Low-Shear Rheology and Delayed Sedimentation of Colloidal Systems

Steven Paul Meeker

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy to the University of Edinburgh 1998
Abstract

Low-shear viscometry and visual observation are used to study the rheology and sedimentation behaviour of colloid-polymer transient gels. The delay to sedimentation (or latency time) exhibited by the transient gels increases strongly with both polymer concentration and colloid volume fraction. Two distinct types of transient gel behaviour are observed; those displaying a latency time independent of sample height (lower polymer concentration), and those for which latency time markedly decreases with increasing sample height (higher polymer concentration). The transient gel displays power-law fluid behaviour for low shear rates ($Pe \lesssim 1$), the viscosity strongly increasing as the shear stress is reduced. It is suggested that the shear-thinning rheological behaviour of the transient gel is the principle mechanism behind the abruptness of the transient gel collapse. Rheological observations suggest that the strength of the transient gel structure significantly increases then decreases during the latency period, the decrease coinciding with the collapse. Measurements of the low-shear rate viscosity of a model hard-sphere suspension are also presented. Suspension volume fractions are calibrated with respect to the thermodynamic disorder to order, or crystallization, transition. At freezing, the low-shear suspension viscosity is found to be $\approx 53$ times that of the solvent, significantly different to values measured in previous studies.
Declaration

This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me, unless otherwise stated.

November 1998
Acknowledgements

Many thanks go to:

My supervisors Wilson Poon and Peter Pusey, for their enthusiasm and encouragement. I am particularly grateful to Wilson for patiently listening to me during my numerous crises of confidence throughout my doctorate, and placing things back in perspective. His timely advice (science is spikey) enabled me to finish this thesis when I did rather than spending another year on the discussion. I would like to thank Peter, last of the great experimentalists, for his approachable and gentlemanly demeanour. He has a knack of not making me feel stupid even when I say something stupid.

All members of the Squidgy group, both past and present, for being a great bunch of people. Special thanks must go to 'Uncle' Steve Ilett for showing me the ropes four years ago and enduring hundreds of questions from myself in the laboratory. For useful discussions thanks also go to Mark Haw and the two Mikes, Evans and Cates.

Thanks to all the staff here at J.C.M.B — technical, admin., and stores (including free dentistry from Bill) for their support. Special thanks go to Steve Duffield for his work on the Zimm viscometer — a true craftsman.

Thanks to all those who helped me through rough patches in work, music and other stuff — you know who you are.

Finally and most importantly my love to the folks back home, Mum and Mick, Dad, Andy, Danny and Rosie. Long live the Madhouse!
For my family
Contents

1 Introduction

1.1 About this work ....................................... 1
1.2 The colloidal category .................................. 1
1.3 Particle interactions .................................... 4
   1.3.1 London-Van der Waals force and aggregation .......... 4
   1.3.2 Stabilization ..................................... 4
   1.3.3 Depletion force .................................. 5
   1.3.4 Hydrodynamics ................................... 7
1.4 Our Model System ..................................... 7
   1.4.1 The particles and solvent ........................... 7
   1.4.2 Equilibrium phase behaviour ........................ 8
   1.4.3 Volume fraction calibration of samples ................. 9

2 Rheology background .................................. 12

2.1 Introduction ....................................... 12
2.2 Basic rheological concepts ............................ 12
   2.2.1 Deformation, flow and time ........................ 12
   2.2.2 Simple shear .................................. 13
   2.2.3 Viscous laminar flow .............................. 14
   2.2.4 More rheological models ............................ 15
   2.2.5 Time dependency in rheological measurements .......... 16
2.3 Rheology of colloidal systems ........................ 17
2.3.1 Hard-sphere colloidal suspensions ....................................... 17
2.4 Concentric-cylinder viscometry ........................................... 21
  2.4.1 Concentric-cylinder viscometer ...................................... 22
  2.4.2 Laminar flow in a concentric-cylinder viscometer ............... 22

3 The Zimm-Crothers viscometer ............................................. 26
  3.1 Introduction .......................................................... 26
  3.2 The Zimm-Crothers viscometer ....................................... 26
  3.3 Zimm viscometer apparatus .......................................... 28
    3.3.1 Stator-rotor unit .............................................. 28
    3.3.2 The frame ........................................................ 29
    3.3.3 Motor-magnet arrangement .................................... 30
    3.3.4 Angular velocity measurement .................................. 31
  3.4 Calibration and preliminary tests .................................... 33
    3.4.1 Sample loading ................................................... 33
    3.4.2 Water calibration ................................................ 34
    3.4.3 Viscometer alignment .......................................... 36
    3.4.4 Rotor level ....................................................... 37
    3.4.5 Temperature control ............................................ 38
    3.4.6 Reproducibility ................................................. 38
    3.4.7 End effects and surface tension ................................ 40
    3.4.8 Automated rotor angular velocity measurement ............... 42

4 Low-shear viscosity of a hard-sphere suspension ......................... 44
  4.1 Introduction .......................................................... 44
  4.2 Sample preparation .................................................... 45
    4.2.1 Method ............................................................ 45
    4.2.2 Concentration uncertainty ..................................... 45
  4.3 Low-shear limit viscosity measurement ................................ 50
    4.3.1 Method ............................................................ 50
7 Transient gel low-shear rheology

7.1 Introduction ........................................ 100
7.2 Low-shear probing of transient gel ...................... 101
  7.2.1 Yield stress philosophy .......................... 101
  7.2.2 Thoughts about yield stress measurement .......... 101
  7.2.3 Experiment ..................................... 103
  7.2.4 Results ........................................ 105
7.3 Colloid-polymer mixture flow curve — no gelation .......... 108
  7.3.1 Method .......................................... 109
  7.3.2 Results ......................................... 109
7.4 Constant-stress rheology and sedimentation observations . 111
  7.4.1 Samples .......................................... 112
  7.4.2 Method .......................................... 112
  7.4.3 Results .......................................... 112
7.5 Wall Slip ........................................... 117

8 Discussion of transient gel latency and collapse .......... 118
8.1 Introduction ........................................... 118
8.2 Transient gel structural rearrangement in the absence of gravity ..... 118
  8.2.1 Intrinsic rearrangement mechanisms ................. 120
8.3 Structural stability and weight-induced rearrangement in the transient gel . . . 124
  8.3.1 Structural stability ................................ 124
  8.3.2 Hydrodynamics ................................... 126
  8.3.3 Modelling the effect of weight on the transient gel .... 128
8.4 The transient gelation picture: intrinsic and weight-induced rearrangement. 129
8.5 Transient gel sedimentation results ...................... 132
8.6 Transient gel rheology results ........................ 135
8.7 Other systems exhibiting 'delayed sedimentation' .......... 137
8.8 Ideas for future work .................................. 138
9 Conclusion 140

Appendix 142

Bibliography 145

Publications 149
Chapter 1

Introduction

1.1 About this work

This work is experimental. It is a collection of observations and measurements motivated by some simple questions and, by the nature of things, seems to raise more than it answers. Such is life.

The study falls neatly into two parts. The first concerns a clearly defined task that was undertaken — to measure the concentration dependence of the low-shear viscosity of a suspension of hard-sphere colloids, in the face of existing studies with conflicting results. The second part is more investigative and qualitative in nature. It is centred around mixtures of colloid and polymer, and the unusual, aggregating, non-equilibrium behaviour that they exhibit. Much of the work consisted simply of watching the macroscopic settling behaviour of these mixtures, whilst some of it involved noting their response to gentle rheological probing. Before looking at the ideas behind these experiments however, and the results obtained, it is useful to look at some relevant background information on colloidal systems in general and on our system specifically.

1.2 The colloidal category

Though the term colloidal is difficult to define [1], [2], one could describe a colloidal substance as comprising particulate (or ‘bits of’) matter, surrounded by a relatively continuous medium, with a characteristic size that falls within the range 1 nm — 1 µm. A classic example would be pollen grains dispersed in water. Each pollen grain is easily discerned as individual or discrete, whilst the water uniformly surrounds it and its neighbours. Due to their small size the pollen grains remain suspended in the water for a long time. The pollen is described as the dispersed phase whilst the water is the continuous phase.

The size restriction of the particles of the dispersed phase means that they lie above the size range of molecularly-dispersed systems, where quantum mechanical effects are influential, but
are still much smaller than ‘bulk’ matter. The surface-to-volume ratio of a pollen grain is much larger than for an apple, so that surface effects play a greater role in the physics and chemistry of colloids.

Because of their size the dispersed particles, although much bigger than the individual molecules of the continuous phase, still feel their collective influence. Returning to our previous example, we envisage the molecules of water in the continuous phase as being in perpetual motion due to the thermal kinetic energy they possess. The water molecules continually bombard the much larger pollen grains, and because of the statistical nature of their motion at any instant there will be a net imbalance of momentum imparted to the pollen grain. This imbalance, negligible for a beach ball in water, is nevertheless significant for the pollen grain, which moves as a result. Because of the random nature of the direction of the momentum imbalance the pollen grain is jostled and buffeted in all directions, and ends up tracing out a zig-zag pattern, a random walk (see fig.1.1).

This motion was first observed by the botanist Robert Brown (fig.1.2) in 1827 and is known as ‘Brownian motion’.

This random stepwise motion of the particle results in its displacement $\Delta r$ after some time $\Delta t$. Langevin showed, by considering a randomly varying instantaneous force acting on a spherical particle opposed by viscous forces, that the average mean-square displacement is [3]

$$\langle \Delta r^2 \rangle = 6D\Delta t$$

(1.1)\]

where $D$ is the diffusion coefficient, given by

$$D = \frac{k_B T}{6\pi \eta a}.$$  

(1.2)

This equation is known as the Stokes-Einstein relation, where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $\eta$ is the viscosity of the solvent and $a$ is the radius of the particle. Equations 1.1 and 1.2 describe the diffusion of an isolated colloidal particle. In a suspension
of many particles the diffusive motion of each is hampered by the proximity of its neighbours; the particle dynamics become more complex. However diffusive motion can still be described within the framework of equation 1.1, the diffusion coefficient becoming a function of time and length scale.

From equation 1.1 we can see that the time required for a particle to diffuse a distance equal to its own radius is

$$t_R \approx \frac{a^2}{D}. \quad (1.3)$$

Thus an isolated particle, size $\sim 0.1 \mu m$ say, in water would take $\sim 10$ ms to diffuse its own radius. For a concentrated suspension of the same particles however $t_R \gg 10$ ms; e.g. $t_R \approx 1$ s for a concentration of $\sim 50\%$. The time $t_R$ can be thought of as the 'structural relaxation time' of the colloidal suspension — more on this in section 2.2.1.

Brownian motion is central to the definition of a colloid — it keeps the particles suspended in the continuous medium. We can think of colloidal particles jostling around with kinetic energies of $\sim k_BT$. An estimate of the upper limit of the colloidal length scale is provided by the Boltzmann distribution. A colloidal particle of buoyant mass $m = \Delta \rho \frac{4}{3} \pi a^3$ has a probability of being suspended at a height $h$ of $\sim \exp[-mgh/k_BT]$ due to the thermal motion of the fluid molecules. We require $a \lesssim \frac{k_BT}{mg}$ for a particle to be reasonably termed colloidal. For most materials $\Delta \rho \lesssim 1$ g cm$^{-3}$, thus $a \lesssim 1 \mu m$.

So far our only example of a colloidal suspension has been that of pollen in water, a suspension of solid particles in a liquid. This type of suspension is very common, but the dispersed and continuous phases can be any combination of liquid, gas or solid. Thus mist is a dispersion of water droplets in air, emulsion paint consists of oil droplets in water, and foam is a dispersion of gas in a liquid. Colloidal systems can also consist of many components (i.e. mixtures of different particles) and can have particles of any shape that you can imagine.
The physical properties of a colloidal suspension depend not only on the nature of the dispersed and continuous phases individually, but also on their relative concentrations, and on the way the particles interact with one another via the suspension medium. We will now take a closer look at the various ways in which colloidal particles interact.

### 1.3 Particle interactions

#### 1.3.1 London-Van der Waals force and aggregation

The **London-Van der Waals force** (or LVdW force for brevity) is an intermolecular force that has a significant influence on the interaction between colloidal particles [4]. The force originates from the interaction between the fluctuating electron clouds of molecules. The resultant force is attractive, and for two molecules separated by a centre-centre distance \( r \) the attractive potential diminishes as \( U_{LVdW} \sim 1/r^6 \) i.e. short-range.

To calculate the LVdW interaction between two spherical colloidal particles one can use a pairwise additive model, summing the LVdW forces between all possible pairs of molecules. The attractive potential between the particles (when close) now goes as \( -A/r \) (\( A \) is the Hamaker constant — see below) i.e. for particles the LVdW force falls off much more slowly than for single molecules [5].

If the LVdW attraction is the only interparticle force present, it will result in an attractive potential minimum near the particle's surface of many \( k_B T \), with the consequence that particles aggregate.

The Hamaker constant \( A \) is determined by the material properties of the particles and suspension medium, in particular their frequency-dependent polarisabilities. If the particles and liquid have equal polarisabilities (or, equivalently, refractive indices), \( A = 0 \) [4]. Thus one can reduce the LVdW force between particles by matching the refractive indices of the particles and the surrounding medium. However the tendency for particles to aggregate due to these forces normally calls for some kind of repulsive contribution to the particle's potential, to balance the attraction of the LVdW forces. This is achieved by stabilization.

#### 1.3.2 Stabilization

Two approaches are common [6], depending on the type of colloidal system.

Some colloidal particles contain ionisable surface groups. When dispersed in a polar liquid (such as water) these groups dissociate from the particle, leaving the particle charged. The particle can now be thought of as a **macroion**. The small dissociated ions are partially dispersed by Brownian motion, but remain within the influence of the particle's electric field. Effectively we have a macroion surrounded by an ion cloud of opposite charge, an electrical double layer (see fig.1.3(a)). When two macroions approach each other their ion clouds overlap and the particles repel each other, stabilizing the suspension against aggregation. This is known as
CHAPTER 1. INTRODUCTION

charge stabilization.

![Figure 1.3](image.png)

**Figure 1.3.** Two common approaches to suspension stabilization — (a) charge stabilization and (b) steric stabilization.

For particles dispersed in a nonpolar solvent a different approach to stabilization is needed. In steric stabilization polymer chains have one end anchored (grafted) to the surface of the particle (see fig.1.3(b)). The other end consists of lyophilic (solvent loving) group. This means that the free end of the grafted polymer chain prefers to be in contact with the solvent. As two particles approach each other and their grafted polymer chains intertwine a repulsion occurs, enabling solvent to surround the chain end groups. Compression of the rigid grafted polymer layer also contributes to repulsion.

If the stabilizing layer is narrow compared to the radius $a$ of the particle then the particle interaction becomes hard-sphere-like to a good approximation (see fig.1.4).

![Figure 1.4](image.png)

**Figure 1.4.** Hard-sphere pair potential.

1.3.3 Depletion force

So far we have restricted ourselves to looking at ‘colloid only’ systems, yet many important industrial colloidal applications involve adding other components to the dispersion. Here we look at adding small non-adsorbing polymer coils to a hard-sphere colloidal dispersion, a system of important academic interest and one that is used in this study.
It is observed that by adding (relatively) small non-adsorbing polymer to a colloidal suspension one can induce particle aggregation i.e. it seems that attractive forces act between the particles. This is a surprising result. The polymer is assumed to be dissolved in the solvent in the form of small ‘tangled’ coils that are roughly spherical, and it is assumed that their only effect is to exclude the colloidal particles from the volume that the polymer occupies. Why does this lead to aggregation?

The phenomenon can be explained in terms of a **depletion force** model. On an isolated particle the polymer solution exerts an isotropic osmotic pressure $\Pi_p$. However when two colloidal particles come to close proximity (i.e. when their surfaces are less than a polymer coil width apart) there exists a volume $V_{\text{overlap}}$ ‘depleted’ of polymer coils, as the coils are too big to fit between them. (fig.1.5). This leads to a lower osmotic pressure acting on the adjacent surfaces of the particles, resulting in a force that drives the particles together. Alternatively one may think of the depleted volume $V_{\text{overlap}}$ effectively acting as an osmotic membrane permeable only to the solvent. Solvent thus tends to diffuse into the bulk, driven by an osmotic pressure $\Pi_p$, and the particles are drawn together to replace the solvent.

\[ U(r) = \begin{cases} \infty & ; \quad r \leq 2a \\ -\Pi_p V_{\text{overlap}} = U_{\text{dep}} & ; \quad 2a < r \leq 2(a + \delta) \\ 0 & ; \quad r > 2(a + \delta) \end{cases} \quad (1.4) \]

\[ \text{The osmotic pressure } \Pi_p \text{ of the polymer solution is equal to the pressure difference felt by a semi-permeable membrane separating the polymer solution from the pure solvent [7].} \]
where $r$ is the centre-centre separation of the particle pair. The range of $U_{\text{dep}}$ is given by the radius of gyration $\delta$ of the polymer coils, whilst the depth increases with the polymer osmotic pressure, and hence polymer concentration $C_p$ (see section 5.2). Therefore it is experimentally possible to create a colloidal suspension with a 'tailor-made' interparticle potential — fig.1.6.

\[ U(r) \]

\[ \begin{align*}
2a & \quad \delta \\
& \quad \Pi_p V_{\text{overlap}} \\
& \quad r
\end{align*} \]

**Figure 1.6.** Depletion pair potential.

### 1.3.4 Hydrodynamics

As a particle moves it disturbs the solvent surrounding it. This disturbance propagates through the liquid and affects the motions of other particles in the vicinity — i.e. the motions of separate particles are coupled via long-range hydrodynamic forces. The timescale of this interaction is $t_H \sim \rho a^2 / \eta \sim 10^{-7}$ s [10] i.e. effectively instantaneous on the colloidal timescale (set by the structural relaxation time $t_R$ — see equation 1.3). Hydrodynamic interactions have a significant effect on macroscopic properties such as the viscosity of a particle suspension, and excepting all but the most dilute of suspensions (volume fraction $\phi \sim 0.01$) cannot be ignored [11]. However attempts to model the hydrodynamic interactions in particle suspensions are inevitably hampered by the complex many-bodied nature of the problem.

### 1.4 Our Model System

Having considered colloidal systems in general we will now focus our attention on the 'model' system used in this study.

#### 1.4.1 The particles and solvent

Our colloidal suspensions consist of **sterically-stabilized PMMA spheres** (polymethylmethacrylate, or 'perspex') dispersed in the organic (nonpolar) solvent **cis-decalin**. The
stabilizer layer consists of chemically-grafted poly-12-hydroxystearic acid.

The (visible light) refractive indices of PMMA and cis-decalin are close (\(\sim 1.5\) at 20° C) so that London-Van der Waals attractions between the particles are expected to be small.

The stabilizing layer is thin compared to the particle size (\(\approx 10\) nm, typical particle radius \(a = 300\) nm). This combined with the effectiveness of the steric repulsion (cis-decalin is a good solvent for the stabilizing layer) and small LVdW attractions results in the particles behaving effectively as hard spheres. Evidence for hard sphere behaviour of the particles is discussed by Underwood et al.[12]. Their study examined the phase transitions of nearly-monodisperse PMMA suspensions within the size range \(138 < a < 440\) nm and found the freezing-melting concentration difference to be consistent with hard-sphere behaviour (see section 1.4.2). Measurements of the diffusion coefficients and sedimentation velocities of the colloidal fluid at the freezing concentration scale with the power of the particle radius as expected for hard spheres. Relative viscosity measurements were also consistent with those expected for hard-sphere behaviour (see section 2.3.1).

The colloidal suspensions used comprised particles that were virtually identical in size i.e. nearly monodisperse. Most of the experiments in this study were performed on particles of radius \(a = 301\) nm; other systems ranged from \(240 < a < 500\) nm. Their polydispersities (a measure of the width of the size distribution of the particles \(\frac{\text{var}(a)}{\langle a \rangle}\)) were typically 5%.

The densities of bulk PMMA and cis-decalin are 1.188 and 0.894 g cm\(^{-3}\) (at 22° C) respectively — eventually the particles will sink to the bottom of the container.

1.4.2 Equilibrium phase behaviour

We have a model suspension of nearly monodisperse colloidal spheres whose interactions can described by a hard-sphere model. If we mix the suspension well so that the particles are randomly distributed within the dispersion medium, and then leave our sample to stand in a constant temperature environment, what will happen?

One might expect that, macroscopically-speaking, nothing much would change. Initially randomly-distributed hard spheres, wending their way throughout the sample in a random-walk fashion, would seem to stand a good chance of remaining randomly distributed. Amazingly this is not always so.

It turns out that the thermodynamic equilibrium state of the suspension depends on the concentration of particles, or alternatively, the volume fraction \(\phi\) (fractional volume of the total sample occupied by particles)[13], [14]. For \(\phi \lesssim 0.5\) the particles remain randomly dispersed, in a fluid state. However, as we cross \(\phi \approx 0.5\) we observe a disorder-order transition. Groups of particles begin to adopt an ordered configuration, the scale of which is comparable to the wavelength of visible light \(\lambda\) for particles of size \(a \sim \lambda\). As a result small colourful crystallites can be seen sparkling beautifully in such samples due to Bragg reflection. The sample consists of coexisting colloidal fluid and crystal. At first this disorder-order transition seems
counter-intuitive; it becomes clear when one considers the competition between the \textit{configura-tional} entropy $S_{\text{con}}$ and \textit{free volume} entropy $S_{fv}$ \cite{15}. Fig.1.7 illustrates this for two dimensions (i.e. hard discs).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1_7.png}
\caption{Illustrates the difference between configurational entropy $S_{\text{con}}$ and free volume entropy $S_{fv}$ for 2 dimensions (hard discs). In (a) the discs have a high $S_{\text{con}}$ due to their disordered arrangement, but as they are ‘jammed’ their $S_{fv}$ is low. In (b) the converse is true; the crystalline order of the discs gives each disc a greater free volume, hence high $S_{fv}$ and low $S_{\text{con}}$.}
\end{figure}

In fig.1.7(a) the discs are in a disordered configuration, giving a high $S_{\text{con}}$. However this type of configuration leaves no room for movement of the discs as they are jammed, giving a low $S_{fv}$. If we rearrange the discs to give an ordered configuration (i.e. crystalline) as in fig.1.7(b) $S_{\text{con}}$ is decreased. However now the discs have a local freedom of movement — $S_{fv}$ increases. Crystallization occurs at a concentration where the decrease in $S_{\text{con}}$ is more than offset by the increase in $S_{fv}$.

Increasing the concentration of particles further increases the amount of sample that becomes crystalline, the volume of crystal phase increasing linearly with volume fraction until the whole sample is ordered at $\phi \approx 0.55$. Further increase in $\phi$ results in a denser crystal phase, until eventually at a volume fraction of $\phi \approx 0.58$ the particles fail to adopt an ordered configuration and instead assume a frozen amorphous state. This state is metastable (non-equilibrium) and has been identified as \textit{glass-like} \cite{16}.

Computer simulations \cite{17} of hard spheres predict a disorder-order transition at $\phi_f = 0.494$, followed by a region of coexisting fluid and crystal up to a melting point of $\phi_m = 0.545$. If we accept the evidence for hard-sphere behaviour of our particles, we can equate the freezing and melting volume fractions of PMMA suspensions with these values. Fig.1.8 summarizes the phase behaviour of our model system \cite{13}.

\subsection*{1.4.3 Volume fraction calibration of samples}

It follows from the above that if we can measure the proportion of a coexistence sample that is crystalline we can determine its volume fraction $\phi$.

Watching a mixed ‘coexistence’ sample that had been left to stand, one sees small crystallites
nucleate throughout the sample, surrounded by colloidal fluid (deemed to be $\phi = 0.494$), after about a day. Obviously at this point it would be difficult to determine the amount of each phase. However, gravity lends a helping hand, as the particles are denser than the solvent. The crystallites, denser than the surrounding colloidal fluid, sediment faster and a crystal-fluid interface is soon discerned. The fluid, sedimenting at a slower rate, begins to form an interface with the pure solvent. One can plot the height of these two interfaces over time (see fig.1.9).

After a few days, once the crystallites have 'settled out' of the fluid, the height of these interfaces changes linearly with time (the exact form depending on the volume fraction of the coexistence sample, particle size and density differences). It is presumed that the linear change in interface heights are due only to the effects of gravity over time, and that by extrapolating to zero time one can determine the relative amounts of each phase in the absence of gravity, and hence the volume fraction of the sample [18], [12].

Calibrating samples by this method means that volume fractions are accurately reproducible. Coexistence samples can then be diluted (or concentrated) as desired, using literature values for the densities of bulk PMMA and cis-decalin. Further discussion into the validity of this calibration method is left until Chapter 4 section 4.2.2.
Figure 1.9. Height of the colloidal fluid-crystal and colloidal fluid-solvent interfaces over time for a sample of coexisting colloidal fluid and crystal; the particles are denser than the solvent.
Chapter 2

Rheology background

2.1 Introduction

So far we have only considered colloidal systems in thermodynamic equilibrium with their surroundings, unperturbed by any external mechanical disturbance. In many circumstances however it is the deformation and flow of a colloidal system that is of primary interest. The spreading of paint, the flow of blood and the consistency of food are just a few examples. The effort needed to make them flow, and the nature of the flow are clearly important. Our interest in the response of a colloidal system to mechanical disturbance brings us into the realm of rheology, which is the science of deformation and flow.

At the beginning of this chapter we consider some basic rheological concepts and models that help us describe and quantify flow. We also briefly review what is already known about the rheology of colloidal suspensions, and hard-sphere dispersions in particular. Finally we look at concentric-cylinder viscometry, to enable us to interpret our results when using the Zimm-Crothers viscometer to investigate colloidal systems.

