43]}$. They have mainly studied the effects of various concentrations of additives on the behaviour of the ZrO$_2$-suspension at various pH. The different behaviour of the suspension with different additives have been interpreted using various interparticle forces such as charged patch interaction, hydrophobic forces, depletion forces, steric forces and hydration forces.

In the paper entitled *Surface and Rheological Properties of ZrO$_2$ Suspension* which was published in September, 1991$^{[33]}$ they reported the importance of surface chemistry on the rheological properties of concentrated ZrO$_2$-suspensions. The pH and the nature of anions were found to have very significant effect and the variation was well correlated with the change in surface properties of the ZrO$_2$ with pH and anion type and concentration. It was concluded that the ZrO$_2$ suspension flocculate and show plastic flow behaviour at and near the isoelectric point (IEP) of ZrO$_2$ which was noted as pH 6.7. At pH further away from the IEP, the suspensions are dispersed and exhibit low viscosity Newtonian flow behaviour. Reported also was that at low pH, the ZrO$_2$-suspensions are dispersed by hydrochloric acid but not by sulphuric acid and that is attributed to significant sulphate adsorption by the ZrO$_2$ particles which will affect the surface of the particles.
In 1992 in a conference in Honolulu,[34] it was presented that the wet colloidal processing techniques such as milling, spray drying and slip casting require specific rheological behaviour or type of particle interaction which could be achieved by surface chemistry control. Results which show the effect of pH, ionic strength and of addition of adsorbing anionic polyacrylate and cationic polyallylamine hydrochloride on the rheological properties of ZrO₂ suspensions were presented. The pH of maximum yield stress and the deflocculation pH were found to be lowered significantly by adsorbed polyacrylate but the pH was increased by adsorbed polyallylamine hydrochloride. At high concentration of polyallylamine hydrochloride, it was found that the maximum yield stress at isoelectric point (IEP) was greatly reduced. However, at low concentration of the same additive, a slight increase in the maximum yield stress was observed. The reduction of maximum yield stress was attributed to the steric mechanisms which keep the interacting particles further apart, while the increase in maximum yield stress was attributed to the bridging flocculation and hydrophobic interaction of the adsorbed polymer.

Subsequently, the effects of various adsorbing anionic and cationic additives at various concentrations on ZrO₂ suspensions have been extensively studied and various interparticle forces have been invoked to explain and also to speculate the results obtained. The additives that have been used include the following:
poly (sodium-4-styrene sulphonate) or NaPSS which was found to increase the yield stress of concentrated ZrO₂ suspension at low concentrations but decreases the yield stress as the concentration of the additive increases. The result obtained was explained by charged patch interaction\textsuperscript{[22]}. 

Small hydrophilic additives such as low molecular weight polyacrylic acid were found to give rise to mainly steric interaction, whereas high molecular weight polyacrylic acid caused both steric and bridging interaction\textsuperscript{[24][35][36][37]. Steric interaction improves the consolidation of suspension in compression while the bridging interaction has the opposite effect. 

A mixture of an adsorbed polymer with a free polymer was studied using low molecular weight polyacrylic acid as adsorbing polymer and two free polymers, namely, polyvinyl alcohol and polyethylene oxide, used separately in concentrated ZrO₂ suspension, was studied to investigate the depletion interaction\textsuperscript{[26]. A reasonable agreement between experimental and theoretical depletion energies was reached. 

Adsorbed octanoic acid was found to increase the hydrophobic interaction and consequently enhance the shear-thinning behaviour of the ZrO₂ suspension. However, no such enhancement was observed for adsorbed polyacrylic acid\textsuperscript{[38]}. 

The effect of a series of anionic adsorbates on the rheology of a model ZrO₂ concentrated suspension has been studied to examine quantitatively the effect of short range forces. The anionic additives include sulphate, phosphate, pyrophosphate and polyphosphate as well as organic acid anions such as lactate, malate and citrate. The adsorbates were found to shift the pH of
maximum yield stress to lower pH values and also to lower the magnitude of the maximum yield stress\(^{39}\).

- ammonium polyacrylate was found to shift the pH of the maximum yield stress to a lower pH and reduce its magnitude\(^{40}\).