2.2 Basic rheological concepts

2.2.1 Deformation, flow and time

In rheology we are interested in how materials deform when acted upon by external mechanical forces [19], [20]. Initially we might simply classify substances by whether they flow or not, according to our basic notion of liquid and solid. For a model elastic solid under the influence of external mechanical forces essentially instantaneous but finite deformation occurs. We envisage that further distortion is prevented by the 'internal resistance' of the solid, and that this resistance only relaxes when the external forces no longer act, the solid reverting back to its original shape. For a simple fluid the 'internal resistance' to a (non-compressive) deformation relaxes essentially instantly, so that deformation is continuous whilst outside forces are applied
— the substance flows. Now it is the rate of deformation that is limited by the viscous internal resistance of the fluid.

However there are many substances — and these include some colloidal systems — whose response to an external force is dependent on how quickly it is applied. For example, pitch behaves like a solid when hit with a mallet, but will flow like a viscous fluid over many years if left on a slope. Such materials are said to exhibit viscoelastic behaviour. This behaviour is a consequence of a finite characteristic relaxation time of the 'internal resistance' to deforming mechanical forces, $t_{\text{relax}}$, lying between the extremes of an ideal elastic solid ($t_{\text{relax}} = \infty$) and a simple viscous fluid ($t_{\text{relax}} \rightarrow 0$). Comparison of the characteristic relaxation time with the timescale of observation $t_{\text{obs}}$ yields the Deborah number [21]

$$De = \frac{t_{\text{relax}}}{t_{\text{obs}}}$$

which indicates how the substance is likely to behave. For high Deborah numbers the material behaves like a solid, for low ones fluid-like behaviour is observed.

For a colloidal suspension Brownian motion is the mechanism by which the internal resistance to deforming mechanical forces relaxes. Therefore we can say that $t_{\text{relax}} \sim t_R$, the colloidal 'structural relaxation' time, where $t_R \sim a^2/D$ is the time taken for a particle to diffuse its own radius (equation 1.1). This time can be anything from $\sim 1$ ms for a dilute suspension of particles, to $\sim$ hours for concentrated suspensions. Hence colloidal systems can display a wide range of rheological behaviour for $t_{\text{obs}}$ spanning everyday timescales.

We must also be aware that the strength of the deforming mechanical forces has a great influence on the material's rheological behaviour. Many of our colloidal suspensions would exhibit solid-like behaviour for weak deforming forces, but would yield and appear fluid-like for stronger ones.

From an everyday perspective the colloidal systems looked at in this study flow readily. They exist either as fluids or as very soft solids that are unable to support their own weight. In order to understand their rheological behaviour we need to somehow quantify deformation (and the effort required to induce and maintain it). Therefore we shall consider a basic geometry of deformation that occurs continuously during flow — simple shear.

### 2.2.2 Simple shear

Deformation of a substance by simple shear is illustrated in fig.2.1.

The substance, in this example a cuboid before deformation, can be thought of as being made up of many thin, horizontal slices of thickness $\delta y$. Each slice is displaced sidewise relative to its neighbour below by an amount $\delta x$, resulting in the distortion of the cuboid into an rhomboid.

The shear distortion is quantified by the shear strain $\gamma$, where
2.2.3 Viscous laminar flow

We will now look at a simple model of fluid flow. Consider a fluid contained between two infinite parallel plates a distance $Y$ apart (fig.2.2).

The size of the plates allows us to neglect end effects. In an effort to induce flow in the fluid we begin moving the top plate by applying a constant tangential force $F$ per unit area $A$ on it, whilst keeping the bottom plate fixed — a shearing action. The top plate accelerates until it reaches a constant velocity $V$, the applied tangential force balanced by the resistance of the fluid. A steady state has been reached.

We assume that the fluid has 'stick boundary conditions' — that is, the fluid layer immediately adjacent to each plate sticks to it, so we know that the fluid near the top plate is travelling at
velocity $V$ whilst that at the bottom plate is at rest. But what is happening in the rest of the fluid?

As in the previous section we can envisage the fluid as being made up of many thin layers parallel to the plane of the plates, continuously sliding over one another in a shear flow. This model, known as laminar flow, is a reasonable approximation of reality for low enough velocity gradients. The velocity gradient depends on the nature of the fluid. The simplest model is that the fluid flows with a constant velocity gradient throughout the bulk. We can see that the fluid is subject to shear deformation at a constant rate and that this is equal to the velocity gradient

$$\dot{\gamma} = \frac{\delta \dot{z}}{\delta y} = \frac{V}{Y} \quad (2.3)$$

Furthermore, it seems reasonable that the rate of shear deformation $\dot{\gamma}$ would increase with the strength of the tangential force $F$ applied, but would decrease in proportion to the plane area $A$ over which the force is distributed. That is the shear stress

$$\sigma = \frac{F}{A} \quad (2.4)$$

is proportional to shear rate, so that

$$\sigma = \eta \dot{\gamma} \quad (2.5)$$

where the constant of proportionality $\eta$ is known as the viscosity, and is a measure of the fluid's internal resistance to flow deformation. This model is known as a Newtonian fluid.

### 2.2.4 More rheological models

Here we look at some common rheological models. These models are represented by means of flow curves — graphs of shear stress versus shear rate — in fig.2.3(a). Fig.2.3(b) shows the dependence of viscosity on shear stress for each model.

The simplest, the Newtonian fluid (i), has already been described in the previous section. The Newtonian fluid model is an excellent one for most low molecular weight liquids over a very wide range of shear rates. Examples are water and most aqueous solutions, organic liquids, silicones and liquid metals.

Complex fluids, such as concentrated polymer solutions and colloidal suspensions, are generally non-Newtonian in flow behaviour. Their viscosities\(^1\) are often a function of shear rate (or shear stress). If the viscosity decreases with shear rate then the fluid is said to undergo shear thinning (ii). Conversely, a fluid whose viscosity increases with shear rate exhibits shear

---

\(^1\)Strictly speaking we should refer to the apparent viscosity of a non-Newtonian fluid. Reiner and Scott Blair define the apparent viscosity as a coefficient calculated from empirical data as if Newton's law held, when the coefficient is not constant. [22]
Figure 2.3. (a) Flow diagrams of some common rheological models; (i) Newtonian, (ii) shear thinning, (iii) shear thickening and (iv) Bingham; (b) shows the variation of viscosity with shear stress for these models.

Thickening (iii). The Power Law fluid model,

\[ \dot{\gamma} = \psi \sigma^N \]  

where \( \psi, N \) are constants, is often used to represent the non-Newtonian flow behaviour of many polymer solutions and melts; for \( N > 1 \) the model represents a shear-thinning fluid.

The Bingham model essentially represents a solid but alternatively can be thought of as a fluid with a yield stress. In this model the material behaves as an elastic solid for stresses less than a yield stress \( \sigma_y \). For stresses greater than the yield stress flow occurs, the shear rate \( \dot{\gamma} \) being proportional to the difference between the applied shear stress \( \sigma \) and the yield stress \( \sigma_y \),

\[ \sigma - \sigma_y = \eta_{pl} \dot{\gamma} \]  

where the plastic viscosity \( \eta_{pl} \) is the constant of proportionality. The flow curve, (iv), is linear with an intercept \( \sigma_y \) on the stress axis. The viscosity becomes infinite as \( \sigma \to \sigma_y \) from above and approaches \( \eta_{pl} \) as \( \sigma \to \infty \).

2.2.5 Time dependency in rheological measurements

When a constant shear stress is applied to a substance over a period of time a change in strain rate may be observed as a result of the structure of the material changing in some way. Examples are the breaking of particle bonds, alignment of irregularly shaped particles or particles colliding to form aggregates. The strain rate usually increases, but may decrease,
CHAPTER 2. RHEOLOGY BACKGROUND

with time. An irreversible change in viscosity is termed rheomalaxis. Sometimes however a material may be restored to its original condition by resting for a sufficient time free from stress. A reversible time-dependent decrease of viscosity is termed thixotropy, and a reversible time-dependent increase in viscosity is called negative thixotropy. When performing rheological measurements on substances exhibiting such time-dependent effects one must view the results in the context of the shear history.

2.3 Rheology of colloidal systems

Having looked at some useful rheological models we now turn our attention to the rheology of colloidal systems. We focus on the steady shear of nearly-monodisperse hard-sphere colloidal suspensions as the best starting point for understanding the rheology of colloidal systems in general.

2.3.1 Hard-sphere colloidal suspensions

General viscosity dependence

Dilute and semi-dilute hard-sphere colloidal suspensions (\( \phi \lesssim 0.2 \)) behave essentially as Newtonian fluids i.e. the viscosity \( \eta \) is independent of \( \dot{\gamma} \). It is found that the viscosity of such colloidal suspensions depends on two factors; the volume fraction \( \phi \) and the viscosity \( \eta_s \) of the solvent.

The effect of the solvent on the overall viscosity \( \eta \) is merely to give a viscosity 'background' i.e. solvent viscosity \( \eta_s \) can be normalized out to give us the relative viscosity \( \eta_r \) of the suspension

\[
\eta_r = \frac{\eta}{\eta_s}
\]  

so that two hard-sphere colloidal suspensions at the same volume fraction but in different dispersion media will have the same relative viscosity. Hence whenever we talk about the rheology of colloidal suspensions we normally talk in terms of the relative viscosity \( \eta_r \).

Not surprisingly the effect of increasing the volume fraction \( \phi \) of the suspension is to increase the relative viscosity \( \eta_r \). However the dependence of \( \eta_r \) on volume fraction \( \phi \) is only understood to order \( \phi^2 \) (see later).

For concentrated dispersions (for \( \phi \gtrsim 0.2 \)) the flow behaviour becomes non-Newtonian, so that now the relative viscosity \( \eta_r \) depends not only on volume fraction \( \phi \) but also on the shear stress \( \sigma \). Explicitly \( \eta_r = \eta_r(\phi, \sigma_r) \) [23]; \( \sigma_r \) is the dimensionless shear stress \( \sigma_r = \sigma a^3/k_BT \) where \( \sigma \) is the actual stress, \( a \) is the particle radius, \( k_B \) is Boltzmann's constant and \( T \) is the absolute temperature. The dimensionless shear stress takes into account the effect of particle size on the rheology of a hard-sphere dispersion (see below).

The general form of the relative viscosity \( \eta_r \) as a function \( \phi \) and \( \sigma_r \) for a hard-sphere dispersion
CHAPTER 2. RHEOLOGY BACKGROUND

Figure 2.4. The relative viscosity $\eta_r$ of a hard-sphere colloidal suspension as a function of dimensionless shear stress $\sigma_r$. At volume fractions $\phi \geq 0.2$ the suspension displays non-Newtonian behaviour; at low shear stresses the viscosity is a constant, shear thinning occurring at higher shear stresses until a 'second Newtonian plateau' of lower viscosity is reached.

is shown in fig.2.4. At suitably low shear stresses the viscosity at any one volume fraction $\phi$ is a constant $-\eta_r^0$, the low-shear relative viscosity. Shear thinning occurs at higher shear stresses, eventually reaching a 'second Newtonian plateau' of lower viscosity, known as the high-shear relative viscosity $\eta_r^\infty$. This rheological behaviour can be qualitatively understood in terms of the relative importance of diffusion and convection in the microstructure of a colloidal suspension under shear. As previously mentioned the time for a particle to diffuse a distance equal to its radius $t_R \sim a^2/D$ (equation 1.3) can be considered the characteristic time taken for the restoration of the equilibrium microstructure of the colloidal suspension after a disturbance i.e. the relaxation time $t_{\text{relax}}$. The characteristic time for shear flow to have substantial effect on the suspension microstructure is $t_{\text{shear}} = 1/\gamma$. Comparing these characteristic times gives us the shear Peclet number

$$Pe_s = \frac{t_{\text{relax}}}{t_{\text{shear}}} = \frac{6\pi \eta_* a^3 \gamma}{k_B T}. \quad (2.9)$$

For $t_{\text{relax}}/t_{\text{shear}} \ll 1$ the Brownian motion of the particles is hardly effected by the shear. At high shear rates ($t_{\text{relax}}/t_{\text{shear}} \gg 1$) the microstructure is radically altered by the flow, giving rise to the shear thinning behaviour and the high shear viscosity 'plateau'. Examination of equation 2.9 reveals that the dimensionless shear stress $\sigma_r = \sigma a^3/k_B T$ is essentially another way of describing the competition between Brownian relaxation and shear deformation (since $\sigma = \eta \gamma$), so we can see why the relative viscosity $\eta_r$ is a function of the dimensionless shear stress $\sigma_r$. 
19 CHAPTER 2. RHEOLOGY BACKGROUND

Figure 2.5. General form of the low-shear limit viscosity $\eta^0_r$ for a suspension of nearly-monodisperse hard spheres as a function of volume fraction $\phi$; $\eta^0_r$ is a rapidly-rising function of volume fraction as the freezing volume fraction $\phi_f = 0.494$ is approached.

Low-shear limit viscosity

In the low-shear limit a nearly-monodisperse hard-sphere suspension acts as though it were a Newtonian fluid, and the suspension viscosity depends only on volume fraction $\phi$. We can think of the low-shear limit as being a small perturbation from the equilibrium state, so it is a good starting point to attempt to understand the rheology of hard-sphere suspensions.

In attempting to build a theory one would hope to have a definitive set of measurements of the low-shear relative viscosity as a function of volume fraction. Fig.2.5 shows the general form of this dependency.

It can be seen that $\eta^0_r$ is a rapidly-rising function of $\phi$, particularly as the freezing volume fraction $\phi_f$ is approached, i.e. $\phi \rightarrow \phi_f = 0.494(\approx 50\%)$. Since the colloidal fluid becomes thermodynamically metastable with respect to the colloidal crystal above the freezing volume fraction $\phi_f$ the viscosity is strictly speaking not defined above this density.

When it comes to precise quantitative determination of $\eta^0_r(\phi)$ we find a large discrepancy between existing sets of experimental measurements for nearly-monodisperse hard-sphere systems. Table 2.1 lists values for $\eta^0_r$ at $\phi \approx 50\%$ obtained by previous studies. Values range from $\approx 20 - \approx 400$. We believe the main reason for this discrepancy lies with determination of the volume fraction of the suspensions. This will be discussed in more detail later. We also note a lack of understanding shown by previous authors concerning the thermodynamics of suspensions of nearly-monodisperse hard spheres. Equilibrium phase transitions and the metastable glass state are ignored by many earlier studies. However if one considers low-shear limit viscosity measurements as a small perturbation from the equilibrium state it is clear they must be viewed in a thermodynamical context.
Study & Low-shear viscosity $\eta^0_\phi (\phi \approx 0.50)$
---
Papir & Kreiger [24] & $\sim 24$
Kruif et al. [25] & $\sim 21$
Choi & Kreiger [26] & $\sim 70$
Mewis et al. [27] & $\sim 100$
Marshall & Zukoski [28] & $\sim 80 - 400$

Table 2.1. Comparison of existing studies of low-shear viscosity at $\phi \approx 0.50$ for various nearly-monodisperse hard-sphere suspensions.

**Theoretical predictions**

Limited progress has been made in predicting the dependency of the low-shear limit relative viscosity for a suspension of hard spheres. The complex interplay of Brownian motion and hydrodynamics set in a many-body scenario makes the task a formidable one.

A theory by Einstein (1906) [29] for spherical particles at low concentrations predicts

$$\eta^0_\phi = 1 + \frac{5}{2}\phi$$  \hspace{1cm} (2.10)

The increase in viscosity in this model arises from summing up the disturbance to the solvent flow field due to the finite size and rigidity of the individual particles. This can be understood by examining the solvent flow-field in the absence of particles, fig.2.6. Consider a spherical volume of solvent. Under shear flow the sphere distorts and becomes an ellipsoid. If we replaced the sphere of solvent with a rigid particle it is clear that this would disturb the solvent flow-field, causing an increase in viscosity.

Figure 2.6. Solvent flow in the absence of particles. A spherical volume of solvent under shear flow distorts and becomes an ellipsoid. If we replaced the sphere of solvent with a rigid particle it is clear that this would disturb the solvent flow-field, causing an increase in viscosity.
To get accurate theoretical predictions of viscosity for more concentrated suspensions one has to consider the effect of particle-particle interactions. For example, consider two particles in the solvent flow field following paths separated by less than a particle diameter (fig.2.7).

**Figure 2.7.** Particle-particle interactions in a flow-field. The particles have to travel an extra distance in order to maintain the same shear rate. This requires an increased expenditure of energy, increasing the viscosity.

Since there is a velocity gradient in the flow field one particle tries to overtake the other. To do so it has to change its trajectory as shown, requiring extra expenditure in energy which is manifested as an increase in viscosity.

Taking into account these pair interactions and Brownian motion leads to a $\phi^2$ term in the above expression (the probability of close approach of two particles). Batchelor [31] calculated the coefficient for the $\phi^2$ term to be 6.2 for stick boundary conditions; Brady recently corrected it to 5.9 [32]. In general, to take into account many-body interactions one might expect the viscosity to be represented by a series expansion in $\phi$

$$\eta_0^r = 1 + \frac{5}{2} \phi + 5.9 \phi^2 + c_3 \phi^3 + \cdots$$ (2.11)

For volume fractions $\geq 0.1$ many-body interactions become increasingly important and terms of order $\phi^3$ and greater become dominant. A rigorous hydrodynamic theory is not available for such concentrations; however a number of empirical equations exist. One of the most common is the Kreiger-Dougherty equation [33],

$$\eta_0^r = (1 - \frac{\phi}{\phi_m})^{-[\eta]\phi_m}$$ (2.12)

where $[\eta]$ is the intrinsic viscosity of the particles, defined as the limit of $(\eta_0^r - 1)$ as $\phi \to 0$ (5/2 for hard spheres), and $\phi_m$ is the volume fraction at which the low-shear viscosity becomes infinite.

### 2.4 Concentric-cylinder viscometry

For the work reported in this thesis the Zimm-Crothers viscometer, a concentric-cylinder instrument, was used to measure the flow curve $(\sigma, \dot{\gamma})$ of colloidal systems in the low-shear regime. However, before we concern ourselves with the intricacies of the Zimm-Crothers viscometer it will be useful to consider concentric-cylinder (or Couette/Searle geometry) viscometers in
2.4.1 Concentric-cylinder viscometer

Imagine a concentric-cylinder arrangement for a viscometer as shown in fig.2.8, with the fluid of interest contained between the two.

![Figure 2.8. A concentric-cylinder viscometer. The sample is contained between the two cylinders. Here the inner cylinder rotates at angular velocity $\Omega$ when a torque $M$ is applied to it.](image)

We can apply a constant torque $M$ to the inner cylinder (rotor), whilst fixing the outer one (stator). The rotor will begin to rotate, disturbing the adjacent fluid. The disturbance will be imparted to the rest of the fluid via viscous forces. The angular velocity of the rotor will increase until the rotor reaches a constant rate of rotation $\Omega$ say, and the fluid flow-field will remain constant — a steady state.

Now, it seems reasonable to believe that the rate of rotation of the rotor would depend not only on the applied torque but also on the fluid viscosity $\eta$. This relationship will also be dependent on the dimensions of the rotational viscometer. In order to determine this relationship explicitly we need to have a closer look at the nature of the flow inside a concentric-cylinder viscometer.

2.4.2 Laminar flow in a concentric-cylinder viscometer

We assume that the rotor angular velocity $\Omega$ is sufficiently small that the flow can be assumed to be laminar. If we make our viscometer long enough we can neglect any end effects. Therefore we can say that the fluid flow-field will be identical for any plane perpendicular to its axis of rotation. Symmetry then shows us that the direction of flow is confined to a perpendicular plane and also requires the flow-lines to be concentric circles (fig.2.9). This means the angular velocity $\dot{\theta}$ of the fluid depends only on the radial distance $r$. 
We model the fluid by considering it to be made up of a series of concentric cylindrical annuli of position \( r \) and width \( \delta r \), each rotating at an angular velocity \( \dot{\theta} \). Since the system is in mechanical equilibrium, the innermost annulus of fluid must be exerting an equal and opposite torque (due to viscous resistance) on the cylinder, otherwise the cylinder would continue to accelerate. We can also apply the same argument to any cylindrical annulus of fluid — its concave surface must experience a positive torque \( +M \) from its inner neighbour fluid annulus inducing it to rotate, whilst its convex surface must receive a retarding torque \( -M \) from its outer neighbour. (i.e. \( \Sigma M = 0 \) for the whole system).

Considering a finite section of the system of length \( l \), this balance of torques can be expressed as

\[
\eta \dot{\gamma} 2\pi rl r = \eta (\dot{\gamma} + \dot{\gamma}) 2\pi l (r + \delta r)^2. \tag{2.13}
\]

This can be rewritten (ignoring second-order infinitesimals) as

\[
2\pi \eta l (r^2 \delta \dot{\gamma} + \dot{\gamma} 2 r \delta r) = 0, \tag{2.14}
\]

whereby our condition for equilibrium can be described mathematically as

\[
\delta (\dot{\gamma} r^2) = 0. \tag{2.15}
\]

Hence

\[
\dot{\gamma} = C/r^2, \tag{2.16}
\]

where \( C \) is a constant.
Now, in order to glean the dependence of angular velocity $\dot{\theta}$ of the fluid on radial distance $r$ we need to know how the rate of shear $\dot{\gamma}$ of the fluid is linked to its angular velocity and radial distance. We can see that in a small time $\delta t$ the shear strain between two annuli a small radial distance $\delta r$ apart would be $\sim r\delta \theta/\delta r$, so that the stain rate is

$$\dot{\gamma} = r \frac{d\dot{\theta}}{dr}$$  \hfill (2.17)

Equating these two expressions for $\dot{\gamma}$ leads to the general solution

$$\dot{\theta} = C_1/r^2 + C_2$$  \hfill (2.18)

where $C_1$ and $C_2$ are constants.

We now make use of boundary conditions, and we assume that fluid in contact with a cylindrical surface sticks to it (i.e. assumes the same angular velocity), so that for our arrangement (rotor radius = $a$, stator radius = $b$)

$$\dot{\theta}(a) = \Omega$$  \hfill (2.19)

and

$$\dot{\theta}(b) = 0$$  \hfill (2.20)

This converts our general solution to

$$\dot{\theta}(r) = \frac{\Omega(1/r^2 - 1/b^2)}{(1/a^2 - 1/b^2)}$$  \hfill (2.21)

We are now able to link our experimental parameters $M$ and $\Omega$ to shear stress and shear rate, and hence to the fluid viscosity.

We have

$$\sigma = \frac{M}{2\pi r^2 l}$$  \hfill (2.22)

and

$$\dot{\gamma} = \frac{2\Omega/r^2}{(1/a^2 - 1/b^2)}$$  \hfill (2.23)

Hence Margules equation linking the experimental parameters to fluid viscosity,
\[ M = \frac{4\pi \eta \Omega}{(1/a^2 - 1/b^2)} \]  

(2.24)

Narrow annulus

So far we have tacitly assumed the fluid within the concentric-cylinder viscometer to be Newtonian (or to be in a shear-stress regime where it is displaying Newtonian behaviour, e.g. the low-shear limit of a colloidal suspension — see section 2.3.1), as the viscosity \( \eta \) was treated as being independent of shear stress/rate. In this case the fact that the applied shear stress \( \sigma \) in a concentric-cylinder viscometer is a function of radius \( r \) (equation 2.22) is of little consequence for viscosity measurement.

When shearing fluids exhibiting non-Newtonian flow behaviour (e.g. colloid-polymer mixtures — see chapter 7) the viscosity is a function of shear stress and the determination of the fluid flow curve from measurements of the applied torque \( M \) and resultant rotor angular velocity \( \Omega \) becomes complicated. If, however, the annular gap of the viscometer is very small compared with the rotor radius, i.e. \( (b - a)/a \ll 1 \), then the shear stress will be approximately

\[ \sigma = \frac{M}{2\pi R_{av}^2} \]  

(2.25)

at all points in the gap where \( R_{av} \) is some average radius — i.e. the flow is quasi-linear. The shear rate will be (from equation 2.17)

\[ \dot{\gamma} = \frac{\Omega R_{av}}{b - a} \]  

(2.26)

hence an approximate flow curve can be determined (see chapter 7 section 7.2.2 for more discussion on this approximation).
Chapter 3

The Zimm-Crothers viscometer

3.1 Introduction

In the previous chapter we introduced the concepts behind concentric cylinder viscometry. In this chapter we look at a specific (and somewhat unusual) type of concentric-cylinder viscometer, the Zimm-Crothers viscometer, which was used in this study to investigate the low-shear regime of colloidal systems.

3.2 The Zimm-Crothers viscometer

Fig. 3.1 shows a schematic diagram of the Zimm-Crothers viscometer [34] (from now on referred to as Zimm viscometer for short). The arrangement essentially consists of a large ‘test tube’ (the stator) which contains the sample of interest, and a smaller, free-floating ‘test tube’, the rotor. The rotor is neutrally buoyant (i.e. only just floating) and surface forces from the fluid cause it to position itself concentrically within the stator (see section 3.4.1 on sample loading). A disc of non-ferrous metal (aluminium in our instrument) is fixed inside the rotor, and by centering a rotating magnetic field (angular velocity \( \omega_m \), controlled via a stepper motor) on the disc (inducing eddy currents) a torque is generated, causing the rotor to rotate at angular velocity \( \Omega \) and subjecting the sample to shear.

Now, in our analysis of laminar flow in a concentric-cylinder geometry (section 2.4.2) we assumed that we could simply apply a torque \( M \) to the rotor of our choosing. For a Zimm viscometer applying a predetermined torque is not so straightforward. This is because the magnetically-generated torque is proportional to the relative motion of the applied magnetic field and the disc [35],

\[
M = c(\omega_m - \Omega) + d, \tag{3.1}
\]

(where \( c \) is a constant and \( d \) represents a small additional torque due to ferromagnetic impurities;
CHAPTER 3. THE ZIMM-CROTHERS VISCOMETER

Figure 3.1. Schematic representation of the Zimm-Crothers viscometer. The neutrally buoyant inner cylinder (rotor) floats concentrically within the outer cylinder (stator). The rotating magnetic field (angular velocity \( \omega_m \)) induces a torque on the aluminium disc fixed inside the rotor, and causes it to rotate (angular velocity \( \Omega \)), subjecting the sample to shear.

in this study \( d \approx 0 \) — see later). But the rate of rotation of the rotor itself is proportional to the torque applied to it! Equating the above expression for torque with that from Margules equation 2.24 we see

\[
\Omega = \frac{C}{\eta} (\omega_m - \Omega), \tag{3.2}
\]

where \( C \) is an apparatus constant. From this equation it is apparent that we can use this apparatus to measure the viscosity \( \eta \) of a fluid if \( C \) is determined with liquids of known viscosity. The constant \( C \), calculated from theory, depends on the experimental variables [35] as

\[
C \propto \frac{H^2 r_{AI}^4 l_{AI} s_{AI} (b^2 - a^2)}{a^2 b^2} \tag{3.3}
\]

where \( a \) and \( b \) are the radii of the rotor and stator respectively, \( H \) is the applied field strength, and \( r_{AI}, l_{AI}, s_{AI} \) are the radius, height, and conductivity of the aluminium cylinder.

We are also interested in the shear rate \( \dot{\gamma} \) and the shear stress \( \sigma \) at which we are measuring the viscosity \( \eta \), particularly when shearing non-Newtonian fluids. In Chapter 2 we saw that for a concentric-cylinder viscometer the shear rate was inversely proportional to the square of the radius, i.e. \( \dot{\gamma} \propto 1/r^2 \). However, from this expression one can calculate the average shear rate to be

\[
\langle \dot{\gamma} \rangle = G \Omega \tag{3.4}
\]

where the geometric factor \( G = 4b^2 a^2/(b^2 - a^2) \ln(b/a) \) depends only on the dimensions of the
CHAPTER 3. THE ZIMM-CROTHERS VISCOMETER

rotor and stator.

Using the above equation for average shear rate, the Zimm experimental equation linking $\Omega$ to $(\omega_m - \Omega)$ and the equation $\sigma = \eta \dot{\gamma}$ we see that the average shear stress is

$$\langle \sigma \rangle = CG(\omega_m - \Omega)$$

(3.5)

Since the rotor is free floating, all the frictional dissipation of energy occurs within the liquid itself. This permits the measurement of viscosities at very low shear rates with accuracy.

3.3 Zimm viscometer apparatus

In fig.3.2 we show a more realistic representation of the Zimm viscometer apparatus, designed and constructed by Steven Duffield and the author for this study. The apparatus can be broadly described as comprising the stator-rotor unit, temperature control, the frame, and the motor-magnet arrangement with its drive circuit, plus rotation measurement systems.

3.3.1 Stator-rotor unit

The stator-rotor unit is the heart of the viscometer (see fig.3.3). Both the stator and rotor are made of glass. The rotor is essentially a thin-walled glass tube that has had its end closed in the manner of a test tube. The open end is ground smooth and square with the walls of the cylinder. Typical outside diameter was $\approx 19$ mm, length $\approx 60$ mm. The stator is a larger glass cylinder closed off at its base. Its inside diameter was $\approx 22$ mm, giving an annular gap between the rotor and stator of $\approx 1.5$ mm. The (neutrally-buoyant) rotor floats in the sample of interest, which itself is contained within the stator. Surface forces acting on the rotor (from the meniscus which extends from the top face of the rotor to several millimetres above it at the stator wall) cause it to float concentrically with the stator (see later).

An aluminium disc fits snugly within the rotor near its base, on which the rotating magnetic field is centred. Perspex discs are used for density matching.

A ‘solvent well’, (a thin-walled perspex tube with a closed square base) can also be inserted into the rotor. This allows solvent (such as cis-decalin) to be added, which serves the dual purpose of refinement to buoyancy matching and saturation of the air with solvent in order to reduce evaporation of colloidal samples.

The top face of the solvent well is used as a ledge for a thin polished aluminium mirror disc (with a hole in the centre to allow solvent addition to the well) which sits near the top end of the rotor. This segmented mirror is used for measuring the rotation rate of the rotor (more on this later).

The stator (more accurately) is a larger ‘double-walled’ test tube with an inlet and an outlet tube into the cavity between (see fig.3.3). Temperature-controlled water flows through the
3.3.2 The frame

The stator-rotor unit sits in the Zimm frame. The Zimm frame is designed not only for stability but also to ensure the consistency of vertical alignment of the concentric-cylinder stator-rotor unit, and the centering of the aluminium disc in the magnetic field.

The frame consists of a steel base plate, in which three vertical steel rods are planted, arranged triangularly in the horizontal plane. This set up is made rigid and stable by fixing the rods at
CHAPTER 3. THE ZIMM-CROTHERS VISCOMETER

3.3.3 Motor-magnet arrangement

The motor-magnet arrangement essentially provides a horizontal magnetic field that rotates around the central vertical axis of the stator-rotor unit and is centred upon an aluminium disc that sits within the rotor. The rotating magnetic field induces eddy currents within the...
aluminium disc. The interaction of these eddy currents and the rotating magnetic field results in a torque on the aluminium disc, which causes the rotor to rotate and thereby shears the sample.

The magnetic field is provided by two ‘rare earth’ magnets which are placed at the ends of a steel ‘yoke’ (like a square horseshoe), opposite polarities facing.

The magnets are strong by every day standards. Two sizes were used — ’small’ — about the size and thickness of a ten-pence piece, and ‘big’ — about the same size as four of the smaller magnets piled on top of one another. Various magnetic ‘configurations’ could be built up by using either one, two or three small magnets, or one big magnet, on each yoke arm. This allowed a variation of the magnetic flux density by a factor of $\approx 3$ and therefore an increase in the range of applied torques by a factor of $\approx 10$ (since the torque $M \propto H^2$). Table 3.1 gives an idea of the magnetic flux density in each configuration as measured by a Hall probe.

<table>
<thead>
<tr>
<th>Magnet configuration</th>
<th>Magnetic flux density $B$ $(T)$ midway</th>
<th>near magnet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>3 small</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>2 small</td>
<td>0.03</td>
<td>0.25</td>
</tr>
<tr>
<td>1 small</td>
<td>0.02</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 3.1. Flux density of various magnetic configurations.

Various motors were used to rotate the yoke and magnets. In the first part of the study (measurement of the low-shear viscosity of various colloidal fluids) a 1.8° stepper motor and 50 : 1 gearbox (giving effectively smooth rotation) were used in combination with a suitable driving circuit board to obtain rates of rotation from 0.3 to 6 rpm. In the second part of the study (rheology of colloid-polymer gels) two D.C. servo motors plus drive circuit were used. The ‘fast’ motor (using a 8 : 1 ratio gearbox) could achieve rotation rates of between 12 and 750 rpm; for the ‘slow’ motor (111 : 1 gearbox) the range was 4 – 100 rpm.

Control of the rotation rate of the motor(s) was ‘manual’ via a variable potentiometer connected to the drive circuits. The motor-yoke arrangement had a quick inertial response to changes in rotation rates, so that rotational acceleration was limited by the rate the potentiometer can be turned.

The motors were either clamped or bolted to the base of the frame. Alignment was achieved by eye and ruler.

### 3.3.4 Angular velocity measurement

In order to make any quantitative measurements with this set up we need to know the angular velocities of the rotor $\Omega$ and the magnetic field $\omega_m$. 

Initially both were measured 'manually' — marks were made on the motor, rotor and non-rotating reference points and rotation times were measured using stopwatches. Apart from requiring much patience this method is only good for rheological measurements on samples where the shear-rate is time independent for a constant applied shear stress (so that $\Omega$ is a constant for each shear stress). Thus measurements were limited to non-thixotropic samples (simple fluids) or samples which are effectively thixotropic within the experimental stress/timescale regime e.g. low-shear limit steady-shear viscosity measurements on hard-sphere colloidal fluids.

Eventually both measurements were semi-automated. The motor rotation rate was measured by placing a small photo-detector under the path of the yoke arms and measuring the frequency of the resultant output pulse train using a digital oscilloscope.

Measuring the angular velocity of the rotor was more involved. A focused laser beam (from a laser diode mounted on the top frame) was shone through the cover-slip 'port hole' down into the viscometer onto a segmented mirror disc (forty segments) which rested near the top of the rotor (see fig.3.4).

![Diagram of rotor angular velocity measurement](image)

**Figure 3.4.** Rotor angular velocity measurement achieved by shining laser light onto a dull-reflecting segmented mirror and detecting and measuring the frequency of the emergent reflected light pulses.

Reflection of the beam depends on whether it falls on a reflecting or dull portion of a segment, and this varies as the rotor rotates. A photo-detector is placed to detect the emergent, refocused, filtered beam, and the frequency of the output pulse train gives us the rotation rate of the rotor. This output pulse train is 'cleaned up' by a comparator circuit, which converts the analogue pulse train into a 'digital' high-low pulse by comparing the strength of the analogue voltage signal with a threshold level — fig.3.5.

The clean pulse train is fed into the I/O port of a counter-timer board within a computer. Software in the computer initializes the timings and stores the mark-space times in memory. Now we can measure $\Omega$ as a function of time $t$ (at least to the resolution of the segments of the mirror disc), enabling thixotropic samples to be studied.
3.4 Calibration and preliminary tests

3.4.1 Sample loading

Cleaning

Both the stator and the rotor were cleaned thoroughly prior to using the Zimm viscometer. This involved scrubbing the glassware using washing-up liquid and water, rinsing with distilled water, then with acetone and allowing to dry in a clean air cabinet. Once the glassware was cleaned hand contact (with the shearing surfaces) was avoided.

Loading and buoyancy matching

Let us consider the rotor floating inside the stator. The equilibrium position of the rotor relative to the stator depends on the shape of the liquid meniscus between the two [36]. If the liquid extends up above the top of one tube as in fig.3.6(a) or (b), then surface forces cause the inner tube to float concentrically with the outer, as desired for a concentric-cylinder viscometer. If however, the meniscus is below the top of both tubes, then the rotor moves to one side of the stator, as in fig.3.6(c), rendering the viscometer useless. In order to obtain the configuration as shown in fig.3.6(a) (that shown in (b) would make it difficult to seal the viscometer) we need the average density of the rotor to be the same as the sample it is floating in — i.e. neutrally buoyant.

Samples were loaded using Pasteur pipettes (acetone rinsed). The rotor starts off as less dense than the sample, and rises as in configuration (c) as the sample is loaded. Once about half
the sample is loaded either water or cis-decalin (dependent on the sample) is placed within the rotor solvent well in small increments in order to make the rotor neutrally buoyant. As this is achieved the sample meniscus rises above the top face of the rotor and surface forces centre it as in configuration (a). The sample is loaded until the rotor reaches a predetermined level within the stator (see rotor height).

The meniscus is then 'primed' i.e. the pipette end is run through the meniscus resulting in complete wetting of the 'top face' of the rotor. Finally the stator is sealed. Loading a sample typically takes about 10 – 15 minutes (the importance of this will become apparent later).

### 3.4.2 Water calibration

According to theory, by shearing a simple fluid sample and plotting the resultant rotor angular velocity $\Omega$ as a function of the magnetic field/rotor differential angular velocity $(\omega_m - \Omega)$, we should obtain a straight line of positive slope $C/\eta$ that goes through the origin. If the viscosity of the fluid is known, then we can calibrate the viscometer (i.e. get a value for $C$) and then measure the viscosity of other fluids.

In order to test if the viscometer worked as predicted, and to calibrate it, I used the viscometer to shear distilled water using the following procedure. First the sample was loaded, as described above, then allowed to equilibrate to the control temperature. In general samples were allowed at least 15 minutes to equilibrate to the control temperature, the sample being sheared at the maximum rate for the motor being used ($\omega_m \sim 0.6 \text{ rad s}^{-1}$). Then measurements could commence.

The magnetic field was rotated at various rates $\omega_m$ by adjusting the motor angular velocity, and the subsequent rate of rotation of the rotor $\Omega$ noted. Early calibration curves were obtained by using stopwatches to time the rates of rotation (over several revolutions). Deviations in repeated period timings were $\sim 1\%$. Generally the order of measurements was from high to
CHAPTER 3. THE ZIMM-CROTHERS VISCOMETER

Figure 3.7. Water calibration curve for the Zimm viscometer. The slope of the line is $C/\eta_{\text{water}}$, where $\eta_{\text{water}}$ is the viscosity of water and $C$ is the experimental constant to be calibrated.

low rotation rates, although the order was not deemed crucial for non-thixotropic samples.

Fig. 3.7 shows the raw data of a distilled water calibration curve, $(\omega_m - \Omega)$ vs. $\Omega$, at $T = 23.0^\circ$ C, for the big magnet configuration, with a least-squares straight-line fit.

We can see that our viscometer is behaving as expected — the data fit a good straight line that (effectively) goes through the origin. The gradient $C/\eta$ for this particular curve is $2.40 \pm 1\%$ (a fairly typical uncertainty in the gradient for any one calibration curve). Using the literature value for the viscosity of water [37] of $\eta_{\text{water}}(T = 23.0^\circ$ C) = $0.9325$ cp (cp = centipoise = $10^{-3}$ Pa s) yields a calibration constant $C = 2.24 \times 10^{-3}$ Pa s. The straight line fit yields a y-axis intercept of $\Omega \approx -3 \times 10^{-3}$ rad s$^{-1}$. The intercept is only $\sim 1\%$ of the typical $\Omega$ data values, and is comparable to the deviation of the least-squares fit ($\approx 2 \times 10^{-3}$ rad s$^{-1}$). Therefore to all intents and purposes the calibration curve goes through the origin, and our assumption that there are negligible contributions to the torque from ferromagnetic impurities is valid (i.e. $d \approx 0$ in equation 3.1). However, reproduction of calibration curves showed a slight bias toward negative y-axis intercepts (see section 3.4.6).

Also shown on the axes are the average shear stress and shear strain rate scales. We can see that with this calibration curve we are easily achieving shear stresses of $\sim 10^{-3}$ Pa, and that stresses as low as $\sim 10^{-4}$ Pa are obtainable.

Having obtained a calibration curve, I was interested to know how sensitive it was to various experimental uncertainties.
3.4.3 Viscometer alignment

Considering that the annular gap between the rotor and the stator is \( \approx 1.5 \text{ mm} \) over a rotor length of \( \approx 60 \text{ mm} \), it would appear that viscometer alignment is very important. With a vertical alignment deviation of \( \pm (3/60) \text{ rad} \) (\( \approx 3^\circ \)) the ends of the rotor would touch the glass walls of the stator.

However, it was difficult to know just how well the stator (inner surface) was aligned within its glass temperature jacket (outer surface), other than by eye, and the hope that the glass blower had done a good job. If one could assume that stator and jacket were well aligned, then vertical alignment (and thus rotor/stator alignment) would be relatively easy to achieve using a well machined supporting frame aligned by spirit levels.

Attempts to notice misalignment involved using a travelling microscope to observe the rotor/stator annular gap. However the depth of the temperature jacket and the shape of the viscometer made focusing very difficult.

In the end I used my eye to make sure that rotor-stator alignment was not terrible. I then decided to carry out some tests to see the effect on the performance of the viscometer of various types and degrees of viscometer misalignment.

Fig. 3.8 shows the classification of alignments investigated — vertical alignment, depth and centering.

![Figure 3.8. Viscometer alignment; (a) vertical (b) depth (c) centering.](image)

For each alignment classification the ‘true’ alignment was judged by eye. Alignment was then slightly changed, by an amount small enough so that it was still deemed to be ‘true’ by eye. Then alignment was changed by a larger amount so that appeared ‘misaligned’ by eye. An attempt was then made to return to the initial ‘true’ alignment. For each positioning a ‘rough’ water calibration curve (few data points) was obtained. However no clear pattern emerged. Presumably this is because (i) the eye judgement of alignment is not good (ii) it was hard to truly isolate the types (i.e. classification) of deviations (iii) dependence of the calibration curve on alignment is complex (combinations of displacing the aluminium disc within the magnetic field coupled with rotor/stator alignment effects). Therefore table 3.2 summarizes the overall variation of alignment and the total variation in gradient of the calibration curve observed over
CHAPTER 3. THE ZIMM-CROTHERS VISCOMETER

### Table 3.2. Variation in calibration constant $C$ with misalignment.

<table>
<thead>
<tr>
<th>Alignment classification</th>
<th>vertical $\theta$</th>
<th>depth $y$</th>
<th>centering $z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>range of misalignment</td>
<td>$\sim 9^\circ$</td>
<td>$\sim 3$ mm</td>
<td>$\sim 1.5$ mm</td>
</tr>
<tr>
<td>range of variation in $C$</td>
<td>$\sim 20%$</td>
<td>$\sim 10%$</td>
<td>$\sim 10%$</td>
</tr>
</tbody>
</table>

the course of the tests, to give a rough guide.

My main fear in the variation in performance of the viscometer with vertical alignment was that the viscometer would only work true for a perfect alignment and that small deviations from this would result in a rapid deterioration in performance. Fortunately this did not seem to be the case, the performance of the viscometer being fairly robust against misalignment. Particularly surprising is that for the (relatively) large maximum vertical misalignment a reasonable calibration curve was obtained, even though parts of the rotor must have come into contact with the stator.

Thinking about vertical misalignment, one may note that the measurement of viscous resistance is spread over entire length of rotor whilst misalignment effects would only be exaggerated at the ends of a rotor. Also meniscus surface forces might still try to centre the top so that rotor 'wobble' would be concentrated at its lower end. I performed a test to see the effects of rotor ‘wobble’, by deliberately altering the rotor centre of mass so that it would float askew. Somewhat surprisingly this resulted in little change to the water calibration curve, which again suggested that the viscometer’s performance is fairly robust.

Eventually I suspected that consistency of good alignment was more crucial than absolute alignment.

#### 3.4.4 Rotor level

The relative height $h_{rot}$ of the rotor within the stator was changed to see if it significantly altered the performance of the viscometer. The gap between the rotor base and the stator base was changed from 6 mm to 0.5 mm, and a ‘rough’ water calibration curve was obtained at each relative rotor height. The magnets were adjusted each time to ensure the magnetic field remained centered on the Al disc.

For $6\text{ mm} < h_{rot} < 1\text{ mm}$ the calibration curve gradients varied by only $\sim 3\%$ i.e. rotor height is unimportant within this range. At a rotor height of $h_{rot} = 0.5$ mm however the calibration curve gradient was significantly reduced by $\sim 10\%$.

I decided to select a rotor height of $h_{rot} = 5$ mm as the norm for experimentation.
3.4.5 Temperature control

Concerning temperature control one has to consider what one actually needs — absolute temperature control or just consistency of temperature. When attempting to use the viscometer to measure absolute viscosities, absolute temperature control is important for viscometer calibration, as different liquids have different dependencies of their viscosity on temperature. However, for the measurement of the low-shear relative viscosity of colloidal suspensions, only consistency of temperature is important, if one uses the suspension solvent to calibrate the viscometer.

Early calibrations and low-shear relative viscosity measurements of hard-sphere colloidal fluids used temperature control of $T = 23.0^\circ \text{C}$ whilst later shearing of gels used $T = 20.0^\circ \text{C}$.

Bearing in mind that the temperature of the viscometer was controlled using an external flow mechanism (i.e. flow tubes connected to the stator arms) I was interested in knowing (i) variation in the temperature of the recirculating bath (ii) the temperature difference between the bath and the sample (water) in the stator.

Laboratory temperature variation would be important for (ii). It was found that over the period from the beginning of December to half-way through March the average laboratory temperature was $24^\circ \text{C}$ with a deviation of $\pm 1^\circ \text{C}$.

The recirculating bath temperature varied by $\pm 0.1^\circ \text{C}$, whereas the bath-stator temperature difference was $\Delta T \approx 0.1^\circ \text{C}$ at most. Temperature control was therefore good to $\pm 0.2^\circ \text{C}$.

Temperatures were measured using a normal mercury thermometer and a platinum resistance thermometer.

3.4.6 Reproducibility

Obviously it was important to gain some insight into how reproducible the Zimm viscometry measurements were. Therefore over the course of several months (whilst performing low-shear viscosity measurements on colloidal fluids) I took a series of cis-decalin and water calibration curves to see how much they would vary. A least-squares fit was applied to the data — the results are summarized in tables 3.3—3.5. The gradients of successive cis-decalin calibration curves showed a standard deviation of $\approx 2 \%$ (table 3.3). By looking at the y-axis ($\Omega$) intercepts and the deviation we can say that all the curves pass through the origin within error, with perhaps some bias towards negative intercepts.

Looking at table 3.4 we see that repeated water calibration curves varied by $\approx 3 \%$. Using the average gradient for each set of calibration curves, and the literature value for the viscosity of water ($\eta_{\text{water}} = 0.9325$ cp at $T = 23.0^\circ \text{C}$) yields the viscosity of cis-decalin at this temperature to be $\eta_{\text{cis}} = 3.06$ cp. This compares with the literature interpolated experimental value of 3.18 cp [38] — agreement to within $4 \%$, which is quite good. However, looking at the y-axis intercepts we see a definite bias towards negative values, which means positive x-axis intercept or shear stress intercept values (table 3.5). I became concerned about this apparent ‘extra’ stress needed to shear the water samples, so I decided to investigate further.
### Table 3.3. A series of cis-decalin calibration curves.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>gradient (= C/\eta )</th>
<th>% gradient uncertainty</th>
<th>y-axis ( \times 10^{-3} ) intercept</th>
<th>int. ( \times 10^{-3} ) uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.731</td>
<td>0.7</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.726</td>
<td>0.4</td>
<td>-1</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>0.726</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0.722</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0.703</td>
<td>2</td>
<td>-2</td>
<td>2</td>
</tr>
</tbody>
</table>

### Table 3.4. A series of water calibration curves.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>gradient (= C/\eta )</th>
<th>% gradient uncertainty</th>
<th>y-axis ( \times 10^{-3} ) intercept</th>
<th>int. ( \times 10^{-3} ) uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.40</td>
<td>1</td>
<td>-3</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>2.44</td>
<td>2</td>
<td>-11</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>2.38</td>
<td>3</td>
<td>-10</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>2.24</td>
<td>3</td>
<td>-3</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 3.5. Stress-axis intercepts for the water calibration curves.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>x-axis ( \times 10^{-3} ) intercept</th>
<th>shear stress int. ( \times 10^{-5} ) N m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>
3.4.7 End effects and surface tension

In order to see if the stress intercept was real rather than a consequence of error in curve fitting I decided to use the small magnet configuration to perform a water calibration curve at lower shearing stresses. If the stress intercept stayed the same magnitude then it would be much more obvious on the calibration curve. Fig. 3.9 shows this calibration curve.

A stress-axis intercept is clear. In order to see if this was due to the meniscus I decided to perform another water calibration but this time using a smaller rotor (a ≈ 8 mm) to exaggerate any possible meniscus effects. I then added a small predetermined amount of surfactant (washing-up liquid) to the meniscus in order to lower its surface tension, and then performed the water calibration again. The two calibration curves are shown in fig. 3.10.

The first curve again clearly shows a stress-axis intercept. However the second curve goes through the origin (within error). This seems to suggest that the meniscus is the cause of the stress-axis intercept. Certainly the meniscus has an important effect on the performance of the viscometer — it was found that 'priming' the meniscus could increase the rotor rotation rate by as much as 10%. Finally I decided to look at the distribution of stress-axis intercepts for all calibration and colloidal fluid low-shear viscosity flow curves (fig. 3.11).

Again on average there seemed to be a definite, if small, stress-axis intercept of ≈ 7 × 10^{-5} Pa. This would have implications for later rheological measurements on colloid-polymer transient gels (see chapter 7) where I was attempting to measure their yield stresses $\sigma_y$; any 'yield stress' measurement of $\sigma_y \sim 10^{-4}$ Pa could be due to end effects/meniscus rather than the sample proper.
Figure 3.10. The effect of reducing the meniscus surface tension on the water calibration curve for a sample with a large meniscus (small rotor); (*) is the normal calibration curve, whereas for (+) the meniscus surface tension has been reduced (surfactant added). The stress-axis intercept disappears, indicating its presence is due to meniscus surface tension.

Figure 3.11. Distribution of stress-axis intercepts for all calibration and colloidal fluid low-shear viscosity flow curves. On average there is a small stress-axis intercept of \( \approx 7 \times 10^{-5} \) Pa.
3.4.8 Automated rotor angular velocity measurement

Fig. 3.12 shows the measurement of the rotor angular velocity $\Omega_{\text{auto}}$ over time as determined by the automated system for two different constant rotor rotation rates, $\Omega \approx 0.5 \text{ revs s}^{-1}$ and $\approx 1.1 \text{ revs s}^{-1}$. Although on average the automated measurements $\Omega_{\text{auto}}$ are constant, they are also noisy. The sinusoidal variation is due to imperfect alignment of the segmented mirror within the rotor.

![Figure 3.12](image)

**Figure 3.12.** Measurement of the rotor angular velocity $\Omega_{\text{auto}}$ over time as determined by the automated system for two different constant rotor rotation rates, $\Omega \approx 0.5 \text{ revs s}^{-1}$ and $\approx 1.1 \text{ revs s}^{-1}$.