- various alkyl chain lengths and various concentrations of surfactants were found to vary the yield stress-pH behaviour of ZrO\(_2\) suspension. A higher surfactant concentration leads to a higher yield stress but the maximum yield stress was found to be insensitive to the chain length and the ionic strength of the suspension\(^{41}\).

- both concentration and chain length, n, of the bolaform surfactants, [HOOC(CH\(_2\)_nCOOH], were found to increase the yield stress and the results were explained in terms of particle bridging model\(^{42}\).

In 1995, Leong et. al published a paper which examines the effects of particle concentration and size on the yield stress of ZrO\(_2\) suspensions at a well defined surface chemistry condition of the isoelectric point (IEP)\(^{43}\). It was found that the use of particle concentration based on the fine size fraction instead of volume fraction provided a better correlation, because the fine particles govern the properties of the flocculated network structure.

J. Zajac et.al\(^{44}\) have also studied ZrO\(_2\) suspensions. They studied the interfacial properties of crystalline zirconium dioxide in aqueous solutions of anionic surfactants. They found that the patchwise-like topography of zirconia surface brings about a non-uniform distribution of surface charge and activates tail-tail attraction even at relatively low surface coverages.
Evelyn M. Deliso et al\cite{45} have studied the interaction between Al$_2$O$_3$ and ZrO$_2$ powder in a concentrated suspension. The electrophoretic mobility of Al$_2$O$_3$ and two types of ZrO$_2$ powder were measured and correlated with viscosity measurements. Slip casting was performed at several total powder concentrations and it was found that the slips dispersed well at pH 3 where the electrophoretic mobility of both Al$_2$O$_3$ and ZrO$_2$ were high and therefore a good quality dispersion was produced.

The literature report on the rheological studies of TiO$_2$ suspension, was scanty when compared to ZrO$_2$. Most of the research done were on adsorption studies of various additives on TiO$_2$ powder. For example, in 1989, A.Tentorio\cite{46} had investigated the adsorption of L-glutamic acid, L-(+)-lysine and DL-serine on amorphous TiO$_2$ as a function of pH. It was found that serine did not adsorb in the pH range between 3.5 and 8, whereas the adsorption of the other two amino acids showed a complex dependence on the pH and occurred under conditions of strong electrostatic repulsion at pH\textgreater;8. Hydrogen bonding between deprotonated amino groups and surface hydroxyl groups was suggested as possible explanations for the observed adsorption when electrostatic repulsion prevailed.

Later, in 1991 the adsorption of polyacrylic acid (PAA) of two molecular weights (M$_w$) on TiO$_2$ and ZrO$_2$ were investigated as a function of pH over the range 3 to 10 and in the presence of added electrolyte\cite{47}. It was found that the plateau adsorption decreased with increasing pH and for the PAA with low M$_w$ approached zero above the isoelectric points of the surfaces, which were both near 6.5. Desorption of the polyelectrolytes adsorbed at pH 3.3 by increasing the pH

Chapter 1
indicated that the PAA with low $M_w$ was reversibly desorbed but the PAA with high $M_w$ was only partially desorbed by this procedure.

Subsequently, the adsorption of various additives\textsuperscript{[48][49][50]} on the TiO\textsubscript{2} powder has been investigated and various types of explanations based on the surface charges of the TiO\textsubscript{2} and the nature of the additives themselves have been given to interpret the various types of adsorption plateau obtained.

George A. Smith \textit{et. al.}\textsuperscript{[51]} have characterized the interaction of allyl polyglycoside (APG) surfactants with TiO\textsubscript{2} pigments by a variety of different experimental techniques. Rheological measurements have been used to determine the viscosity of concentrated TiO\textsubscript{2} pigment slurries as a function of surfactant concentration (which is similar to the work done in this project). Adsorption experiments have been used to understand how APG surfactants interact with the surface of the pigment on a molecular level. In addition, zeta potential measurements were performed to determine how APG surfactants affect the electrostatic potential at the TiO\textsubscript{2} particle surface. Taken together, the experimental results indicated that APG surfactants are effective dispersants for TiO\textsubscript{2} particles in aqueous solution. In general, it was found that the effectiveness increases with increasing alkyl chain length. It was concluded that APG surfactant molecules adsorb on the particle surface by hemimicelle formation.