The automated rotor angular measurement was tested by performing a water calibration and comparing the 'automated' calibration curve with the 'manual' one (i.e. $\Omega$ measured using a stopwatch). Fig. 3.13 compares the two calibration curves; their gradients agree to within $\approx 2\%$. However, the 'automatic' data points (o) are averages of at least a whole revolution of the rotor. The error bars show the deviation in $\Omega_{\text{auto}}$ over forty segments (i.e. one revolution), due to the sinusoidal variation, which on average is around 13%. If the automated measurement of $\Omega$ is determined from just a few segments (i.e. small rotor rotation), as may be the case for very viscous samples, this is the kind of error we must assign to the rotor angular velocity measurement.
Figure 3.13. Comparison of 'automated' and 'manual' water calibration curves. For (o) \( \Omega \) is determined by the automated rotor angular velocity measurement system; for (\( \times \)) \( \Omega \) is measured manually with a stopwatch.
Chapter 4

Low-shear viscosity of a hard-sphere suspension

4.1 Introduction

In Chapter 2 we highlighted the importance of understanding the rheology of colloidal systems. We focused our attention on the rheology of a hard-sphere suspension in the low-shear limit, as the first step to an understanding of the flow of colloidal systems in general. However it was soon apparent that present knowledge is poor, with a dearth of good (non-empirical) theories for anything other than the most dilute suspensions, and a lack of consensus between existing data sets [24]-[28] (table 2.1). This disagreement between existing experimental studies of the low-shear relative viscosity of (nearly) monodisperse hard-sphere suspensions is perhaps most worrying, as there is no standard with which to compare any new theories. It was decided therefore to measure carefully the concentration dependence of the low-shear viscosity of sterically-stabilized nearly-monodisperse PMMA spheres dispersed in cis-decalin — a well-characterized model hard-sphere suspension — and to compare the results with previous studies.

The first step was to ascertain why existing data sets disagree; i.e. what are the difficulties associated with such measurements, and what can be done to overcome them? We think the most important factor is the precision to which the volume fraction of the suspension can be determined. As previously noted the low-shear viscosity rapidly increases as the volume fraction approaches 0.50 — an uncertainty of only $\approx 0.025$ in concentration could lead to an error in low-shear viscosity of a factor of $\approx 2$ or more. However, our system has the advantage of a readily reproducible volume fraction ‘marker’ — $\phi_f$, the freezing volume fraction of a collection of hard spheres (see chapter 1). We calibrate our suspensions by referring them to this disorder-order, or freezing, phase transition.

Another important factor when attempting to obtain such data is the measurement of the low-shear viscosity itself. Many viscometers are not capable of imposing small enough shear stresses to reach the low-shear regime of concentrated suspensions. Here we use the Zimm-Crothers viscometer which, as shown in the previous chapter, is suited for measurements requiring small
4.2 Sample preparation

4.2.1 Method

The first step was to prepare batches of colloidal stock solution with concentrations within the coexistence region. This was achieved by filling teflon centrifuge containers (volume $\approx 30 \text{ cm}^3$) with uncalibrated colloidal stock solution ($\phi \sim 0.3$), centrifuging down the particles into a close-packed 'hard' sediment and removing the excess solvent. This sediment was assumed to be at $\phi \approx 0.66$ (for polydispersities of $\approx 5\%$ — see [39]). Then an amount of solvent calculated (using literature values for the density of cis-decalin $\rho_{\text{cis}} = 0.894 \text{ g cm}^{-3}$ and bulk PMMA $\rho_{\text{pmma}} = 1.188 \text{ g cm}^{-3}$) to bring the samples into the coexistence region was added. The samples were then mixed and tumbled in order to redisperse the particles.

The batches were calibrated, as described in chapter 1 and below, by taking small samples in glass cuvettes (sample volume $\approx 2 \text{ cm}^3$) and monitoring the amount of crystal phase over a period of a week (two to three weeks for the suspensions of the largest particles, which were harder to calibrate due to slower crystallization and greater sedimentation rates). Once the batch was calibrated amounts were removed and diluted to the desired volume fractions (cis-decalin added by weight), again calculated using literature values for the densities of PMMA and cis-decalin.

In order to have a semi-independent method of sample preparation a number of samples were also prepared by carefully removing the colloidal fluid (deemed to be at $\phi = 0.494$) from batches with coexisting fluid and crystal and then diluting to the required concentrations.

The principal system studied consisted of particles of radius 301 nm, with a polydispersity of approximately 0.05. Measurements were also performed on suspensions with 240 nm and 500 nm particle radii, with polydispersities of 0.04 and 0.07 respectively. The particle sizes were determined by dynamic and static light scattering.

4.2.2 Concentration uncertainty

Sample calibration

We will now take a closer look at the calibration method to gain an insight into its accuracy.

In chapter 1 we noted that the model hard-sphere colloidal suspension exhibits colloidal fluid-crystal coexistence phase behaviour between volume fractions of $\approx 0.50$ and $\approx 0.55$ (designated as $\phi_f = 0.494$ and $\phi_m = 0.545$ in the light of hard-sphere simulations). Furthermore, the relative amounts of crystal and fluid phase vary linearly with volume fraction in this region, so that if we can measure the amount of crystal phase in a coexistence sample we can determine its volume fraction $\phi$. 
Figure 4.1. A coexistence sample after several days standing. Two interfaces can be clearly defined; a colloidal crystal-fluid interface at height $h_c$ and a colloidal fluid-solvent interface at height $h_f$. $h_{mb}$ is the height of the sample meniscus base. $h_T$ is the effective total sample height.

Fig.4.1 depicts a coexistence sample that has been left to stand for a period of time (~ days). As previously described in chapter 1 colloidal crystallites form and 'sediment out' of the colloidal fluid, resulting in a colloidal crystal-fluid interface at height $h_c$. The fluid also sediments out of the solvent, creating a colloidal fluid-solvent interface at height $h_f$. It is known that in the absence of gravity crystallization occurs rapidly i.e. the sample reaches thermodynamic equilibrium within a day. Gravity helps us to ascertain the amount of crystal phase by settling out the crystallites from the fluid, but also confuses as both the fluid and crystal phases sediment as time goes by.

Figs.4.2 and 4.3 show the height of these interfaces monitored over time (many days), which were measured using a vernier caliper arrangement and magnifying glass. Initially crystallites are formed and are spread throughout the 'bulk' of the colloidal fluid, so time is required (3 to 10 days depending on concentration and size of the particles) for them to settle and form homogeneous regions. Once these homogeneous regions are formed one of two changes can occur to the position of the crystal-fluid interface — an increase or a decrease in height. A decrease in height can only be due to the compression of the colloidal crystal by gravity. An increase must be caused by the sedimentation of the fluid phase 'against' the crystal face, creating new crystallites. Whether the interface increases or decreases in height will depend on the sedimentation rate of each phase, and this will vary according to the particle size and the volume fraction of the sample. If the sedimentation rates of the homogeneous phases are eventually constant with time, this would lead to the interfaces changing linearly with time. Figs.4.2 and 4.3 indicate that this is the case. Therefore we can extrapolate the interface heights to zero time and determine the relative amounts of each phase in the absence of gravity [18].

It is interesting to note that for the larger particles ($a = 500$ nm) the crystal-fluid interface height $h_c$ increases with time (fig.4.3) whilst for smaller particles ($a = 301$ nm) the height of the interface stays fairly constant (fig.4.2). Even smaller particles ($a = 240$ nm) exhibited a decreasing crystal-fluid interface height with time (not shown). Presumably this is because the
**CHAPTER 4. LOW-SHEAR VISCOSITY OF A HARD-SPHERE SUSPENSION**

Figure 4.2. Colloidal crystal-fluid interface height $h_c$ over time for two different sample concentrations; ($\times$) $\phi \approx 0.52$, ($\Diamond$) $\phi \approx 0.51$. Particle radius $a = 301$ nm. The linear portion of the curve is extrapolated to zero time in order to determine the equilibrium amount of crystal phase in the absence of gravity and hence the sample volume fraction $\phi$.

Figure 4.3. Colloidal fluid-solvent interface height $h_{lf}$ and colloidal crystal-fluid interface height $h_c$ over time for two different sample concentrations; ($\times$) $\phi \approx 0.51$, ($\Diamond$) $\phi \approx 0.50$. Particle radius $a \approx 500$ nm; note the longer time taken for the crystal-fluid interface height to start changing linearly with time for the larger particles.
sedimentation rate of the coexistence colloidal fluid is more sensitive to particle size than that for the coexistence colloidal crystal. This would lead to crystal compression being the dominant change in crystal-fluid interface height for smaller particles, and creation of new crystallites due to colloidal fluid sedimentation dominating for larger particles.

Once the amount of crystal phase is determined the sample can be calibrated using the simple relation

\[ \phi = \frac{V_c}{V_T} (\phi_m - \phi_f) + \phi_f \]  

(4.1)

where \( V_c \) is the volume of the crystal phase (in the absence of gravity) and \( V_T \) is the total sample volume. The fractional volume of crystal is replaced by the fractional height of crystal phase \( h^0_T / h_T \), where \( h^0_T \) is the zero-time crystal-fluid interface height. The ‘effective’ total height of the sample \( h_T \) has to be calculated due to the presence of the meniscus. This can be expressed as \( h_T = h_{mb} + \Delta h \), where \( h_{mb} \) is the meniscus base height (a well-defined reference point) and \( \Delta h = m_{men} / A \rho_{cis} \), where \( m_{men} \) is the mass of solvent above the meniscus base, \( A \) is the sample cell cross-sectional area (\( 1 \text{ cm}^2 \)) and \( \rho_{cis} \) is the solvent density (\( 0.894 \text{ g cm}^{-3} \)). Fig.4.4 shows the determination of \( m_{men} \); this gave \( \Delta h = 0.84 \text{ mm} \).

![Figure 4.4. The determination of \( m_{men} \), the mass of solvent above the meniscus base by extrapolation of the total mass of a pure cis-decalin ‘sample’ as a function of meniscus base height \( h_{mb} \). The ‘meniscus’ mass \( m_{men} = 0.075 \text{ g} \).](image)

Generally in order to reduce errors in this calibration method it is good to have tall samples and to avoid those with concentrations falling near the extremes of the coexistence region. Typically \( h_T \approx 20 - 30 \text{ mm} \). The vernier calipers were capable of measuring to a precision of \( \pm 0.1 \text{ mm} \), although judgement of the position of the interface realistically doubles this error. The extrapolation to the zero-time crystal-fluid interface height \( h^0_T \) typically deviated by \( \pm 1 \text{ mm} \). The effect of solvent loss (evaporation) was generally negligible. The effect of any uncertainty in the freezing and melting volume fractions \( \phi_f \) and \( \phi_m \) is discussed later. The total uncertainty in the calibration method was deemed to be \( \Delta \phi_{cal} = \pm 0.002 \text{ on average} \).
Evaporation

Once the colloidal batches were calibrated, amounts could be taken as desired, diluted down and used for experimentation. However these batches were used over many days, so that it was important that solvent evaporation was minimised. Teflon centrifuge containers were used to contain both the colloidal batches and the individual diluted samples. The weights of all colloidal batches and samples were periodically measured to monitor any solvent evaporation. The resultant error in concentration due to solvent loss varied from negligible to $\Delta \phi_{\text{evap}} \approx +0.001$ over the life time of the batches/samples.

Evaporation of the sample whilst in the Zimm viscometer was also a concern. A rubber bung was used to seal the viscometer, which was not ideal as there may be some solvent imbibition. However measurements rarely lasted more than six hours, and cis-decalin evaporation tests indicated that the amount of solvent loss over this period of time for samples of $\approx 7$ g would have negligible effect on even concentrated suspensions. Also the inclusion of the cis-decalin solvent well in the rotor would further reduce evaporation. The biggest concern regarded the integrity of the sample on a local scale, i.e. the meniscus, for samples close to the freezing volume fraction. Here there was a danger of crystallization occurring locally, especially at the lowest shear rates. However, one would expect to see some time-dependency in viscometry measurements if this were important, and this was not observed.

Unknown particle density

The dilution of the colloidal batch to make samples of desired concentration for experimentation further increases the uncertainty in volume fraction. This is because the density of the particles is assumed to be $\rho_{\text{pmma}} = 1.188 \text{ g cm}^{-3}$ — i.e. the same as bulk PMMA. However there is uncertainty in this estimate of the particle density, and hence calculated volume fraction, as it does not include the solvated stabilizer layer, whose thickness and density are not known precisely. Possible solvent imbibition by the particles is a further complication. Calculation (see appendix [40]) gives an estimate of this contribution to the fractional uncertainty in volume fraction:

$$\frac{\Delta \phi_{\text{dil}}}{\phi} = \frac{(\phi - \phi_f) \Delta x}{(1 + \alpha x) z}$$

where $x = \rho_{\text{pmma}}/\rho_{\text{cis}}$ is the particle-solvent density ratio, $\Delta x$ is the uncertainty in this ratio, and $\alpha$ is the fractional increase in the mass of the particle by solvent imbibition. This 'dilution' error in volume fraction is quadratic in form. Assuming a worst case of $\Delta x/x \approx 3\%$ (stabilizer layer $\approx 10$ nm at liquid density, core of particle $a \approx 290$ nm at bulk PMMA density), with the particle taking up say 10% of its mass in solvent, gives an error that is zero at $\phi = 0$, increasing to a maximum error of $\pm 0.002$ at $\phi = 0.247$, and decreasing to zero at the reference volume fraction $\phi_f = 0.494$. 
CHAPTER 4. LOW-SHEAR VISCOSITY OF A HARD-SPHERE SUSPENSION

4.3 Low-shear limit viscosity measurement

4.3.1 Method

Colloidal fluids were loaded and their viscosities measured using essentially the same method as described in sections 3.4.1 and 3.4.2. The samples were temperature controlled at 23.0±0.2°C.

4.3.2 Viscosity uncertainty

There are basically two main concerns regarding the low-shear limit viscosity measurements; whether we are truly measuring the viscosities in the low-shear limit and the accuracy of the measurements themselves.

When we are in the low-shear regime the suspension is essentially behaving like a Newtonian fluid, so all the (shear stress, shear rate) data points will fall on a straight line that goes through the origin (at least to the error of the fit, excepting any small end effects). This is observed. Also a useful guide to the low-shear regime is the Peclet number, effectively the dimensionless shear rate (see equation 2.9). This gives us a measure of the relative importance of diffusive motion versus shear motion imposed on the particles. Viscosity measurements were performed in the $Pe_0 < 0.01$ range i.e. $Pe \ll 1$.

Examining the other concern, the accuracy of the measurements, we assume that the reproducibility of the measurements is the same as for the repeated cis-decalin calibration curves that were taken over the same period i.e. 2%. Furthermore we can take the standard deviation of the least-squares straight-line fit of our low-shear viscosity data as the random error in measurement.

4.4 Results

Some examples of the shear stress $\sigma$ versus strain rate $\gamma$ curves obtained for dispersions of volume fractions 0.430 to 0.494 ($a = 301$ nm) are shown in fig.4.5. Emergence from the shear-thinning regime into the low-shear viscosity limit can clearly be seen; data points in the low-shear limit at each volume fraction lie on a straight line extrapolating through the origin. The slope of this straight line gives the low-shear viscosity, whilst the standard deviation of the slope is the random error.

Fig.4.6 displays the relative low-shear viscosity $\eta_0^\phi$ as a function of volume fraction $\phi$. We obtain a relative viscosity $\eta_0^\phi$ of $\approx 50$ at the freezing volume fraction $\phi_f = 0.494$ for our suspensions comprising particles of radii 240 nm and 301 nm. A higher value of $\eta_0^\phi(\phi_f) = 59$ was measured for the larger particles ($a = 500$ nm). This variation in result is consistent with the uncertainty in volume fraction $\phi$ of our suspensions, as $\eta_0^\phi$ is such a rapidly rising function of $\phi$ around the freezing phase transition. Averaging these results gives $\eta_0^\phi = 53 \pm 6$. The data show no dependence of $\eta_0^\phi$ on particle size, as expected for a hard-sphere suspension. Consistent results were achieved between samples that were prepared by diluting coexistence fluid and those
CHAPTER 4. LOW-SHEAR VISCOITY OF A HARD-SHERE SUSPENSION

Figure 4.5. Shear stress $\sigma$ versus strain rate $\dot{\gamma}$ for several concentrated PMMA suspensions (particle radius $a = 301$ nm). At low rates of strain (or stresses) the points in each case lie on a straight line (shown), the slope of which is the low-shear viscosity. All of these lines extrapolate through the origin to within experimental error. At higher rates of strain deviations from linearity are observed — this is the beginning of shear-thinning.

Figure 4.6. The dependence of the low-shear viscosity $\eta^0$ on volume fraction $\phi$. Most of the data is for particles of size $a = 301$ nm; ($\square$) indicate samples that were diluted from batches consisting of coexisting fluid and colloidal crystal, whereas ($\bigcirc$) indicate samples diluted from the coexistence fluid ($\phi_f = 0.494$). Measurements at other particle sizes are ($\times$) $a = 500$ nm, ($\Delta$) $a = 240$ nm.
calibrated by measuring crystal amount. Deviations in the viscometer calibration curves led to a systematic error of 2% in viscosity. The aforementioned uncertainty of the density of the composite shell-core PMMA particle, any swelling through solvent absorption, plus uncertainty in the reference concentration and any solvent evaporation led to a maximum uncertainty of ±0.003 in volume fraction.

4.5 Discussion

One can compare our value for the relative low-shear limit viscosity $\eta_0^0 = 53 \pm 6$ at the freezing concentration with those determined by previous studies at $\phi \approx 0.50$ volume fraction shown in table 2.1 ($20 \leq \eta_0^0(\phi \approx 0.50) \leq 400$).

An attempt must be made to reconcile the different values reported. It is possible that not all the systems studied can be modelled accurately as hard spheres. Papir and Kreiger [24] report iridescence in their dispersions at volume fractions in excess of 0.30. This would seem to be a departure from hard sphere behaviour, where we would expect to see ordered structure only at volume fractions in excess of 0.494.

In some of the studies significant polydispersity may have an effect. It is also possible that the true low-shear regime may not have been reached in all cases. The most likely cause of the discrepancy, however, is the determination of the suspension volume fractions.

Previous studies measure the mass concentrations of the particles and convert these into volume fractions using literature or experimentally determined values for particle and solvent density. However, it is not clear that volume fraction can be related to mass concentration so simply. As mentioned before the suspensions are likely to have an 'effective' volume fraction arising from solvation of the stabilizing layer or the particle itself.

Some of the previous studies (de Kruif et al. [25], Mewis et al. [27]) attempt to convert particle mass concentration into volume fraction by determining a particle specific volume $q$ from specific viscosity measurements in the dilute limit. As mass concentration $c \rightarrow 0$

$$\eta_{sp} = \eta_r - 1 = K c = [\eta] \phi,$$

where $K$ is a constant determined by the dilute viscometry measurements and $[\eta]$ is the intrinsic viscosity. Then $[\eta]$ is equated to the Einstein value of $5/2$ (by assuming hard sphere behavior) which yields a particle specific volume $q = 2K/5$. However, care has to be taken that such measurements are truly in the dilute limit. At $\phi$ as low as 0.02 the Batchelor term $5.9\phi^2$ [31], [32] contributes $\approx 5\%$ to the specific viscosity $\eta_{sp}$ which would be directly passed on as error in $\phi$ if ignored. Such discrepancy would have grave consequences when relating low-shear viscosity measurements to (calculated) volume fractions. Even if measurements are on sufficiently dilute suspensions great accuracy is required [12]. For $\phi \approx 0.01$, $\eta_{sp}$ accounts for only $\approx 3\%$ of the relative viscosity. In order to achieve an estimate of $\eta_{sp}$ (and thereby $\phi$) to a minimum precision of $\pm 2\%$ one would have to measure $\eta_r$ to $\pm 0.06\%$.

By calibrating our samples with respect to their freezing concentration we have a clearly defined
This work.

Figure 4.7. The dependence of the relative low-shear viscosity $\eta^0_r$ on volume fraction $\phi$ measured in this work, and the data of de Kruif et al. [25], and Choi and Kreiger [26] with volume fraction multiplied by a constant factor in each case (0.91 and 1.02 respectively). All the data falls on a single curve, supporting the claim that uncertainty in volume fraction is the main cause of the discrepancy between the studies summarised in table 2.1.

Support for our contention that volume fraction uncertainty is the single most important cause of discrepancy between existing data sets comes from the plot shown in fig.4.7.

Here we show again the dependence of the relative low-shear viscosity $\eta^0_r$ on volume fraction $\phi$ measured in this work. On the same plot, however, we also show the data of de Kruif et al. [25], and Choi and Kreiger [26] with volume fraction multiplied by a constant factor in each case (0.91 and 1.02 respectively). The three data sets fall on a single curve. The data of Mewis et al. ($a = 238$ nm) [27] failed to agree with our results when rescaling of their volume fractions was attempted. Our only explanation is possible deviation of their particles from the hard-sphere ideal, or uncertainty in determining the low-shear viscosity. The data of Marshall et al. [28] did not readily lend itself to such comparison, as the bulk of the measurements made were on suspensions near the glass transition.

It is tempting to seek a closed form expression for the 'master curve' shown in fig.4.7. An obvious candidate is the empirical Kreiger-Dougherty equation:

$$\eta^0_r = (1 - \phi/\phi_m)^{-[\eta] \phi_m}.$$  \hspace{1cm} (4.3)

The intrinsic viscosity, $[\eta]$, is expected to take the Einstein value for hard spheres, $[\eta] = 2.5$. The other parameter, $\phi_m$, is the volume fraction at which the low-shear viscosity diverges.
the colloidal fluid becomes thermodynamically metastable with respect to the colloidal crystal above the freezing volume fraction \( \phi_f = 0.494 \), the viscosity is strictly speaking not defined above this density. If one nevertheless wants to enquire about the viscosity of the metastable colloidal fluid, the expectation might be (in common with the well-known situation in simple atomic and molecular fluids [41]) that it should diverge at the glass transition, which occurs in this system at \( \phi_g \approx 0.58 \) [16]. Certainly one would not expect the low-shear viscosity to diverge at a lower volume fraction. An unconstrained fit, returning the values \( [\eta] = 3.2 \) and \( \phi_m = 0.55 \), gave good agreement with the data in Fig. 4. However, we deem the fitted values of the parameters \([\eta]\) and \( \phi_m \) to be unphysical. Constraining \([\eta]\) to the Einstein value and fitting to \( \phi_m \) alone (returning a best-fit value of \( \phi_m = 0.525 \)) did not produce satisfactory agreement.

We note that in associating the observed freezing volume fraction of our samples \( \phi_f \) with the hard-sphere computer value of 0.494 we neglect possible effects of polydispersity of the particles on observed freezing volume fraction. Recent simulations ([42]) suggest that the effect of 5% polydispersity is to increase observed \( \phi_f \) by \( \sim 2\% \), so that the volume fractions in this study may be underestimated by this amount. We also note that polydispersity may affect the value of viscosity at a well-defined volume fraction. It seems however that at the very least we have placed an upper bound on the low-shear rate relative viscosity at \( \phi = 0.494 \); in reality the value is likely to be substantially above \( \sim 20 \) and a little below \( \sim 50 \).

4.6 Conclusion

The low-shear limit relative viscosity \( \eta^0 \) of nearly-monodisperse sterically stabilized PMMA spheres dispersed in cis-decalin, a hard-sphere suspension, was found to be \( \approx 50 \) at the hard sphere freezing concentration \( \phi_f = 0.494 \). This, as well as the general volume fraction dependence (referenced to the freezing concentration) of the low-shear relative viscosity, was found to be significantly different to previous measurements on hard-sphere suspensions. However, two previous data sets were brought into agreement with our measurements with a simple scaling of volume fractions in each case. Elsewhere the results are discussed in relation to dynamic light scattering (DLS) measurements. An intriguing relationship was found between the low-shear viscosities and the rates of structural relaxation determined by DLS [43].

Finally we mention other work that corroborates our results. Rodriguez et al. [44] measured the low-shear viscosity of highly cross-linked polystyrene microgels dispersed in bromoform, a hard sphere-like system. From his measurements it can be seen that \( \eta^0 \) lies between 40 - 50 at the freezing concentration. Similar results have been obtained by Reuvers [45]. His hard-sphere system consists of monodisperse polystyrene particles dispersed in sodium chloride solution and stabilized by surfactant. His measurements of the low-shear viscosity at the freezing volume fraction of the suspension yield \( \eta^0(\phi_f) = 49 \pm 4 \), in close agreement with our value of 50. The most significant confirmation however comes most recently from See-Eng Phan et al. [46], who performed similar measurements on sterically-stabilized PMMA suspensions. They obtained \( \eta^0 = 45 \pm 3 \) at \( \phi = 0.50 \) after correcting \( \phi \) for both the polymer layer thickness and polydispersity.
Chapter 5

Colloid-polymer mixtures

5.1 Introduction

It has long been known that the addition of enough free (non-adsorbing) polymer to a suspension of colloidal particles can lead to phase separation. Apart from the fundamental interest of this, many industrial products are essentially colloid-polymer mixtures, so an understanding of their behaviour is desirable.

A theoretical model was first suggested by Asakura and Oosawa (1958)[9], and also independently by Vrij (1976)[47] — the depletion force, which we have already met in chapter 1. In this chapter we review the predicted and observed equilibrium phase behaviour for a ‘model’ colloid-polymer mixture, and the variety of non-equilibrium aggregation behaviour seen.

5.2 Depletion potential

We recall (chapter 1) that the addition of small, non-adsorbing polymer coils to a hard-sphere suspension results in an effective attractive force — the depletion force — between the particles. The pair potential is given by

\[ U(r) = \begin{cases} 
\infty & ; \quad r \leq 2a \\
-\Pi_p V_{\text{overlap}} = U_{\text{dep}} & ; \quad 2a < r \leq 2(a + \delta) \\
0 & ; \quad r > 2(a + \delta) 
\end{cases} \] (5.1)

where \( 2a \) is the particle diameter, \( \delta \) is the polymer coil radius of gyration and \( \Pi_p \) is the osmotic pressure of the polymer. \( V_{\text{overlap}} \) is the volume of the overlapping depletion zones between two particles at an intercentre separation of \( r \) (see fig.1.5 chapter 1). Explicitly

\[ V_{\text{overlap}} = \left\{ 1 - \frac{3r}{4a(1 + \xi)} + \frac{1}{2} \left[ \frac{r}{2a(1 + \xi)} \right]^3 \right\} \times \frac{\pi}{6} (2a)^3 (1 + \xi)^3 \] (5.2)
CHAPTER 5. COLLOID-POLYMER MIXTURES

where the polymer-colloid size ratio $\xi = \delta/a$.

An expression is required for the osmotic pressure $\Pi_p$ of the polymer solution. For a dilute polymer solution (i.e. polymer volume fraction $\phi_p \ll \phi_p^*$, where $\phi_p^* \sim 1$ is the volume fraction at which the polymer coils overlap) there exists a temperature, known as the 'theta temperature' $T_\theta$, at which the polymer coils effectively interact as interpenetrable spheres. The osmotic pressure is then given by Van't Hoff's law [48] (the colloidal analogue of the perfect gas law)

$$\Pi_p = \frac{N_p (k_B T)}{V_{\text{free}}}$$

(5.3)

where $N_p/V_{\text{free}}$ is the number density of polymer coils in the free volume i.e. the volume accessible to the centre of a polymer coil.

As can be seen in fig.5.1, the free volume $V\{r_C\}_{\text{free}}$ depends on the positions of all colloidal particles, as particles can overlap their depletion layers. We can write

$$V_{\text{free}} = \alpha\{r_C\} V$$

(5.4)

where $V$ is the total system volume, $\{r_C\}$ denotes the position of all colloidal particles and the 'free volume fraction' $\alpha\{r_C\}$ contains the particle position dependency. One can make a mean-field approximation and take the average value of the free volume in the corresponding unperturbed (polymer-free) system of colloidal particles.

$$\alpha\{r_C\} \rightarrow \langle \alpha \rangle = \alpha(\phi)$$

(5.5)

The interaction between the polymer and colloid is contained solely in the dependence of $\alpha$ on
\( \phi \). Through work in scaled particle theory \cite{49} an approximate closed-form expression for \( \alpha(\phi) \) can be obtained —

\[
\alpha = (1 - \phi) \exp[-A\gamma - B\gamma^2 - C\gamma^3]
\]

(5.6)

where \( \gamma = \phi/(1 - \phi) \), \( A = 3\xi + 3\xi^2 + \xi^3 \), \( B = 9\xi^2/2 + 3\xi^3 \) and \( C = 3\xi^3 \).

We link the polymer osmotic pressure \( \Pi_p \) and hence the depletion potential 'strength' \( U_{dep} \) to the experimental parameter polymer mass concentration \( C_p \).

\[
\frac{\Pi_p}{k_BT} = \left( \frac{N_A}{M_W} \right) \left( \frac{M_p}{\alpha V} \right)
\]

(5.7)

where \( N_A \) is Avogadro's number, \( M_W \) is the molecular mass of the polymer and \( M_p \) is the total mass of polymer in the system. Hence

\[
\frac{\Pi_p}{k_BT} = \left( \frac{N_A}{M_W} \right) C_p^{\text{free}}
\]

(5.8)

where \( C_p^{\text{free}} \) is the polymer concentration in the free volume and is simply linked to polymer concentration \( C_p \) by

\[
C_p^{\text{free}} = \frac{C_p}{\alpha}
\]

(5.9)

We can see that in our model \( C_p^{\text{free}} \) is proportional to \( \Pi_p \) and hence \( U_{dep} \).

### 5.3 Predicting equilibrium phase behaviour

We have already looked at the hard-sphere system and seen its phase behaviour. How does the addition of an attractive well to the bare hard-sphere potential affect the equilibrium phase behaviour?

Any fixed-volume system will try to minimise its total Helmholtz free energy \( F \), and this determines its equilibrium phase behaviour. Following Lekkerkerker et al. \cite{50} the free energy density of a colloid-polymer mixture is a function of the colloid volume fraction \( \phi \), and the polymer chemical potential \( \mu_p \). For a fixed temperature \( T \) the polymer chemical potential is a function of the number density of polymer coils in the free volume \( N_p/V_{\text{free}} \) only, and hence \( C_p^{\text{free}} \). Therefore the free energy density \( f \) can be expressed as a function of \( \phi \) and \( C_p^{\text{free}} \) i.e. \( f = f(\phi, C_p^{\text{free}}) \). This can be calculated, within a mean-field framework, for a disordered arrangement of colloids and polymers, the 'fluid branch', and an ordered arrangement of colloids with polymers randomly dispersed, the 'crystal branch'. For a given pair-potential strength determined by \( C_p^{\text{free}} \) one can plot the free energy density for each phase as a function of colloid volume fraction \( \phi \), which (for low \( C_p^{\text{free}} \)) has the form as shown in fig.5.2.
Figure 5.2. For a fixed free-volume polymer concentration $C^\text{free}_p$ one can plot the free energy density $f$ as a function of colloid volume fraction $\phi$ for a disordered arrangement of polymer and colloid (fluid branch) and an ordered arrangement of colloids with polymers randomly dispersed (crystal branch). For low $C^\text{free}_p$ (as shown) both branches exhibit a single minimum. This gives rise to either single-phase fluid, fluid-crystal coexistence or single-phase crystal. The colloid concentrations in the coexisting fluid and crystal phases are obtained by the common tangent construction \cite{51}; the amounts of each phase by the lever rule.

Figure 5.3. Predicted phase diagram (polymer concentration $C_p$ vs. colloid volume fraction $\phi$) for a colloid-polymer mixture where the polymer-colloid size ratio $\xi = 0.08$. Tie lines are shown in the two-phase crystal-fluid coexistence region. The oblique tie lines imply considerable polymer partitioning among the coexisting phases. Figure reproduced from \cite{52}.
To determine the concentrations of the (potentially) coexisting phases one performs the common tangent construction as shown [51]. This is a geometrical solution to the equilibrium conditions for coexisting phases, namely equal chemical potentials (and hence $C_p^{\text{free}}$) and pressures. From this construction we can see that an initially randomized sample (i.e. fluid) of concentration $\phi_1$ in between $\phi_1, \phi_2$ can lower its initial free energy density $f_i$ by separating into coexisting phases of fluid at concentration $\phi_1$ and crystal at concentration $\phi_2$. The volume of each phase $(V_1, V_2)$ will be determined by the lever rule, i.e. $V_1/V_2 = b/a$.

This process can be repeated for different free-volume polymer concentrations $C_p^{\text{free}}$, hence we can determine the equilibrium phase behaviour as a function of particle concentration $\phi$ and free polymer concentration $C_p^{\text{free}}$ (and hence $C_p$ from equations 5.6 and 5.9) for a specific potential range $\xi$. When the polymer-colloid size ratio $\xi \leq 0.3$, added polymer is predicted to expand the fluid-crystal coexistence region. When $\xi \geq 0.3$ fluid-fluid separation is also possible. In this study however we shall only be using systems with small polymer-colloid size ratios (i.e. $\xi < 0.1$).

Fig.5.3 displays a typical predicted phase diagram for $\xi = 0.08$ [52]. Essentially the effect of increasing the potential depth is the broadening of the coexistence region.

### 5.4 Observed equilibrium phase behaviour

Comparison is made between the predicted phase diagram $(\phi, C_p)$ (fig.5.3) and an experimentally observed one, for PMMA spheres plus polystyrene (PS) in cis-decalin at room temperature ($19 \pm 2^\circ \text{C}$), studied by Poon et al. [52] (fig.5.4). The theta temperature for polystyrene in cis-decalin is $T_\theta = 12.5^\circ \text{C}$ [53]; Poon et al. assume coil interpenetrability as a first approximation. The particle size was 217 nm, whilst the polymer ($M_w = 390,000$) radius of gyration was $\delta \approx 19$ nm, giving $\xi \approx 0.09$.

With no polymer added we have the familiar hard-sphere phase diagram as described in chapter 1 with freezing and melting volume fractions at $\phi_f = 0.494$ and $\phi_m = 0.545$ respectively.

If we take a pure colloidal fluid sample and add a (relatively) small amount of polymer very little seems to change. These samples remain single phase and homogeneous. They are apparently fluid-like, and individually particles can explore the whole sample by diffusion.

Adding more polymer to the sample $(C_p > C_p^{\text{coex}}(\phi))$ eventually induces phase separation — visually we see crystallization occurring within the sample. The sample eventually separates out into coexisting phases of colloidal crystal and fluid. In fact over the phase diagram as a whole we can see that the addition of polymer broadens the fluid-crystal coexistence region, as predicted by theory. However, addition of yet more polymer $(C_p > C_p^{\text{coex}}(\phi))$ results in the suppression of crystallization. Immediately after mixing the samples resemble single-phase fluids. Dramatically however, these samples settle very rapidly, some immediately, some after a 'latency' time of ~ hours, leaving a supernatant of solvent visually devoid of particles. This rapid settling halts fairly abruptly as the particles form a metastable sediment that slowly compactifies over weeks. This behaviour is not predicted by equilibrium thermodynamics, and hence is labelled non-equilibrium behaviour.
Figure 5.4. The experimental phase diagram for a mixture of PMMA colloid (volume fraction $\phi$) and polystyrene (concentration $C_p$). The polymer-colloid size ratio $\xi \approx 0.09$; (o) single phase colloidal fluid, (□) fluid-crystal coexistence, (△) non-equilibrium aggregating state, (×) fully crystalline and (○) glass. Figure reproduced from [52].

All colloid-polymer samples above the non-equilibrium boundary were characterised by the exhibition of a small-angle light scattering ring which brightens and collapses as a function of time. This small-angle ring is the hallmark of large-scale correlations or inhomogeneities in the colloidal structure (twenty or so particles), such as may develop in an aggregating colloidal suspension.

5.5 Observed non-equilibrium phase behaviour

The non-equilibrium aggregating behaviour of a colloid-polymer system was investigated by Poon et al. [54], using similar particles and polymer as above ($a = 240$ nm, $M_w = 370,000$) but with a mixture of cis-decalin and tetralin for solvent (ratio $\approx 3 : 1$), nearly index-matching the particles and the suspension medium, enabling the investigation of the structure and dynamics of the colloid-polymer mixtures using various light-scattering techniques. The detailed studies of the time-dependent position and intensity of the small-angle scattering peak shows that the behaviour of the samples above the non-equilibrium boundary can be classified into three regimes [54],[55] — fig.5.5.
CHAPTER 5. COLLOID-POLYMER MIXTURES

Figure 5.5. Non-equilibrium phase behaviour for an index-matched PMMA-PS colloid-polymer mixture, $\xi \approx 0.08$. The non-equilibrium behaviour can be classified into three regimes; spinodal-like (SD), transient gelation (TG) and nucleation-like (N). The various boundaries are: fluid-crystal coexistence $C_p^{\text{coex}}(\phi)$ (lower solid line), non-equilibrium boundary $C_p^{\text{neq}}(\phi)$ (upper solid line), nucleation-spinodal crossover $C_p^S(\phi)$ (long dashes) and transient gelation line $C_p^T(\phi)$ (short dashes). Figure reproduced from [54].

Spinodal-like

Just above the non-equilibrium boundary $C_p^{\text{neq}}(\phi)$ and at moderate colloid volume fractions the small-angle peak collapses continuously and completely. The behaviour of the time-dependent peak position is reminiscent of classical spinodal decomposition in fluids; i.e. the system is unstable to small density fluctuations, leading to particle aggregation. Macroscopically these samples show no delay before rapid sedimentation occurs.

Transient gel

At higher polymer concentrations ($C_p > C_p^S(\phi)$) a period of 'latency' is exhibited before rapid sedimentation occurs. Chapters 6 and 7 are devoted to a detailed study of this phenomenon of 'delayed sedimentation'. The latency time grows with increasing polymer concentration. The collapse of the small-angle scattering peak is now incomplete. In these samples the 'ring' appears 'frozen' to the naked eye after initial collapse. Temporal fluctuations in the speckles on this 'frozen ring' are very slow. Preliminary dynamic light scattering suggests that while the structure is frozen on large length scales (i.e. a 'gel'), motion still occurs on the single particle level. After a fixed period of time coincident with the onset of rapid gravitational settling of the particles, the fluctuation of the speckles suddenly speeds up and the ring disappears within seconds, leaving peaked forward scattering.
Nucleation-like

A sample just across the non-equilibrium boundary and at low colloid volume fraction shows a third kind of behaviour. Here, a small-angle scattering ring only appears after an initial latency period. Direct observation under the microscope showed disconnected droplets. The sedimentation behaviour is similar to spinodal-like samples. Further increase of polymer concentration led to spinodal-like behaviour.

5.6 Discussion of non-equilibrium behaviour

We envisage that the crossover from equilibrium to non-equilibrium behaviour in colloid-polymer mixtures occurs because the particles aggregate. Here we take a look at the aggregation model, and then view it in a wider quasi-thermodynamical context.

5.6.1 Aggregation picture

In order to get a better understanding of aggregation we can look at attempts to understand aggregating colloids through computer simulation. A simple but useful model for aggregation is diffusion-limited cluster aggregation (DLCA) [56]. It is appropriate for systems with a strong, short-range attraction between aggregating particles. In the DLCA model identical particles are initially set diffusing in a fixed region of space. When two particles collide they are permanently bonded together, and thereafter diffuse as a cluster. Similarly when two clusters collide they bond and subsequently diffuse as a larger cluster.

The structure of each growing cluster in DLCA is found to be fractal — i.e. the number of particles in a cluster scales with its radius \( R \) as

\[
 n \sim \left( \frac{R}{a} \right)^d
\]

where \( d \) is the fractal dimension (which must be less than the spatial dimension \( D \)) and \( a \) is the particle radius. For 3 dimensions DLCA gives \( d \approx 1.8 \).

![Figure 5.6. Schematic diagram illustrating the fractal growth of a cluster. The average density of the cluster decreases as it grows.](image)
We can see that as a cluster grows fractally its average density (or average volume fraction \((\phi)_{cl}\)) decreases as it grows i.e. the cluster becomes more tenuous as its size increases (fig.5.6). One can see that when the average volume fraction of each cluster \((\phi)_{cl}\) is the same as the total sample fraction \(\phi_0\) the sample must have gelled — i.e. all clusters meet to span the sample, fig.5.7.

![Figure 5.7](image)

**Figure 5.7.** Schematic diagram illustrating gelation in an aggregating system. Clusters grow until they form one sample-spanning cluster.

At the gel point

\[
(\phi)_{cl} \sim \frac{na^D}{R^D} \sim \phi_0
\]

Substituting for \(n\) gives us the radius of the clusters at the gel point

\[
\frac{R_{gel}}{a} \sim \phi_0^{1/(d-D)}
\]

It can be seen that \(R_{gel}\) is a strong function of sample volume fraction. In this model a gel is an assembly of fractal clusters of size \(R_{gel}\). The above equation indicates that the size of the clusters forming the gel decreases with increasing sample volume fraction.

The above model is good for systems with very strong pair potentials. At lower depletion potentials however the situation is different. The bonds are sufficiently weak that they can be broken by the thermal energy \(\sim k_BT\) that the particles possess, i.e. thermal rearrangement. Hence aggregation and thermal rearrangement would compete in such a system. This can be modelled by DLCA with finite bond energies (reversible DLCA), where the probability of a particle bond being broken is given by the Boltzmann distribution \(\sim \exp(-U/k_BT)\). Figure 5.8(a)-(c) show examples from a 2D reversible DLCA simulation by Haw et al. [57]. The number of particle steps used corresponds to a ‘real’ time of \(\sim\) minutes after randomization. The results fall broadly into three categories:
Figure 5.8. Reversible DLCA simulations with varying bond strength; (a) $U_{\text{dep}} \gg k_B T$, (b) $U_{\text{dep}} \approx 3k_B T$ and (c) $U_{\text{dep}} \approx k_B T$. Reproduced from [57].
(i) Fig. 5.8(a) Irreversible DLCA, $U_{\text{dep}} \gg k_B T$ — the system spanning cluster is made of thin, single-particle links.

(ii) Fig. 5.8(b) Intermediate bond strength, $U_{\text{dep}} \approx 3k_B T$ — we see growth of clusters occurring simultaneously with thermally-driven compactification on short length scales. Over time the particles form relatively stable double and triple bonded local structure: the filaments in the evolving structure grow fatter. However on longer length scales the structure of the clusters is still ramified. The clusters grow fractally until they form a space-spanning structure. This structure however continually breaks apart (into two or three large clusters) and reforms due to the thermal motions of the particles. Such a structure could be termed a transient gel. In a real system such thermally-driven rearrangements coupled with fluid flow and gravity would probably lead to collapse.

(iii) Fig. 5.8(c) At lower bond energies ($U_{\text{dep}} \approx k_B T$) thermal compactification occurs more quickly, such that clusters do not have time before they compactify to grow large enough to fill an appreciable fraction of space and form a gel. This is analogous to our spinodal-like samples. We can identify the gel-sol crossover between cases (ii) and (iii) with transient gelation line in the absence of gravity.

5.6.2 Non-equilibrium line

We have seen the sharp transition from equilibrium phase behaviour to non-equilibrium aggregation behaviour at high enough polymer concentrations, but as yet have not speculated about the reasons for the existence of the non-equilibrium boundary $C_p^{\text{eq}}(\phi)$. Poon has suggested that it is possible to understand aggregation within a quasi-thermodynamic framework [52], [55]. He suggests that non-equilibrium behaviour is 'switched on' by the presence of a 'hidden' gas-liquid binodal within the equilibrium crystal-fluid coexistence region in the phase diagram. This can be understood as follows.

We have already seen how we can predict equilibrium phase behaviour by plotting the free energy density of the disordered fluid phase and ordered crystal phase, and by using the common tangent construction. At higher polymer concentrations however the fluid branch of the free energy shows a double minimum structure, fig. 5.9. The points on the equilibrium phase boundary at this polymer concentration, coexisting fluid and crystal phases, are still obtained by constructing the lowest common tangent between the fluid and crystal branches. However one could still plot the liquid-gas binodal, performing the double tangent construction on the fluid branch alone, constructing a gas-liquid binodal. It has been found that both the equilibrium phase boundary and the hidden gas-liquid binodal compare well with the experimental crystal-fluid phase boundary and the non-equilibrium boundary respectively. It is possible therefore that the hidden gas-liquid binodal should be identified with the experimentally determined non-equilibrium boundary $C_p^{\text{eq}}(\phi)$. If this identification is true we would expect the initial behaviour of homogeneous fluids above the non-equilibrium boundary to be similar to simple fluids undergoing phase separation. We would expect to see 'nucleation' (of amorphous clusters) close to the binodal and 'spinodal decomposition' further in (a result of 'negative curvature' in the fluid branch of the free energy density leading to instability to small density fluctuations.
and hence aggregation). This kind of non-equilibrium behaviour is indeed observed for our colloid-polymer mixtures, giving support for identification of the 'hidden' gas-liquid binodal with the experimental non-equilibrium line.

5.6.3 Onset of gelation

In section 5.6.1 we briefly discussed the reversible DLCA model and identified (transient) gelation with percolation (i.e. existence of a single network-spanning cluster) in a system where aggregation competes with cluster compactification due to thermal rearrangement. However so far we have ignored the effect of gravity in aggregating systems, which will certainly play a significant role in non-density matched systems. Indeed gravity is responsible for the spectacular 'collapse' in a transient gel. Here we present a simple model inspired by the work of Allain et al. [58] and reworked by Poon [55] in order to have some understanding of the effect of gravity on the transient gelation line $C_p$.

We can imagine clusters growing in a DLCA model as described in section 5.6.1, gelation occurring when the clusters 'meet' once they have grown to size $R_{gel}$. One might hope to determine the effect of gravity on such a system by considering the gravitational Peclet number $Pe_g$ on a cluster of size $R$. The gravitational Peclet number measures the relative importance of Brownian motion to gravitational settling, by comparing the time it takes a cluster to diffuse its own radius $t_R$ to the time it takes to sediment the same distance $t_S$. For simplicity we treat each cluster as a sphere of radius $R$ and density difference $\Delta \rho_{cl} \sim \Delta \rho \left( \frac{a}{R} \right)^{d-B}$, where $\Delta \rho$ is the particle-solvent density difference. Equation 1.3 gives us $t_R$ whilst the Stokes velocity for a
spheres [59] $V_s = 2\Delta \rho_d g R^2 / 9 \eta = R / t_s$ gives us $t_s$. Hence

$$P_{e_g} = \frac{t_R}{t_s} \approx \frac{6 \pi \Delta \rho a^4}{9 k_B T} \left( \frac{R}{a} \right)^{d+1}$$  \hspace{1cm} (5.13)

Our condition for gelation to occur in a system under gravitational influence is that $P_{e_g} \leq 1$ (i.e. sedimentation does not dominate diffusion) for clusters of size $R_{gel}$ (i.e. the cluster size at the gelation point in the absence of gravitational influence). Hence we set $P_{e_g} = 1$ and substitute the expression for cluster size $R_{gel}$ from the DLCA model for gelation, equ.5.12. Rearranging the expression gives us the volume fraction of the sample (at infinite bond energy) $\phi^*$ below which we should not see gelation,

$$\phi^* \approx \left( \frac{6 \pi \Delta \rho a^4}{9 k_B T} \right)^{\frac{1}{d+1}}$$  \hspace{1cm} (5.14)

where $d \approx 1.8$ for DLCA in 3 dimensions.

This infinite bond-energy limit of **gravity-dependent transient gelation line** is visualized in a schematic experimental non-equilibrium diagram, fig.5.10.

![Figure 5.10. A schematic non-equilibrium diagram for a colloid-polymer mixture. The effect of gravity (through particle size $a$ and particle-solvent density difference $\Delta \rho$) is to increase the minimum volume fraction (in the infinite bond energy limit) $\phi^*$ for transient gelation to occur.](image)

The model predicts that the effect of increasing the influence of gravity on the system (e.g. increasing the size of the particles $a$ or increasing the particle-solvent density difference $\Delta \rho$) is to increase $\phi^*$. In fact $\phi^*$ is particularly sensitive to the particle size $a$.

For samples with $\phi < \phi^*$ gravitational settling dominates before gelation can occur. Rapid sedimentation then takes place, the size of the sedimenting cluster size being determined by the competition between aggregation and destruction by shear flow [60]. For finite bond-energies (i.e. less than the infinite $C_p$ required at $\phi^*$ in fig.5.10) increasing volume fractions will be needed for gelation to occur as the bond-energy (or polymer concentration) is decreased, as
clusters are compactified by thermal rearrangement (i.e. $d$ increases from 1.8 to 3 as polymer concentration is decreased).

The predictions of this simple model are compared with experiment in Chapter 6, section 6.5.1.
Chapter 6

Delayed sedimentation observations

6.1 Introduction

We saw in the previous chapter that particular mixtures of colloid and polymer undergo transient gelation, presumably a detour on their journey to an equilibrium state of coexisting fluid and crystal. Qualitatively the (macroscopic) sedimentation behaviour of these transient gels was known; after a period of delay the gel becomes gravitationally unstable (i.e. 'collapses') and the colloidal bulk undergoes rapid sedimentation. Once sufficient compactification of the colloidal bulk occurs rapid sedimentation ceases abruptly — the sediment becomes metastable with respect to gravity. The metastable sediment then gradually compactifies over time.

Quantitatively however only preliminary measurements had been obtained [54]. It was decided therefore to perform some detailed measurements of sedimentation behaviour for various transient gels, with a primary interest in measuring latency time (delay to sedimentation), and to relate these measurements to the sample concentration variables \( \phi \) and \( C_p \). This information would then provide a useful context for planned low-shear rheological measurements of the transient gel. The first step therefore was to make some colloid-polymer transient gels.

6.2 Model system

Our samples comprise the same sterically-stabilized nearly-monodisperse ‘hard’ PMMA spheres (radius \( a = 301 \text{ nm} \)) dispersed in cis-decalin as described in chapter 1, with the addition of (relatively) small non-adsorbing polymer — in this case polystyrene (PS). The polystyrene is dissolved in the cis-decalin, a near theta-solvent at room temperature, so now our PMMA particles are dispersed in a polymer solution.

Each polymer molecule is envisaged as a long chain that adopts a ‘random-coil’ configuration
Figure 6.1. Schematic realization of a polymer coil. The polymer adopts a ‘random-coil’ configuration. The spherical volume defined by the radius of gyration $\delta$ of the coil is effectively an excluded volume for a colloidal particle.

(see fig.6.1). In the simplest approximation (valid for near-theta conditions) the polymer coils are assumed to be freely interpenetrable coils. The centre of a polymer coil is, however, excluded from coming closer than a distance $\delta$ from a colloidal particle, where $\delta$ would be something like the radius of gyration of the polymer molecule.

The polystyrene is of molecular weight $M_w = 370,000$, and when dissolved in cis-decalin at room temperature ($T = 19 \pm 2^\circ$ C) previous studies have determined its radius of gyration to be 19 nm [52]. Therefore our polymer-colloid size ratio is $\xi \approx 0.06$ i.e. the polymer coil is much smaller than the colloidal particle. The theta temperature of PS in cis-decalin is $T_\theta = 12.5^\circ$ C, so it is reasonable to assume coil interpenetrability as a first approximation under our experimental conditions ($T = 20^\circ$ C) [52]. In reality there will be departures from this ideal; effects of polymer nonideality in a colloid-polymer mixture are discussed by Warren et al. [61].

Adding small non-absorbing polymer to a hard-sphere suspension leads to the depletion potential between colloidal particles as discussed in chapter 1, and results in the equilibrium and nonequilibrium phase behaviour previously discussed in chapter 5.

6.3 Sample preparation

First a polymer stock solution was prepared. An amount of ‘dry’ PS (typically 0.3 g) was placed inside a ‘leak-proof’ teflon container, and then cis-decalin was added by weight in order to obtain a polystyrene stock solution of concentration $C_p^{\text{stock}} \sim 20$ mg cm$^{-3}$.

A batch of PMMA colloidal particles suspended in cis-decalin was prepared, with concentration in the coexistence region. This batch was prepared and calibrated as previously described in chapter 4.

Amounts (by weight, calculated using literature density values) of batch colloidal suspension, PS stock solution and cis-decalin were mixed in glass cuvettes to give a colloid-polymer mixture.
CHAPTER 6. DELAYED SEDIMENTATION OBSERVATIONS

2cm

1 cm

1 cm

Figure 6.2. The 'standard' colloid-polymer mixture sample used in this study; square cross-sectional cell (1 cm²), cell height ≈ 4 cm, the mixture half-filling the cell.

of desired colloid volume fraction $\phi$ and polymer concentration $C_p$ (in mg cm⁻³).

It should be noted for clarity that the volume fraction $\phi$ is the fractional volume of the total sample volume occupied by colloid, and that the polymer concentration is the mass of polymer per total sample volume, not the polymer mass per unit volume of solvent.

Most of the sample cuvettes were of square cross-section (= 1 cm²) and were ≈ 4 cm tall (see fig.6.2). They were sealed with a teflon stopper which had a viton o-ring fitted on the neck, greatly reducing solvent evaporation. Typically cuvettes were half filled with colloid-polymer mixture. The cuvette walls were optically smooth i.e. typically flat to better than 1 μm (~ particle diameter) over the whole window area. All newly-made samples were slow tumbled over a day to ensure good mixing.

Approach to concentration selection

The approach to sample concentration selection ($\phi, C_p$) was to choose several nominal colloidal volume fractions ($\phi = 0.10, 0.20, 0.30$) and to vary the polymer concentration $C_p$, rather than the converse. The reasons for this are:

(i) Our 'prejudiced' model-view focuses on the colloidal particles and views the polymer primarily as a mediator of an effective attractive force between the particles.

(ii) The difficulty in relating the experimental parameter $C_p$ to the 'strength' of the depletion potential between different sample volume fractions. As previously mentioned in chapter 5 it is the polymer concentration in the free volume that is proportional to depletion potential strength. However the precise determination of the free volume depends on all colloidal particle positions, and is a complex problem. Our estimate is a mean-field approximation. Table 6.1 displays values of the free volume fraction $\alpha$ (calculated using equ.5.6) for the various volume
Table 6.1. Free volume fraction $\alpha$ as a function of colloidal volume fraction $\phi$ calculated using equ.5.6.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$\alpha(\phi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.88</td>
</tr>
<tr>
<td>0.15</td>
<td>0.84</td>
</tr>
<tr>
<td>0.20</td>
<td>0.76</td>
</tr>
<tr>
<td>0.30</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Concentration uncertainties

Uncertainty in the final sample concentrations $\phi, C_p$ can occur due to (i) concentration uncertainty in the colloid and polymer solution batches and (ii) subsequent solvent evaporation once the sample has been made.

The uncertainty in the colloid batch has been discussed before in chapter 4. The calibration method, batch solvent evaporation and unknown particle density lead to an uncertainty in volume fraction $\phi$ of ±0.003.

Uncertainty in polymer stock solution concentration could arise from two sources; stock solution solvent evaporation and PS weighing errors. The former had negligible effect on $C_p^{stock}$. However a not insignificant error in stock concentration can arise in initial preparation. This is because preparation of the polystyrene stock solution involves weighing a small mass of PS (~0.3 g) in a heavy container (~35 g) and adding a large mass of cis-decalin (~15 g). A reasonable estimate of uncertainty in mass measurement (using precision scales) is ±0.0030 g, which would result in an error of ~1% in $C_p$. For a typical transient gel ($\phi = 0.20$) of polymer concentration $C_p = 5.25 \text{ mg cm}^{-3}$ this would lead to an uncertainty in $C_p$ of ±0.05 mg cm$^{-3}$. Significant changes are seen in sample behaviour over a concentration step of 0.25 mg cm$^{-3}$, so we can see that this is not a negligible error. However, this is an absolute error in polymer stock concentration. Samples made from the same stock (as most are within any one volume fraction) will not be affected relatively.

In general solvent evaporation from samples was negligible. With a few marked exceptions, solvent evaporation lead to an uncertainty in $C_p$ of ±0.01 mg cm$^{-3}$, and had no significant effect on volume fraction $\phi$.

6.4 Experimental method

The simple apparatus for measuring the solvent-sediment interface position $z(t)$ is shown in fig.6.3. The sample is suspended (vertically aligned by eye) in a tall glass-walled water tank,
which itself sits in a recirculating bath. This maintains the sample’s temperature at $T = 20.0 \pm 0.2$° C. The sample cuvette faces square to a CCD camera linked to a time-lapse video recorder which records the sample’s macroscopic sedimentation behaviour.

Prior to experiment the sample is slow tumbled for at least an hour in order to randomize the particles (often preceded by a few minutes of vigorous vortex mixing to redisperse stubborn compact sediments). Unfortunately there is an inevitable delay time between slow tumbling and transferral of the sample to the water tank and commencement of recording. An effort was made to continue the slow tumbling by hand. However this delay is tiny compared to the observation time; the main concern was to ensure a ‘smooth transition’ from slow tumbling to rest in the water tank to minimise unwelcome disturbance to the gel structure as it forms (this happens very quickly, ~ seconds i.e. the time for the small-angle light-scattering ‘frozen’ ring to appear). Once the randomized sample is set in place it is simply left alone to evolve, whilst the VCR records.

Once the ‘rapid’ sedimentation is complete (i.e. sediment is metastable) the data is obtained from the video recording. The video is played back on a large (16 x 12 inch) television set, resulting in a magnified image (typically 5 - 10x). The (magnified) position of the solvent-sediment interface $Z(t)$ was then measured straight from the screen using a ruler (see fig.6.4). Measurement was in relation to the base of the sample meniscus, the most clearly defined and reproducible reference point ($Z = 0$ at the meniscus base, $Z(t) < 0$ for the sediment below the meniscus base). The ratio of the cuvette cell’s onscreen width $W$ and real width $w$ determined the magnification. The shape of images on the screen was found to be slightly distorted from reality; vertical distances were increased by ~ 3 % in relation to their width. The ‘real’ interface position $z(t)$ is then

$$z(t) = (0.97)\frac{w}{W}Z(t)$$ (6.1)

Conversion of interface position $z(t)$ to ‘height’ $h(t)$ is simply achieved by adding the height of the meniscus base $h_{mb}$.

Typical measurement time intervals were ~ 30 mins, but this varied according to the stage
CHAPTER 6. DELAYED SEDIMENTATION OBSERVATIONS

Figure 6.4. Acquisition of sediment-interface position $z(t)$ data from the video recording.

of sedimentation from 20 mins to 12 hrs (the determining factor was resolution of change in sediment position).

There are some points to note in the measurement of the sediment interface position. Early measurements take place in the ‘corner’ of the meniscus (for square sample cells this typically extends up a distance of $\sim 5$ mm from the meniscus base). During the latency period there was often some variation in the position of the interface across the sample width (see section 6.5.2), particularly towards the end of latency where ‘buckling’ of the interface often occurred (deviations were typically $\pm 2$ mm on screen). In such instances an average or ‘representative’ position was judged. However during the collapse the interface was very level. A more detailed pictorial description of the the transient gel latency and collapse is given later in this chapter.

The ‘raw’ data then consists of measurements of $z(t)$ vs. $t$ for each sample at $\phi, C_p$.

Errors

For time measurements $t$ after randomization there are essentially no errors, as the timescale for transferral to the setup is negligible compared to the timescale of experiment, and the time between each height measurement is large (at least 20 mins).

Onscreen interface position measurements $Z(t)$ — distances on screen can be measured to an accuracy of $\pm 1$ mm, whereas the typical total screen distance is at least 100mm — therefore the error is $\pm 1\%$.

Real interface position measurements $z(t)$ — conversion of screen to real interface position data involves determination of the screen magnification. The screen magnification was judged by scaling the screen width ($\pm \sim 3\%$) of the sample cell to the real width ($\pm 2\%$). Combination of these errors leads to a real interface position error of $\sim 4\%$. 


6.5 Results

6.5.1 Basic categorization of sedimentation behaviour

The sedimentation behaviour of nonequilibrium colloid-polymer samples clearly fell into two distinct categories; those that exhibited a period of 'latency' (delay to sedimentation) before rapid sedimentation (transient gels) and those that did not (spinodal-like or nucleation-like). The exhibition of latency is equated with the transient gelation of the colloidal particles.

The dependency of transient gelation on colloid volume fraction $\phi$ and polymer concentration $C_p$ is shown in in fig.6.5, a nonequilibrium diagram shown for comparison with the experimentally obtainable equilibrium phase diagram for this system. We can compare it with fig.5.5, a similar

![Diagram showing the relationship between $\phi$ and $C_p$.](image)

**Figure 6.5.** Nonequilibrium diagram for the PMMA-PS colloid-polymer mixture (in cis-decalin) used in this study. The particle radius $a = 301$ nm, the polymer radius of gyration $\delta \approx 19$ nm, hence the polymer-colloid size ratio $\xi = 0.06$. Below the transient gelation line $C_p^I(\phi)$ samples immediately sediment at fast rates; above $C_p^I(\phi)$ a delay to rapid sedimentation is observed.

diagram obtained by Poon et al. [52] for a PMMA-PS system with a comparable colloid-polymer size ratio, but using smaller particles ($a = 240$ nm) dispersed in a mixture of cis-decalin and tetralin (for index matching). Here identification of transient gelation was made primarily on
CHAPTER 6. DELAYED SEDIMENTATION OBSERVATIONS

<table>
<thead>
<tr>
<th>Study</th>
<th>$\Delta \rho$ (g cm$^{-3}$)</th>
<th>$a$ (nm)</th>
<th>Experimental $\phi^*$</th>
<th>Predicted $\phi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allain et al. [58]</td>
<td>1.7</td>
<td>70</td>
<td>$\sim 0.003$</td>
<td>0.03</td>
</tr>
<tr>
<td>Poon et al. [52]</td>
<td>0.3</td>
<td>240</td>
<td>$\sim 0.02$</td>
<td>0.10</td>
</tr>
<tr>
<td>This study</td>
<td>0.3</td>
<td>300</td>
<td>$\sim 0.1$</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 6.2. Comparison experimental and predicted values of the minimum volume fraction $\phi^*$ required for gelation to occur for high bond energies.

observation of a ‘frozen’ small-angle light scattering ring. The transient gelation line, $C^*_t(\phi)$, is a sharply decreasing function of volume fraction in both cases. However, in our system higher volume fractions are required to see transient gelation at moderate polymer concentrations. This can be explained as a result of the greater influence of gravity on the gelation process due to larger particle size $a$ as described in section 5.6.3 chapter 5.

We might attempt to quantify the change in the transient gelation line $C^*_t(\phi)$ by comparison of the minimum volume fraction $\phi^*$ required for gelation in the high bond energy limit as described in section 5.6.3. However it is not clear from fig.6.5 what this value should be. Also we might not expect to see a clearly defined value of $\phi^*$ in a colloid-polymer system as the assumption of polymer-coil ideality (i.e. interpenetrability) and hence the depletion-potential model will break down as the overlap polymer concentration ($\approx 14$ mg cm$^{-3}$ for this system) is approached. However, for the sake of comparison values of $\phi^* \sim 0.02$ and $\sim 0.1$ are judged respectively for the system of Poon et al. and of this study. These values are compared with the predicted values of $\phi^*$ from equ.5.14 in table 6.2. Also included is the value obtained by Allain et al. [58] for a dispersion of dense calcium carbonate particles in water, aggregating via the Van der Waals attraction.

Quantitatively the model of section 5.6.3 fails to predict the experimentally observed values of $\phi^*$. This is not surprising considering its simplicity, as well as difficulty in judging the experimental value of $\phi^*$. Qualitatively however the model remains good as regards the observed increase of $\phi^*$ with increasing particle size $a$.

Brief mention is made of the nonequilibrium line $C^*_{p}^{\text{eq}}(\phi)$. In the previous study by Poon et al. (fig.5.5) the onset of nonequilibrium behaviour was sharply marked by the appearance of a small-angle ring (with the suppression of crystallization and rapid sedimentation of (apparently) all colloidal material in the sample). In this investigation however all categorization was based on visual observation of macroscopic phase and sedimentation behaviour only. It is noted that the crosses (+) just over the ‘nonequilibrium line’ represent samples whose macroscopic behaviour appeared ambiguous to me. Their rapid sedimentation behaviour was identical to other (nonlatency) nonequilibrium samples, yet two factors pointed towards their classification as coexistence samples. The first was the clear existence of a dilute fluid phase once rapid sedimentation of most of the colloidal material had begun (instead of the usual visually clear supernatant). The second was the observation of very small closely-packed crystallites in the metastable sediment after several days. These crystallites were hard to see and were only clearly identified on the top and in the corner of the sediment. However one ‘had the feeling’ that they existed throughout the bulk. This may be a sign that nonequilibrium behaviour is merely a detour on the samples’ journey to an equilibrium state of coexisting gas and crystal
6.5.2 Images and description of transient gel latency and collapse

In an attempt to understand the transition from latency to subsequent rapid sedimentation in a transient gel sample an effort was made to obtain images that might reveal the detailed mechanism leading to the 'collapse'. The following images are of a 'weak' transient gel sample (see later) $\phi = 0.20$, $C_p = 5.5 \text{ mg cm}^{-3}$, exhibiting a latency period of $t_{\text{lat}} \approx 3\frac{1}{2} \text{ hours}$. The sample is lit from the right with a thin plane of white light across the front of the sample; the images are of the top half of the sample plane adjacent to the front glass wall. Excepting the first two, all pictures were image-enhanced using a computer image-enhancing program to increase the contrast of the texture and structure observed by eye (image-enhancing involved subtracting the 'background' image (a) at $t=0$ and magnifying the difference, hence enhancing poor-contrast inhomogeneities). The sample was not temperature controlled. Here the images are merely presented and described with a little interpretation; speculation of the physics behind the cause of the transient gel collapse are left until chapter 8.
(a) time $t=0$ mins. The sample appears homogeneous. The white arc of the meniscus can be clearly seen. The black edges on the left and right are the sides of the sample container (width = 1 cm). Within minutes we expect the sample to have 'gelled', and would see a 'frozen' small-angle light scattering ring.

(b) $t=10$ mins. Rapid sedimentation has already occurred in the corners of the meniscus. This 'early' sedimentation is purely a meniscus effect. The rest of the sample remains homogeneous.

(c) $t=2$ hours. The following pictures are image-enhanced. Over half the latency period has passed, yet visually there is no obvious change in the structure of the bulk, which essentially remains homogeneous. However a faint graininess can be discerned through the sample bulk; it is not known whether this is the gel structure or an effect of image-enhancement. The solvent-colloid interface is clearly defined; the interface shows signs of 'buckling' i.e. uneveness. The colloidal material near the interface appears brighter, perhaps indicating that this region is denser (perhaps containing the colloidal material from the meniscus corners).

(d) $t=3$ hrs 40.5 mins. The sample is nearing the end of the latency period and approaching collapse. A vertical inhomogeneity or 'channel' can clearly be seen, ending in a bright (dense?) region of material in the corner of the colloidal sediment. Other recordings of transient gels exhibit similar channels and 'fingers' moving upwards through the bulk. 'Motion' can often be detected along these channels, perhaps indicating that solvent/colloidal material is flowing up through them. Slow sedimentation of the interface has continued, and the unevenness persists. The top corners of the sediment are also beginning to show a 'coarse structure', perhaps indicating strong density variations. Typical length scale (real) $\sim 0.1$ mm i.e. $\sim 100$ particle diameters. We are now seeing 'structure' locally; the rest of the bulk however still remains essentially homogeneous.
After \( \approx 3 \) hours 40 minutes of very little happening on this scale of observation, the next 10 minutes ((e)-(i)) is very dramatic. The 'dense' region in the top-right of the sediment (large aggregate?; size (real) \( \sim 1 \text{ mm} \sim 1000 \) particle diameters) appears to fall through the homogeneous bulk at a velocity of \( \sim 3 \mu \text{m s}^{-1} \), leaving a 'coarsened structure' in its wake. The coarse region in the top-left begins to extend through the bulk too. We see macroscopic (i.e. on the length-scale of the sample cell) convective-like flow in the sample, appearing to 'break up' the transient gel structure. Note the extreme unevenness of the interface.
The coarse region has the appearance of many individual clusters, which proceed to 'fall through' the homogeneous region. The interface has smoothed out (hard to see due to image-enhancement). Note that the interface position does not change much.
(m) \( t=4 \text{ hrs 22 mins} \). A coarsened structure now appears throughout the bulk of the sediment, and rapid sedimentation begins.

(n) \( t=5 \text{ hrs 28.5 mins} \). Considerable change in sediment position now occurs. Note that the top layer of the sediment appears free of structure.

(o) \( t=6 \text{ hrs 13.5 mins} \). The sediment is now approaching the metastable phase. The structureless region has extended further into the bulk; any remaining structure is at the bottom half of the sediment.
6.5.3 Sedimentation behaviour — interface position over time

We now focus on the macroscopic sedimentation behaviour of the nonequilibrium colloid-polymer mixtures. Figs. 6.6, 6.7 and 6.8 show a selection of ‘sedimentation profiles’ — position $z(t)$ against time $t$ — for varying polymer concentrations at the chosen volume fractions of $\phi = 0.10$, $0.20$ and $0.30$ respectively. Broadly speaking, samples at $\phi = 0.10$ showed no latency, whilst most of the samples at volume fractions of $\phi = 0.20$ and $0.30$ did exhibit a delay to sedimentation.

First we turn our attention to fig. 6.6, $\phi = 0.10$. We see rapid sedimentation beginning immediately for these samples, at velocities $V_r, \sim 1 \mu m s^{-1}$. This rapid sedimentation velocity is well defined, and can be seen to decrease with increasing polymer concentration. The rapid sedimentation ends quite abruptly and the sediment becomes metastable, slowly compactifying at $\sim 10 \text{ nm s}^{-1}$. A latency can be observed at this volume fraction, but requires (relatively) very high polymer concentrations, $C_p \approx 12 \text{ mg cm}^{-3}$, to achieve a latency of just a few hours. This is around the polymer overlap concentration at this volume fraction.

Looking at fig. 6.7 ($\phi = 0.20$) we see latency exhibited for polymer concentrations not far over the nonequilibrium boundary $C_{p}^{\text{neq}}$. During the latency period there is not a complete cessation of sedimentation; rather one sees slow sedimentation at $\sim 10 \text{ nm s}^{-1}$. However, it must be noted that the sediment interface is at this stage residing in the ‘corners’ of the sample meniscus. This 'sedimentation' is probably just local collapse and compactification of the gel structure (see later section on meniscus). However for the gel samples with high polymer concentrations this slow sedimentation continues below the base of the meniscus — here the sedimentation must be ‘real’. As one would expect, the latency period increases with polymer concentration.
Figure 6.7. Sediment position $z$ over time $t$ for $\phi = 0.20$ colloid-polymer mixtures of varying polymer concentration $C_p$. Latency times $t_{lat}$ are typically $\sim$ hours.

The latency period is typically $\sim$ hours.

The end of latency is marked by a sharp transition to rapid sedimentation (or 'collapse'). Here the rapid sedimentation velocity is fairly well defined and is of the same order as for nonlatency samples. It also seems to be independent of polymer concentration. As in nonlatency samples the rapid sedimentation ends quite abruptly, the sediment becoming metastable. Interestingly all the sedimentation curves show a close similarity of form.

Finally we look at fig.6.8, showing sedimentation profiles for $\phi = 0.30$. The most striking feature is the huge increase in the latency periods for these samples, ranging from $\sim$ hours to $\sim$ days. Again, the rapid sedimentation velocity seems to be independent of polymer concentration (excepting the sample with the greatest polymer concentration).

We will now take a closer look at the three stages of transient gel life — latency, rapid sedimentation and slow compactification — in order to glean quantitative information about the transient gel sedimentation behaviour and its dependency on sample volume fraction $\phi$ and polymer concentration $C_p$. 

6.5.4 Latency

The exhibition of a latency period is a fundamental property of the transient gel; measurement of the latency time $t_{\text{lat}}$ and the determination of its dependency on experimental variables is therefore of primary interest. It is the period of time that elapses before the collapse or rapid sedimentation of the transient gel — effectively the gel lifetime. During the latency period the colloidal mesostructure is effectively frozen in a single sample-spanning cluster. End of the latency period signals the destruction and collapse of this structure.
The latency time $t_{\text{lat}}$ was obtained from the sedimentation profile in two different ways (see fig. 6.9). The first method involved fitting straight lines to the linear sections of the sedimentation profile during latency and collapse. The $x$-coordinate of the point of intersection of these lines gave the latency time $t_{\text{lat}}$. The second method involved simply selecting the data point preceding the greatest change in sedimentation velocity i.e. the sharp transition between latency and collapse. The $x$-coordinate of this data point gave a second estimate of the latency time $t_{\text{lat}}$. The two different methods gave close agreement. Method 1 was easier when a sharp transition was hard to judge. Method 2 was better for comparing the latency times of samples of very different heights — see later.

The dependency of the transient gel latency time $t_{\text{lat}}$ on polymer concentration $C_p$, for samples at volume fractions $\phi = 0.20$ and 0.30, is shown in figs. 6.10 and 6.11.

To first order all samples were the same height, $\sim 2$ cm (this will be of importance later). Essentially latency time has an exponential-like dependence on polymer concentration for 'moderate' volume fractions. The dependence becomes more sensitive as the volume fraction $\phi$ increases. It is worth noting the variation in latency time for each sample. The standard deviation in $t_{\text{lat}}$ for each sample ranged from $\sim 20 - 10\%$ (over 2-3 measurements). This is probably due to a
Figure 6.11. Latency time $t_{\text{lat}}$ as a function of polymer concentration $C_p$ for $\phi = 0.30$ samples. Again the dependency is exponential-like; however $t_{\text{lat}}$ is much more sensitive to polymer concentration than for $\phi = 0.20$ samples.

Figure 6.12. Latency time $t_{\text{lat}}$ as a function of free polymer concentration $C_p^{\text{free}}$ for various volume fractions $\phi$. 
combination of experimental method (e.g. variations in randomization) and an inherent vari-
ation due to the 'statistical nature' of the transient gel de-percolation. We note that for sample
$\phi = 0.30, C_p = 5.00 \text{ mg cm}^{-3}$, latency time becomes difficult to define; the ‘slow sedimentation’
of the latency period takes the interface to the height at which slow compactification begins,
h_{\text{fn}} — see later.

Fig.6.12 displays the latency times for volume fractions $\phi = 0.10, 0.15, 0.20$ and $0.30$ as a
function of the free polymer concentration $C_p^{\text{free}}$, for comparison. This highlights the strong
dependency of the transient gel lifetime on volume fraction $\phi$. We see that for lower volume
fractions $t_{\text{lat}}(C_p^{\text{free}})$ has a linear dependency, evolving into a dependency that becomes much
more acute on free polymer concentration as the volume fraction increases.

Here we resist attempting to make quantitative predictions on the nature of the dependence of
$t_{\text{lat}}$ on $\phi, C_p^{\text{free}}$; as we shall see later the latency times measured are not ‘fundamental’ to the
sample only but can be affected by other experimental parameters.

6.5.5 Rapid sedimentation/collapse

On examination of the collapse section of the transient gel sedimentation profiles it can be seen
that the rapid sedimentation velocities are (to first order) the same, at least for samples of
the same volume fraction. For $\phi = 0.20$, the collapse velocity ranges from $0.5 - 0.8 \text{ \mu m s}^{-1}$,
with a tendency for those gels with greater polymer concentrations to have the higher collapse
velocities. For $\phi = 0.30$ collapse velocity ranges from $0.3 - 0.7 \text{ \mu m s}^{-1}$, with a tendency for
those gels with intermediate polymer concentrations to have the higher collapse velocities. For
collation, the Stokes velocity of a single PMMA particle of radius $\approx 300 \text{ nm}$ in cis-decalin
is $\approx 0.02 \text{ \mu m s}^{-1}$. Closer inspection of the collapse reveals slight acceleration of the sediment
during this phase.

Due to experimental limitation and the nature of the collapse phase, there is no noticeable
pattern to be found in the collapse velocities of the transient gel samples. However, one does
see a pattern in the rapid sedimentation of the nonlatency or spinodal-like samples of $\phi = 0.10$.
These samples have well defined rapid sedimentation velocities.

Fig.6.13 shows the rapid sedimentation velocity as a function of polymer concentration. This
shows a decrease in the sediment velocity with increasing polymer concentration. At first this
seems surprising. The size of a cluster during sedimentation will depend on the competition
between aggregation (due to the depletion force) and break-up of clusters due to shear-flow
[60]. As the strength of the depletion force is increased one might expect larger clusters, with
correspondingly greater masses, sedimenting at higher velocities. The increase in background
viscosity does not compensate for the decrease in rapid sedimentation velocity (the increase in
polymer solution viscosity is only $\approx 20 \%$, whilst the velocity falls by half). However we expect
the clusters to become more ramified as the strength of the interparticle bonds increases (i.e.
increasing polymer concentration). The ratio of drag to weight for a cluster would increase as
it becomes less compact, resulting in a corresponding decrease in sedimentation velocity.
Figure 6.13. Rapid sedimentation velocities of nonlatency samples, $\phi = 0.10$, as a function of polymer concentration.

6.5.6 Compactification

Rapid sedimentation eventually comes to a halt; the sediment then very slowly compactifies at $\sim 10$ nm s$^{-1}$, and at progressively slower rates. The transition point from rapid sedimentation to metastable sediment is not as easily defined as for the collapse. The deceleration is smoother than the sharp change in velocity often seen at the end of latency. The position, $z_{\text{fn}}$, at which this ‘final’ sediment was reached was defined as the point at which the sediment velocity became an order of magnitude smaller than the characteristic collapse velocity of the sample.

The final sediment position $z_{\text{fn}}$ is converted to a height $h_{\text{fn}}$, and is displayed (as a percentage of the total sample height $h_{\text{tot}}$) in fig.6.14 as a function of free polymer concentration $C_{p}^{\text{free}}$ for the various volume fractions $\phi$ studied. The graph includes final sediment heights for nonlatency samples as well as for transient gels.

First we note the tendency for $h_{\text{fn}}$ to increase with increasing polymer concentration. To first order this increase is linear, and is continuous between nonlatency and transient gel samples (to experimental accuracy). This is consistent with the picture that the clusters become (and remain) more ramified as the depletion force is increased, resulting in a more voluminous metastable sediment. The final sediment height $h_{\text{fn}}$ also increases linearly with volume fraction $\phi$ (first seen by A.Pirie [62]), shown in fig.6.15 for a fixed bond strength ($C_{p}^{\text{free}} = 6.0$ mg cm$^{-2}$). This graph seems to imply that a transient gel of $\phi \approx 0.50$ would not collapse (for this bond strength).

Fig.6.16 displays the metastable sediment volume fraction $\phi_{\text{fn}}$ ($= \phi [h_{\text{tot}}/h_{\text{fn}}]$) as a function of $C_{p}^{\text{free}}$ for various volume fractions $\phi$. Somewhat surprisingly there is a large variation in $\phi_{\text{fn}}$ at lower polymer concentrations between different sample volume fractions $\phi$. For example, at ‘low’ polymer concentrations a sample of $\phi = 0.10$ has a metastable sediment volume fraction
Figure 6.14. Metastable sediment heights $h_{\text{fin}}$ (expressed as a percentage of the total sample height $h_{\text{tot}}$) as a function of free polymer concentration $C_p^{\text{free}}$ for various volume fractions $\phi$. The circled symbols indicate nonlatency samples.

Figure 6.15. Metastable sediment heights $h_{\text{fin}}$ (expressed as a percentage of the total sample height $h_{\text{tot}}$) as a function of volume fraction $\phi$ for a fixed depletion potential ($C_p^{\text{free}} = 6.0 \text{ mg cm}^{-3}$)
Figure 6.16. Metastable sediment volume fractions $\phi_{fn}$ as a function of free polymer concentration $C_{p}^{\text{free}}$ for various sample volume fractions $\phi$. The circled symbols indicate nonlatency samples.

$\phi_{fn} \approx 0.35$, compared with $\phi_{fn} \approx 0.50$ for a $\phi = 0.30$ sample. It is not clear why $\phi_{fn}$ should exhibit such a strong volume fraction dependence. Here we simply note that $\phi_{fn}$ is both volume fraction and polymer concentration dependent.

Tentatively one might use fig.6.14 to predict the free polymer concentration required to avoid transient gel collapse for a sample of volume fraction $\phi$. For example, by extrapolation fig.6.14 implies that a sample of $\phi = 0.30$, $C_{p}^{\text{free}} \approx 12$ mg cm$^{-3}$ would not collapse, i.e. the entire sample is a metastable sediment.

6.5.7 Sample size and geometry

All of the observations so far presented have been the result of experiments performed on samples of identical geometry and similar size i.e. ~ 2 cm high in square cross-section glass cuvettes (1 cm $\times$ 1 cm). However, if we envisage the destruction of the gel structure occurring due to, or being affected by, its own weight, we might expect to see a dependency of the latency time on sample size, e.g. height. Therefore preliminary investigations were undertaken into the effect of sample size and geometry on sedimentation behaviour in order to shed light on the processes behind the gel collapse.

Height

The height dependency of sedimentation behaviour was investigated for three different samples listed in table 6.3.

Doubling the height of samples 1 and 2 had no obvious effect on the latency time of the sample,
CHAPTER 6. DELAYED SEDIMENTATION OBSERVATIONS

<table>
<thead>
<tr>
<th>Sample type</th>
<th>$\phi$</th>
<th>$C_{\text{free}}^\text{mg cm}^{-3}$</th>
<th>Latency time (standard sample) $t_{\text{lat}}$ (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>7.22</td>
<td>$\approx 2$</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
<td>5.84</td>
<td>$\approx 5$</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>7.02</td>
<td>$\approx 16$</td>
</tr>
</tbody>
</table>

Table 6.3. Samples used for investigating the effect of height on latency time.

as can be seen in fig.6.17. The only effect, not surprisingly, was to increase the distance over which rapid sedimentation occurred. A slight increase in $\phi_{\text{fin}}$ was also seen. Sample type 3

![Figure 6.17. Sedimentation profiles for sample type 2; (x) sample height $h_{\text{tot}} \approx 2 \text{ cm}$, (black □) sample height $h_{\text{tot}} \approx 4 \text{ cm}$. No change in the latency period is seen.](image)

however displayed a markedly different response to a change in sample height, as can be seen in the sedimentation profiles shown in fig.6.18. Essentially latency time $t_{\text{lat}}$ decreases with increasing sample height $h_{\text{tot}}$ (fig.6.19), indicating that for this sample its own weight plays a role in determining when it will collapse.

This clear difference in height dependency of sedimentation behaviour suggests that transient gels can be divided into two categories. For 'weak' transient gels (standard latency $t_{\text{lat}} \leq 10 \text{ hrs}$ say) 'thermal rearrangement' leads to de-percolation and collapse. For 'strong' transient gels the sample's own mass leads to a premature end to the gel structure, before thermal rearrangement causes de-percolation. Therefore one would expect an 'inherent' latency time significantly greater for strong transient gels (perhaps obtained by extrapolation of data shown in fig.6.19) than previously measured for our standard samples, leading to an even more acute dependency of latency time $t_{\text{lat}}$ on $\phi, C_{p}^\text{free}$ than shown in fig.6.12.
Figure 6.18. Sedimentation profiles for sample type 3. The total sample height was varied, $1 \, \text{cm} \geq h_{\text{tot}} \geq 4 \, \text{cm}$. Decreasing the sample height significantly increases the latency time $t_{\text{lat}}$.

Figure 6.19. Latency time $t_{\text{lat}}$ as a function of sample height $h_{\text{tot}}$ for sample type 3.
Meniscus

It is evident that much of the 'slow sedimentation' that occurs during the latency period is taking place in the corners of the meniscus. It was therefore desirable to 'remove' the meniscus for two reasons; firstly, to see if its presence had any strong influence on the latency time and secondly, to see if the slow sedimentation is merely an ornamentation due to the meniscus or whether it would occur in its absence.

In order to 'remove' the meniscus samples were made that filled the sample cuvettes. A small square of stainless steel (~ 3 mm x 3 mm) was included to enable mixing of the sample. Unfortunately total exclusion of air from the samples was not achieved; each sample contained a 'small' air bubble ~ 2 mm radius. However, this still resulted in a large reduction in the meniscus. Fig. 6.20 compares the initial sedimentation behaviour of a standard 'weak' transient gel (sample type 1) with its 'no-meniscus' equivalent. We see no significant change in the latency time within error. It also appears that most of the slow sedimentation is purely a meniscus effect, at least for the weak gels — the sample without a meniscus does not show any settling before collapse. We do however see some slow sedimentation occurring for a no-meniscus transient gel with a long lifetime (i.e. a 'strong' gel, sample type 3), as is seen in fig. 6.21.
CHAPTER 6. DELAYED SEDIMENTATION OBSERVATIONS

Figure 6.21. Initial sedimentation behaviour of a no-meniscus strong transient gel (sample type 3). Some slow sedimentation is seen during latency ($h_{tot} \approx 4$ cm).

Width

The effect of the sample width on sedimentation behaviour was also investigated for the weak transient gel. Since the weak gel shows no significant height dependency, it was easy to take the no-meniscus sample of the previous section and observe its sedimentation behaviour in a horizontal orientation, effectively increasing its width by a factor of four. This approach was improved by taking a wide cuvette (2 cm $\times$ 1 cm cross-section) and recording the sedimentation behaviour in vertical and horizontal orientations (fig.6.22).

Figure 6.22. Vertical and horizontal orientations of the wide cuvette (2 cm $\times$ 1 cm cross section) used in the investigation of the effect of sample width on latency period (weak gel).

The results are shown in fig.6.23. No significant effect on latency time was observed.
Figure 6.23. Sedimentation profiles of a weak gel (sample type 1) with sample cells in vertical and horizontal orientations to investigate the effect of sample width on latency time. 1 cm x 1 cm cross-section cell (×) horizontal orientation (○) vertical; 2 cm x 1 cm cross-section cell (+) horizontal (filled ○) vertical. No significant change in latency time is seen.

Figure 6.24. Comparison of the standard sedimentation behaviour of the weak gel sample type 2 (×) with that in a thin cell of 0.2 cm x 1 cm cross-section (†). The latency time is essentially unaltered.
The above experiments increase the width. However one might expect to see an increased latency time for a sample in a sufficiently 'narrow' sample cell. Fig.6.24 compares the standard sedimentation behaviour of the weak gel (sample type 2) with that in a thin cell of 0.2 cm × 1 cm cross section. Although there is some difference in the initial slow sedimentation (very different meniscus shapes) the latency time is essentially unaltered.

Unfortunately equivalent experiments were not performed on the strong gel. Considering a clear height dependence was observed it seems likely that one would see a strong width dependence too. Preliminary measurements of strong gel samples in cylindrical containers of varying width seem to suggest a 'critical' width dependence — see following section.

Circular cross-section

The sedimentation behaviour of transient gels in cylindrical containers was briefly investigated to see if any change in sample latency time occurred. Any differences would have important ramifications for transient gel experiments in the Zimm viscometer, essentially a cell of circular cross-section. Fig.6.25 compares the sedimentation profiles of the weak gel sample type 2 in the standard and cylindrical cells (cylindrical cell diameter ≈ 0.8 cm).

![Figure 6.25](image)

**Figure 6.25.** Comparison of the standard sedimentation behaviour of the weak gel sample type 2 (×) with that in a cylindrical cell of 0.8 cm diameter (○). The latency time of the sample in the cylinder was consistently half that of the sample in the standard square cross-section cuvette.

Somewhat surprisingly the latency period of the weak transient gel in the cylindrical cell was consistently about half that of the sample in the standard square cross-section cuvette. Why this should be is not clear, especially in light of the height/width independence observed for
CHAPTER 6. DELAYED SEDIMENTATION OBSERVATIONS

<table>
<thead>
<tr>
<th>Cell no.</th>
<th>Description</th>
<th>width/diameter (cm)</th>
<th>( t_{\text{lat}} ) (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Square cross-section cuvette</td>
<td>1</td>
<td>( \approx 20 )</td>
</tr>
<tr>
<td>2</td>
<td>Cylindrical cuvette</td>
<td>0.8</td>
<td>( \approx 20 )</td>
</tr>
<tr>
<td>3</td>
<td>Measuring cylinder</td>
<td>1.5</td>
<td>( \approx 5 )</td>
</tr>
<tr>
<td>4</td>
<td>Sample jar</td>
<td>3</td>
<td>( \approx 6 )</td>
</tr>
</tbody>
</table>

Table 6.4. Latency times of a strong transient gel in various cylindrical containers.

The weak transient gel in containers of a cuboid cross-section. Perhaps the circular 'boundary conditions' effect the aggregation process and result in a different gel structure. This seems unlikely however as the wall curvature is small on the scale of the particle size. Perhaps the corners in a cuboid cross-sectional cell somehow lead to an increased latency period, by increasing the rigidity/strength of the gel structure; however, this seems inconsistent with the observed height/width independence (there was also no height dependency for the weak gel in a cylindrical cell).

The picture becomes even more confusing when one considers the sedimentation behaviour of a strong gel in various cylindrical cells (note: larger particle size \( a = 326 \text{ nm} \) — see next chapter). Samples were placed in a standard square cross-section cuvette, cylindrical sample cell (\( \approx 0.8 \text{ cm diameter} \)), measuring cylinder (\( \approx 1.5 \text{ cm diameter} \)) and a sample jar (\( \approx 3 \text{ cm diameter} \)). All samples were the same height (\( \approx 2 \text{ cm} \)). The results of this brief investigation are summarized in table 6.4.

Now there is no difference between the latency times of samples in cells 1 and 2 as there was for the weak gel. Instead there would appear to be a critical width dependence, as the latency time falls dramatically for cells 3 and 4. It is possible that this large difference in latency period is partially due to differences in cell wall roughness for the various containers. Both cells 1 and 2 are designed for light-scattering, and hence are smooth on the length scale of the particles, whereas cells 3 and 4 would appear rough.

The cylindrical container results are somewhat puzzling; further investigation is certainly warranted. Certainly we can expect that the sedimentation behaviour of transient gel samples in the Zimm viscometer will be significantly different to that observed in the standard cells.

6.5.8 Miscellany

Macroscopic flow

In order to gain some insight into the mechanisms behind the transient gel collapse attempts were made to start it prematurely. A small steel ball bearing (diameter \( \sim 1 \text{ mm} \)) was included in a strong transient gel sample (\( \phi = 0.30, C_p = 4.49 \text{ mg cm}^{-3}, t_{\text{lat}} \approx 16 \text{ hrs} \)), which rested in a corner of the sample after randomization. With each experiment the ball bearing was passed through the sample (either vertically or horizontally) and returned to its starting position (using a strong magnet) in order to destroy the gel structure locally. This was done at different times in the latency period for each experiment.
This failed to start the gel collapse; the passage of the ball bearing through the sample probably randomized the sample locally allowing gelation to reoccur. However, around the time of collapse the ball bearing often moved from its resting place, rolling along as far as half the sample width over a period of $\approx 2$ hrs. This is due to the macroscopic convective-like flow in the sample at the time of collapse. From this motion we can estimate that these flow rates must be of the order of $\sim 1 \mu m s^{-1}$ ($\approx 100$ times the Stokes velocity of a single sphere), with shear rates $\dot{\gamma} \sim 10^{-3} s^{-1}$. The motion of the ball bearing coincides with the apparent 'stress release' in the sample, as flow motion is seen on the uneven solvent-colloid interface which then smooths out.

**Vigorous shaking**

The randomization procedure of the samples was altered to see if any change in sedimentation behaviour occurred. Instead of slow tumbling before experimentation the samples were vigorously shaken by hand. For most of the samples investigated no change in sedimentation behaviour was seen. However for one sample, $\phi = 0.30$, $C_p = 4.49 \text{ mg cm}^{-3}$ a drastic change was observed (fig. 6.26).

![Figure 6.26. Sedimentation behaviour of $\phi = 0.30$, $C_p = 4.49 \text{ mg cm}^{-3}$, colloid-polymer mixture (x) after normal randomization and (o) after vigorous shaking. A dramatic change is seen, latency period and collapse ceasing to occur for the vigorously-shaken sample. This may be the effect of many small air bubbles slowly rising through the viscous sample, disrupting the gelation process.](image)

The distinctive latency period and collapse is no longer seen. Instead the initial sedimentation rate is faster, but gradually slows down. No rapid sedimentation stage is seen. This change in sedimentation behaviour could be the result of many small air bubbles slowly rising through
the viscous sample, disrupting the gelation process. Perhaps when the bubbles have either dissolved or risen to the top of the sample gelation may occur, but by this stage the colloidal particles/clusters have sedimented considerably, increasing the volume fraction of the colloidal bulk so that collapse does not occur and only slow sedimentation is seen. The sample returned to normal transient gel sedimentation behaviour after normal randomization. Vigorous shaking had no effect on the sedimentation behaviour of samples of lesser latency time; perhaps for these samples any bubbles rose quickly to the surface of the sample, thereby not disrupting the gelation process.
Chapter 7

Transient gel low-shear rheology

7.1 Introduction

In the previous chapter we looked at the unusual sedimentation behaviour of colloid-polymer transient gels. In this chapter we examine the rheological response of the transient gel to small shear stresses.

The rheological behaviour of any substance is essentially a consequence of how its 'internal structure' responds to external bulk forces. For the transient gel (during its latency period) we envisage aggregating colloidal particles having formed a space-spanning network; essentially many connected clusters extending across the whole sample. The particles are bonded to one another by the depletion force.

How would such a structure respond to macroscopic shearing forces? For any macroscopic flow to occur the network would have to de-percolate i.e. a certain number of particle bonds would have to be broken. One might expect an amount of rigidity from such a structure. If small enough shear stresses were applied, the gel would behave according to the Bingham model (equ.2.7), resisting flow below a finite (albeit small) shear stress i.e. the gel would have a yield stress.

It would be interesting to measure the yield stresses of transient gels of varying strength and to see if these could be related to their delayed sedimentation behaviour, particularly latency times. The Zimm viscometer seemed perfectly suited to such a task. It was decided therefore to attempt to measure the yield stresses of transient gels of varying polymer concentration at fixed volume fraction.
7.2 Low-shear probing of transient gel

7.2.1 Yield stress philosophy

As mentioned before in chapter 2, the rheological behaviour of a substance often depends on the timescale of the observation. For a substance subjected to shear stresses below its yield stress we envisage the body suffering limited deformation (elastic), further deformation being halted by internal stresses balancing the applied shear stress. However, in reality the internal stresses will eventually relax (on the timescale of the relaxation time of the material). That is to say, wait long enough and even mountains will flow. So discussions about yield stress and flow have to be placed in the context of the timescale of observation.

From a practical point of view accurate yield stress measurements are, in general, difficult to achieve. Often it is found that the yield stress is not well defined, and amongst other things depends on the apparatus used and the shear history of the sample [63]. In fact the concept of the yield stress as a true material property is a controversial one. Scott Blair (a rheological pioneer) proposed a practical definition of the yield stress as 'any critical stress below which no flow can be observed under the condition of experimentation' [64].

These factors aside, let us assume that there is a well-defined yield stress fundamental to the transient gel (as described in the introduction) that could, in principle, be measured. How would one approach this task?

7.2.2 Thoughts about yield stress measurement

Extrapolation

How does one determine when a substance has 'yielded'? One necessary criterion is the detection of flow of the substance, but how long does one wait to see if flow occurs?

Any measurement has a limit to its resolution. Practically one has to define a maximum measurement time (or waiting time) $\Delta t_{\text{max}}$ for each stress applied, and detection of deformation will be limited to $\Delta \gamma$. This results in a minimum shear rate that can be detected, $\dot{\gamma}_{\text{min}} = \Delta \gamma / \Delta t_{\text{max}}$. Therefore it is not sufficient to define the yield stress for a substance as the stress at which flow is first detected, as we could simply be measuring the stress at which we could first detect the flow of a very viscous Newtonian fluid (see fig. 7.1(i)).

Surely what we really mean when we envisage a yield stress (as something meaningful to do with the substance rather than surroundings) is that it is the stress at which the viscosity shows a sharp transition to a much lower value, with respect to increasing shear stress. That is to say, the stress at which a substantially large decrease in viscosity occurs over a relatively small range of applied shear stress (linked to important structural changes), the subsequent flow curve then remaining either at constant viscosity (as in Bingham model — see fig. 7.1(ii)) or decreasing at a much slower rate than measured in the region of 'yielding'.

It is likely therefore that the yield stress, $\sigma_y$, will be detected indirectly, involving some form
CHAPTER 7. TRANSIENT GEL LOW-SHEAR RHEOLOGY

Figure 7.1. Measurement of a yield stress \( \sigma_y \). The minimum shear rate that can be detected \( \dot{\gamma}_{\text{min}} \) results in a minimum stress \( \sigma_{\text{min}} \) that can be applied for each sample below which flow is not detected. Hence flow curve extrapolation is needed in order to differentiate between, say a viscous Newtonian fluid (i) and fluids exhibiting a yield stress (ii), (iii).

of extrapolation of the flow curve ‘above yield’. This will ensure that non-detection of flow has some real meaning rather than being the result of experimental limitation. However, extrapolation would be more difficult for fluids that are non-Newtonian above the yield stress, especially those whose viscosity is a rapidly decreasing function of shear stress (fig.7.1(iii)).

The experimental measurement limit \( \dot{\gamma}_{\text{min}} \) means that for each sample there will be a lower-limit stress we can apply \( \sigma_{\text{min}}(> \sigma_y) \) and still detect flow within the time limit \( \Delta t_{\text{max}} \). Obviously the closer our measurements are to the true yield stress \( \sigma_y \) the more likely we are to detect it. Therefore measurement of this minimum or 'benchmark' stress \( \sigma_{\text{min}} \) for each sample at the lower limit of experimentation is a good starting point. This will also give us a 'feel' for the rheological behaviour of the transient gel in the experimentally closest approach to the true yield stress e.g. whether the viscosity is time-dependent; values for viscosity \( \eta_{\text{bm}} \) \( (= \sigma_{\text{min}}/\dot{\gamma}_{\text{min}}) \) at this benchmark (both absolute and relative between different gel samples). Further experiments can then sketch the flow curve above the benchmark: the shape of this flow curve and its extrapolation may indicate the existence of a yield stress for the transient gel.

Time dependency of samples

The internal structure of the transient gel is, as its name suggests, time dependent. Consequently we would expect its low-shear rheological behaviour to be time dependent. Therefore if flow curve 'sketches' (many \( \sigma \) vs. \( \dot{\gamma} \) measurements) are to be of any use they must be performed within a period of time significantly less than the gel latency time. It is also important to note that applying even very small shear stresses affects the gel lifetime, as does the geometry of
the Zimm viscometer (see later). The latency times of the samples investigated were typically \( \sim \) hours (as measured in the square cross-section cuvettes). Generally one has to balance the need to complete flow curve measurements well within gel lifetime with the desire to apply small shear stresses (taking a long time to measure due to limited resolution of shear).

**Non-Newtonian fluids in Couette geometry**

Since in our system the annular gap is small compared with the radius of the rotor \( ((b - a)/a = 0.17) \) to first order we can assume the shear stress will be approximately

\[
\sigma = \frac{M}{2\pi lR_{av}^2} (7.1)
\]

at all points in the gap where \( R_{av} \) is some average radius. Similarly the shear rate will be approximately

\[
\dot{\gamma} = \frac{\Omega R_{av}}{(b - a)} (7.2)
\]

and a flow curve can be derived directly from the values of applied torque \( M \), rotor angular velocity \( \Omega \) and the geometry of the system. However here we note that *this is a first order approximation only*. Although relatively the annular gap is small, it is not very small, and we could expect significant deviations from this ideal if the fluid flow curve is a very sensitive function of the shear stress e.g. a power-law fluid. For example, across the annular gap \( ((b - a)/a = 0.17) \) the variation in applied shear stress is \( \Delta\sigma \approx \pm 15\% \) (from equation 2.22). For a power-law fluid \( \dot{\gamma} \sim \sigma^N \) with \( N \approx 3 \) (see later) this would result in a variation in shear rate of as much as \( \Delta\dot{\gamma} \approx \pm 50\% \) across the annular gap. However we will use this simple approximation for the transformation of torque \( M \) and rotor angular velocity \( \Omega \) to shear stress \( \sigma \) and strain rate \( \dot{\gamma} \) as a first step toward understanding the form of the transient gel flow curve.

### 7.2.3 Experiment

**Samples**

Table 7.1 lists and describes the transient gel samples investigated. The system is identical to that used in the delayed sedimentation observations of chapter 6. All samples were of volume fraction \( \phi = 0.30 \). Samples were made in the same fashion as those made for delayed sedimentation measurements, except here the quantities of sample used were much greater (\( \sim 10 \text{ cm}^3 \), stored in teflon containers). All samples were slow tumbled prior to experimentation. Unfortunately it was necessary to re-use transient gel samples on repetition of rheology experiments, due to lack of colloidal material and time. However much effort was made to try to maintain the integrity of samples (cleanliness and minimizing solvent evaporation).
CHAPTER 7. TRANSIENT GEL LOW-SHEAR RHEOLOGY

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>$C_p$ (mg cm$^{-3}$)</th>
<th>Latency time $t_{lat}$ (standard cuvette $\approx$ 2 cm high)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>$\approx$ 2 hrs</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>$\approx$ 8 hrs</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>$\approx$ 16 hrs</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>$\approx$ days</td>
</tr>
</tbody>
</table>

Table 7.1. Transient gel samples ($\phi = 0.30$) used in low-shear rheology measurements.

Method

Based on the reasoning on yield stress measurements in the earlier section, experiments were grouped into 'benchmark' stress/viscosity measurements, or flow-curve sketching. All experiments were started on transient gel samples in the early stages of their life-cycle (i.e. $\approx$ 1 hr old).

Prior to each experiment the sample was slow tumbled, then loaded into the viscometer as in chapter 4. Loading the viscometer takes at least ten minutes, whereas gelation takes place within seconds. Therefore some attempt at randomization of the sample was required. For these experiments a fine nichrome wire was drawn through the sample to try to achieve this. The sample was then sealed and left for $\sim$ 1 hour (although different samples would be in different stages of their life-cycles, they should all be in the first half).

Benchmark measurements

After the gel had been left for an hour I could attempt to find the benchmark stress $\sigma_{min}$.

The laser, mirror and detector was set up for early detection of flow. The laser was shone onto the middle of a reflecting surface (see fig.7.2). Flow is first detected when the laser hits a non-reflecting surface, so that the limit of resolution for initial detection of shear deformation was $\approx 1/4$ of a segment, i.e. $\approx 1/160$ of a revolution, $\Delta \gamma \approx 0.2$.

The practical maximum waiting time for initial detection of flow of a gel at any one applied shear stress was defined as $\Delta t_{max} \approx 10$ mins, bearing in mind transient gel lifetimes and the probable need to apply several different shear stresses before the benchmark was reached. A suitably low shear stress would be guessed (hopefully below $\sigma_{min}$) and applied. If flow was not detected within 10 minutes, the applied stress would be increased and so on until detection of flow had occurred within $\Delta t_{max}$.

Sometimes it was necessary to reattempt or repeat benchmark measurements (starting from fresh but reusing the transient gel sample) if the first stress applied was above the benchmark, or simply to refine the measurement. An effort was made to keep track of the shear history during each experiment and to keep them similar, hopefully hitting the benchmark stress as soon as possible. Once the benchmark stress was hit the experiment was left to run, to monitor the time dependency of the sample in this low-stress regime.
CHAPTER 7. TRANSIENT GEL LOW-SHEAR RHEOLOGY

Figure 7.2. The laser and mirror set up for early detection of flow. The laser is shone onto the middle of a reflecting surface. Flow is first detected when the laser hits a non-reflecting surface, so that the limit of resolution for initial detection of shear deformation is \( \approx 1/4 \) of a segment, i.e. \( \approx 1/160 \) of a revolution, \( \Delta \gamma \approx 0.2 \).

Flow-curve sketching

Again the sample was left for an hour. Measurements then began at around twice the benchmark stress. Experimentation involved making measurements at increasing shear stresses, then repeating for decreasing stresses. Data was obtained relatively quickly at these higher stresses, in under 1 hour.

7.2.4 Results

The benchmark stress \( \sigma_{\text{min}} \) and viscosity \( \eta_{\text{bm}} \) for each sample of polymer concentration \( C_p \) (\( \phi = 0.30 \)) are shown as circles in fig. 7.3. The cross underneath each benchmark stress is the penultimate stress applied before the benchmark was reached, indicative of the applied stress increments. The shear histories of the samples were fairly similar and 'short' (~ 2 previous stress steps, ~ 20 mins in all).

Although in practice relatively crude, these measurements allow some comparison of the (initial) resistance to deformation of transient gels of different strength in the low-shear regime. The benchmark stress \( \sigma_{\text{min}} \) for each gel is the (upper bound) stress required to flow the sample at the 'minimum' shear rate \( \gamma_{\text{min}} \approx 3 \times 10^{-4} \) s\(^{-1} \), a Peclet number of \( Pe \approx 10^{-4} \). Excepting the weakest transient gel the benchmark stress \( \sigma_{\text{min}} \) has a linear dependence on polymer concentration. Examination of the benchmark viscosities \( \eta_{\text{bm}} \) shows we are dealing with very viscous samples; for sample no.4 \( \eta_{\text{bm}} \approx 20,000 \) cp.

It is interesting to note the time-dependent rheological behaviour of the samples whilst the benchmark stress is applied (fig. 7.4). The strongest two samples show a marked fall in viscosity over two hours — at least an order of magnitude. Clearly the rheological behaviour of the gel in this stress regime is very time dependent.

We now consider the flow curve for the strongest transient gel, sample no.4, shown in fig. 7.5.
Figure 7.3. The benchmark stress $\sigma_{\text{min}}$ and viscosity $\eta_{\text{bm}}$ for transient gels of polymer concentration $C_p$ ($\phi = 0.30$). The benchmark stress for each gel is the (upper bound) stress required to flow the sample at the 'minimum' shear rate $\dot{\gamma}_{\text{min}} \approx 3 \times 10^{-4}$ s$^{-1}$, a Peclet number of $Pe \sim 10^{-4}$. Excepting the weakest transient gel the benchmark stress $\sigma_{\text{min}}$ has a linear dependence on polymer concentration.

Figure 7.4. Time dependency of the viscosity $\eta$ of the transient gel samples whilst the benchmark stress is applied.
The starting stress was $\approx 2\sigma_{\text{min}}$. The flow curve was sketched over a magnitude of stresses, increasing then decreasing. There was little or no time dependency for each measurement, and the flow curve appears to be relatively unaffected by shear history. The whole experiment took less than an hour to perform.

Figure 7.5. Flow curve for transient gel sample no.4, for increasing then decreasing shear stresses. On the broad scale the flow curve appears to be Bingham-like. The viscosity converges to a plastic viscosity $\eta_{\text{pl}} \approx 17$ cp (dotted line). Extrapolation of the linear ('plastic') portion of the flow defines the plastic stress $\sigma_{\text{pl}}$.

On the broad scale the flow curve appears Bingham-like. The viscosity converges to a plastic viscosity $\eta_{\text{pl}} \approx 17$ cp. Taking into account the background viscosity of the polymer solution gives a relative viscosity $\eta_r \approx 3$, equal to the low-shear relative viscosity of a hard-sphere suspension of volume fraction $\phi = 0.30$. The viscosity begins to move away from $\eta_{\text{pl}}$ around Peclet number $Pe \approx 1$. One can extrapolate a Bingham-like 'yield stress' on this scale, $\approx 0.1$ N m$^{-2}$. However, since stresses of this magnitude result in significant shear flow ($Pe \approx 1$) this is clearly not the 'true' yield stress $\sigma_y$ we are looking for. We shall define this stress-axis intercept as the plastic stress $\sigma_{\text{pl}}$.

At lower shear stresses the viscosity begins to increase very rapidly. The question is, is it diverging at a finite shear stress? Plotting the data in log-log form helps us to look at the low-stress region of the flow curve (fig.7.6). Also displayed are the range of (time-dependent) shear-rate measurements taken at the benchmark stress $\sigma_{\text{min}}$, and half the benchmark stress $\frac{1}{2}\sigma_{\text{min}}$. The data appears to be following a power law

$$\dot{\gamma} = \psi \sigma^N,$$  \hspace{1cm} (7.3)
with exponent $N \approx 3$ and $\psi \approx 1100$ — i.e., the shear rate $\dot{\gamma}$ is a sensitive function of shear stress $\sigma$, falling by three orders of magnitude (1 to 0.001 s$^{-1}$) over a decrease of just one magnitude in shear stress (0.1 to 0.01 N m$^{-2}$). If the data were to indicate a yield stress we expect to see the data tending towards the stress axis with an infinite gradient (as with the extrapolation of the linear portion of the flow curve). Therefore if this (relatively strong) transient gel has a true yield stress our present experimental setup is not good enough to detect it. The experimental limitation is a consequence of the high gel viscosity in the low-shear regime and experimental time restriction due to the finite lifetime of the transient gel. The lowest shear stresses applied were $\sigma \sim 10^{-2}$ N m$^{-2}$; if any true yield stress exists its value must be $\sigma_y \leq 10^{-3}$ N m$^{-2}$.

### 7.3 Colloid-polymer mixture flow curve — no gelation

So far all rheological measurements had been performed on one hour old transient gels, and had commenced with low shear stresses and shear rates ($Pe \sim 10^{-4}$). I was curious to know how the flow curve of the colloid-polymer mixture depended on the initial 'state' (i.e. colloidal microstructure), the starting stress and the subsequent shear history. Therefore flow curves were obtained for the various colloid-polymer mixtures starting from higher shear stresses and shear rates ($Pe \approx 3$), decreasing ($Pe \sim 10^{-4}$) then increasing back to higher shear rates again. Hence the initial state of the colloid-polymer mixture was a fluid rather than a gel.
7.3.1 Method

Samples 1, 2 and 4 were used. Torque was applied to the rotor whilst the sample was loaded; hence as soon as the rotor was floating above the stator shear flow occurred, and the mixture was unable to gel. Measurements commenced as soon as the sample was loaded, the shear stress being decreased, and then eventually increased. The whole experiment took less than an hour; sedimentation was minimal.

7.3.2 Results

The 'fluid-start' flow curve is compared with the 'gel-start' flow curve for the strongest sample no.4 in fig.7.7. The two are almost identical, indicating that for the strongest gel, in the stress regime investigated and for total experimentation time ~ 1 hour, the flow curve appears independent of the initial state of the sample and subsequent shear history.

![Figure 7.7. Comparison of the 'fluid-start' flow curve with the 'gel-start' flow curve for the strongest sample no.4. The two are almost identical, indicating that for the strongest gel, the flow curve appears independent of the initial state of the sample and subsequent shear history under the experimental conditions (total experimentation time ~ 1 hour).](image)

Whilst the strongest sample seems fairly robust, time-dependency/shear-history leaves a mark on the flow curve of the weaker samples, as can be seen in fig.7.8 for sample no.2.

We compare the decreasing stress flow curves for the different colloid-polymer mixtures in fig.7.9. Quick experimentation times (~ 10 mins) for the higher stress portion of these flow curves and similar starting conditions (Pe \( \approx \) 3) means that time dependency should not be
Figure 7.8. Time-dependency/shear-history leaves a greater mark on the flow curve of the weaker samples, as can be seen for sample no.2 (C_p = 4.0 mg cm⁻³).

Figure 7.9. Comparison of the decreasing stress flow curves for the different colloid-polymer mixtures. One can extrapolate a plastic stress σ_pl from the linear portion of each flow curve.
significant. Again we see Bingham-like behaviour on the broad scale, and we can extrapolate a plastic stress $\sigma_{pl}$ for the linear portion of the flow curve for each colloid-polymer mixture. Fig. 7.10 shows the dependence of the plastic stress $\sigma_{pl}$ on polymer concentration. Again a linear dependence is seen for 'comparative' stresses of colloid-polymer mixtures. The plastic stress $\sigma_{pl}$ ($Pe \approx 1$) increases by a factor of $\approx 2$ over the polymer concentration range 3.5 to 5.0 mg cm$^{-3}$. However comparison with the benchmark stresses (fig. 7.3) shows that the increase in stress with polymer concentration is greater for lower shear rates ($Pe \approx 10^{-4}$), as the benchmark stress $\sigma_{min}$ increases by a factor of $\approx 16$ over the same increase of polymer concentration.

![Graph showing plastic stress $\sigma_{pl}$ as a function of polymer concentration for polymer colloid mixtures ($\phi = 0.30$). A linear dependence is observed.]

**Figure 7.10.** Plastic stress $\sigma_{pl}$ as a function of polymer concentration for polymer colloid mixtures ($\phi = 0.30$). A linear dependence is observed.

### 7.4 Constant-stress rheology and sedimentation observations

The experimental results discussed so far have shed light on the rheological behaviour of the transient gel. However, experiments were complicated by factors such as the time dependency of the gel structure and the shear history of the experiments. Perhaps most crucially the sedimentation behaviour of the gel is significantly altered from earlier 'cuvette' observations by (i) the geometry of the Zimm viscometer and (ii) the applied shear stress itself. This means that it is difficult to relate rheology measurements with sedimentation behaviour i.e. the 'life-cycle' of the gel. It was decided therefore to record the sedimentation behaviour of a transient gel whilst conducting some simple, well-defined low-shear rheology experiments on it. The following measures were taken to achieve this aim:
1. One very strong transient gel ($\phi = 0.30, C_p \approx 9 \text{ mg cm}^{-3}$) would be looked at. The high strength of the sample ensures that the gel has a relatively long lifetime ($t_{\text{lat}} \approx 13 \text{ hrs}$) in the Zimm viscometer (much reduction in latency time is observed between samples in small cuvettes and those in larger, cylindrical geometries). This gives plenty of time for experimentation.

2. Each experiment would use a new gel sample i.e. no reusing of samples, ensuring sample integrity.

3. To ensure a simple shear history each experiment would be carried out under a 'small' constant shear stress $\sigma_c$. One could then see the resulting time-dependent sedimentation and rheological behaviour of a gel as a function of constant applied shear stress.

### 7.4.1 Samples

The transient gel samples were made as described earlier, but this time using slightly larger particles ($a = 326 \text{ nm}$). A large batch of the transient gel ($\phi = 0.30, C_p \approx 9 \text{ mg cm}^{-3}$) provided all the samples for experimentation.

### 7.4.2 Method

As usual, all samples were slow tumbled before experimentation. The sample was loaded and then the viscometer was sealed. The 'randomization' of the colloid-polymer mixture was achieved by 'fast' shearing for $\approx 15 \text{ mins}$ at Peclet no. $Pe \approx 3$. Whether this 'truly' randomizes the mixture is not known; nevertheless it gives a highly reproducible starting state for each sample. After randomization the sample was left undisturbed for a period of $\approx 1 \text{ min}$ i.e. the gel has only just formed. During this period the laser was aligned on a reflecting surface ready for early detection of flow. The magnetic field was then rotated at a constant angular velocity for the duration of the experiment, subjecting the sample to a small but continuous steady shear stress $\sigma_c$.

Throughout the experiment the viscometer is monitored using the CCD camera linked to the time-lapse VCR, recording the sample's sedimentation behaviour.

The above experiment was conducted for zero applied stress, at $\sigma_c \approx 0.004 \text{ N m}^{-2}$ (considered low), an order of magnitude higher and then at various stresses in between.

### 7.4.3 Results

Sedimentation behaviour as function of shear stress

Fig.7.11 shows how the sedimentation behaviour of the very strong transient gel is affected by shear stress. The unstressed sample shows typical transient gel sedimentation behaviour, showing a latency period (with no slow sedimentation), rapid collapse followed by slow compaction (albeit not slowing down as quickly as in a square cuvette, probably due to the
Figure 7.11. The effect of various constant applied shear stresses $\sigma_c$ on the sedimentation behaviour of a very strong transient gel.

curved base of the viscometer). The latency time for the unperturbed sample was $\approx 13$ hrs.

There was no discernible change in the sedimentation behaviour for the lowest stress applied (0.004 N m$^{-2}$).

The next step to a stress of $\sigma \approx 0.0120$ N m$^{-2}$ had a significant affect on the sedimentation behaviour, roughly halving the latency time. Increasing the stress had the effect of further decreasing latency (although at a slower rate) as might be expected — see fig.7.12(a). Greater shearing stresses also had the effect of increasing the collapse velocity and increasing the 'final' volume fraction $\phi_{fn}$ — as displayed in figs.7.12(b), 7.12(c). This behaviour is consistent with the idea that shear flow breaks up ramified clusters and only allows more compact clusters to survive, which have less drag per unit density (thereby increasing collapse velocity) and will form a denser metastable sediment (hence increased $\phi_{fn}$).
Figure 7.12. The effect of applied shear stress $\sigma_s$ on (a) the latency time $t_{lat}$, (b) the rapid sedimentation velocity $V_{rs}$, and (c) the metastable sediment volume fraction $\phi_{\text{fin}}$ of the very strong transient gel.
Rheological behaviour as a function of shear stress

The observed rheological behaviour fell into three categories.

1. (virtually) No flow. For the lowest stress applied the amount of shear flow was very small. Only two segments registered, a shear deformation of $\gamma \approx 2$ over a period of $\approx 30$ hours.

2. Much flow. The higher stresses resulted in much shear flow (fig.7.13). The viscosities, starting around $\sim 5,000$ cp, gradually decreased to a (relatively) stable value of $\sim 2,000$ cp (the oscillations are due to deviations in segmented mirror alignment).

3. Intermediate. These stresses displayed the most interesting rheological behaviour (fig.7.13). Again, viscosities began at $\sim 5,000$ cp, but, over a period of $\approx 3$ hrs, increased markedly by an order of magnitude. After reaching a peak the viscosities decline markedly again at about the same rate, until compactification led to a cessation of shear flow. It was felt that here a good experimental compromise was reached; small enough shear stresses that the rearranging gel structure affects the motion of the rotor, but not so small that the shear flow is beyond instrument detection resolution. This rheological behaviour is consistent with the picture of a rearranging gel structure slowly strengthening and then weakening.
Sedimentation and rheology

Figs. 7.14(a)-(d) compare the sedimentation and rheological behaviour for the very strong transient gel for increasing stresses (intermediate to much flow). Essentially the rheological behaviour for the higher shear stresses does not seem to be linked to the sedimentation behaviour. For the intermediate stresses however the weakening of the sample does seem to correspond to the onset of the transient gel collapse. In general it is somewhat surprising that the samples can sustain such significant amounts of shear flow before collapse occurs. Perhaps the transient gel can effectively 'heal itself' against structural rearrangement due to shear flow if the shear rates are low enough.

Figure 7.14. Comparison of the time-dependent sedimentation and rheological behaviour of the very strong transient gel for several applied shear stresses.
7.5 Wall Slip

Slip can occur in the flow of two-phase systems because of the displacement of the disperse phase away from the walls of the viscometer. Large particles in the disperse phase (or clusters), with a large dependence of the viscosity on concentration of the dispersed phase can lead to slip, especially if coupled with smooth walls and small flow dimensions [65]. The effect is usually greatest at low flow rates. Therefore our transient gels would appear to be susceptible to slip whilst under shear forces.

Attempts to eliminate or alter slip can be achieved by physically roughening the walls of the viscometer. In order to test if slip was occurring the flow curves of a pure colloidal fluid $(\phi \sim 0.3)$ and a transient gel were measured using first a smooth rotor and then a roughened one (the rotor was roughened using a glass grinder).

The flow curves are displayed figs. 7.15(a) and (b). There is no significant difference in the flow curves for the different rotors. It would seem therefore that slip is not a concern in the rheological investigations of colloidal fluid and colloid-polymer mixtures presented in this work.

![Figure 7.15](image-url) — Figure 7.15. Comparison of flow curves obtained using rough and smooth rotors for (a) a pure colloidal fluid and (b) a transient gel colloid-polymer mixture. Differences between the flow curves for rough and smooth rotors are minimal, indicating that wall slip is not a concern in this study.
Chapter 8

Discussion of transient gel latency and collapse

8.1 Introduction

The most spectacular, and perhaps perplexing, aspect of transient gel behaviour is the collapse. It is made all the more dramatic by the quiescent nature of the latency period preceding it. During latency there is little to suggest, either visually or through small-angle light scattering observations, that the collapse is imminent.

In order to understand precisely how and why the transient gel collapses we need to know what physical mechanisms affect the gel structure and its stability during the latency period. Obviously the influence of gravity is important as it is ultimately responsible for any sedimentation or collapse (assuming a finite particle-solvent density difference). However, is it the dominant mechanism determining the latency time, or is it simply exploiting the work of some other mechanism? Is gravity the protagonist or merely the observer [66]? We are still in the process of trying to understand the transient gel behaviour and hence much of this chapter is speculative; nevertheless it is an attempt to construct a simple model of transient gel latency and collapse consistent with experimental observations.

8.2 Transient gel structural rearrangement in the absence of gravity

In this section we speculate on the rearrangement of the gel structure in the absence of gravitational effects i.e. a transient gel comprising density-matched particles and solvent, or a transient gel in the space shuttle (microgravity experiments in collaboration with NASA are in fact underway).

The reversible-DLCA simulations of Haw et al. [57] reveal the significant role of thermal
rearrangement in determining the colloidal structure in an aggregating system at short times (~ minutes). When compared with the tenuous fractal-like structure observed in irreversible-DLCA (fig.5.8(a) — $U_{dep} \gg k_B T$ — no thermal rearrangement) we see that thermal rearrangement results in local compactification of fractal-like structures (as multiple particle bonds are more stable against thermal breakup) and de-percolation of the system-spanning cluster (fig.5.8(b) — $U_{dep} \approx 3k_B T$).

We can speculate on the effect of thermal rearrangement on the structure of a transient gel of higher bond energy, $U_{dep} \approx 6k_B T$ say. Single particle bonds would be more stable against thermal breakup than in the $3k_B T$ system, hence we would expect a more tenuous structure at gelation (fig.8.1(i)). Nevertheless since multiple particle bonds are more stable against thermal breakup than single particle bonds for any aggregating system of finite bond energy we would still see structural compactification (fig.8.1(ii)) and eventual de-percolation (fig.8.1(iii)), albeit over a longer timescale. In the course of time the systems might consist of many discrete compact clusters [54] (fig.8.1(iv)). This is consistent with the knowledge that the equilibrium state of such a system is the coexistence of (compact) colloidal crystals and a very dilute colloidal gas [67].

Figure 8.1. Schematic diagram depicting the expected long-term effect of thermal rearrangement on a 'relatively stable' transient gel ($U_{dep} \approx 6k_B T$ say) in the absence of gravity. (i) The initially tenuous structure (ii) would compactify locally (iii) and eventually de-percolate; (iv) if one waited long enough the system might end up as a collection of compact clusters.

In summary we expect thermal rearrangement to lead eventually to the de-percolation of a system-spanning structure of finite bond energy $U$ after some time $t_{dp}$, related to the probability of thermal bond-breaking given by the Boltzmann distribution $\sim \exp(-U/k_B T)$. However we note that other properties of the system may drive rearrangements that lead to de-percolation (see next section). We shall collectively label all such rearrangements leading to de-percolation at time $t_{dp}$ in the absence of gravity 'intrinsic' rearrangements. Moreover, we shall identify the de-percolation time $t_{dp}$ as the 'latency time' in the absence of gravity, since the de-percolated structure would be unable to support itself in the presence of a gravitational field (for a finite solvent-particle density difference).
8.2.1 Intrinsic rearrangement mechanisms

We can gain insight into possible intrinsic rearrangement mechanisms from the work of Olivi-Tran et al. [68]. They considered the underlying physical mechanisms of sintering [69] in materials made from fractal arrangements of aggregated particles, such as silica aerogels. For such materials the sintering process involves heating the sample for a given time at a temperature smaller than its melting temperature. One observes a net shrinkage of structure and a gradual elimination of pores as the surface area is reduced. We may expect to observe a similar time-dependent morphology in our transient gels, i.e. gradual compactification of the ramified (porous) structure.

They suggest several possible sintering mechanisms; (i) evaporation/deposition, (ii) surface diffusion and (iii) viscous flow. Their work focused on the latter two. We consider these and other possible mechanisms in the context of our own system. First, however, we shall briefly describe our model of the early-time transient gel structure on which the intrinsic-rearrangement mechanisms act.

Simple model of the early-time transient gel structure

In the DLCA model we envisage clusters growing fractally until they meet, at which point the sample has gelled (see section 5.6.1). Therefore we imagine the transient gel to comprise many fractal-like clusters of radius \( R = R_{gel} \) randomly close packed as in fig.8.2 — i.e. the gel is fractal-like up to length scale \( R_{gel} \) and is homogeneous on larger length scales. The large-scale length correlation indicated by the small-angle light-scattering ring can be thought of as arising from the cluster size \( R_{gel} \). The system percolates via numerous ‘backbones’, of width \( b \) say. Within the backbone the arrangement of particles is compact. Thus the gel is fractal within the length scale range \( b < L < 2R_{gel} \). We shall call non-percolating branches of a cluster ‘tendrils’. This simple model neglects many factors such as cluster interpenetration and its effect on subsequent growth, cluster polydispersity and the like; however it neatly describes the gelation phenomenon and and is a useful framework for the description of rearrangement processes.

Evaporation/deposition

At any one instant a particle on the surface of a cluster may acquire sufficient thermal energy to escape the bonds of its neighbours and continue its existence in a ‘gaseous’ state i.e. evaporate. Conversely a free particle may ‘condense’ back to the cluster. This mechanism is similar in origin to the thermal rearrangement displayed in the reversible DLCA simulations.

How would particle evaporation/deposition change the transient gel structure? A collection of drops (e.g. an emulsion) transferring mass via evaporation/deposition displays the phenomenon known as Ostwald ripening or coarsening [70]. Smaller drops contribute more interfacial energy per unit volume than larger ones; hence smaller drops dissolve and transfer their mass to the larger drops. It is not obvious what would occur in our system. Perhaps wider backbones might grow thicker at the expense of thinner backbones and tendrils?
Figure 8.2. A simple model of the early-time transient gel structure. The gel comprises many randomly close-packed fractal-like clusters of radius $R_{\text{gel}}$. The system percolates via numerous backbones of width $b$. Within the backbones the arrangement of particles is compact.

Surface diffusion

On the particulate scale surface diffusion might be regarded as particle 'rolling' driven by the 'surface tension' of the cluster branches — fig.8.3(a). Alternatively it could arise from 'short-range' thermal rearrangement i.e. particle 'hopping' (fig.8.3(b)).

Figure 8.3. Surface diffusion could arise from (a) surface tension-driven 'particle-rolling' or (b) short-range thermal rearrangement (particle 'hopping').

Olivi-Tran et al. investigated the effect of surface diffusion on 2-D mass-fractals. In their simulations diffusive transport of matter along the surface of the fractal object (governed by a diffusion equation) is driven by the pressure inhomogeneities associated with changes of curvature along the surface i.e. surface tension. Hence the sintering process ends when a circular shape (constant curvature) is reached.

The result can be seen at the top of fig.8.4. It is observed that the size (length) of the fractal, which would correspond to the cluster size $2R$ in our model, stays approximately constant.
(except towards the very end of the process) and that the lower cut-off, which is something like the width of the fractal arms (comparable to the backbone width $b$ in our model) increases during the sintering process. Hence a network of percolating fractals objects sintering via surface diffusion would retain the percolation of the network well into the sintering process. Subsequent work [71] has shown that 'sufficiently large' fractal objects sintering via surface diffusion fragment into several smaller pieces during the sintering process.

![Figure 8.4](image)

**Figure 8.4.** The effect on a 2-D mass-fractal (left) of surface-diffusion sintering (top) and viscous-flow sintering (bottom). Both mechanisms continually increase the width $b$ of the fractal 'backbone'; however with surface diffusion the fractal maintains its size (length) $2R$ well into the sintering process, whereas viscous-flow sintering continually decreases the fractal size. Figure reproduced from [68].

**Viscous flow**

Viscous flow is another possible sintering mechanism. Again it is driven by surface tension (so that the end result will be a sphere), but now the matter is transported via viscous flow within the bulk (governed by a Stokes equation).

The bottom of fig.8.4 shows the effect of viscous-flow sintering on a 2-D fractal object. Again the lowercut-off ($\sim$ arm width $b$) continually increases with time. However the fractal size ($\sim$ cluster size $2R$) continually decreases with time. Hence if viscous-flow sintering were the dominant rearrangement process in a network of percolating fractal objects the system would break up after minimal rearrangement.

It would be interesting to consider the viscoelastic-flow sintering process. Varying relaxation times on different length scales might lead to some unusual structural evolution.
Instability of a fluid cylinder

It is well known that a cylinder of fluid longer than its diameter is unstable to small perturbations and breaks up into segments that, under the action of surface tension, form into individual drops (Rayleigh instability [72]). The backbones in our transient gel model, considered as cylinders of very viscous fluid, would similarly be prone to this instability. However, Cates and Evans [73] have suggested that the instability could be held at bay by the steady influx of material from the tendrils of the fractal aggregate (driven by surface tension) continually increasing the width \( b \) of the cylinder — see fig. 8.5. Only once this 'reservoir' is depleted would the break up of the cylinder (and hence de-percolation of the gel network) occur.

![Figure 8.5. The Rayleigh instability held at bay. (i) Schematic representation of a transient gel backbone with tendrils. (ii) Material is steadily drawn into the cylinder, driven by surface tension, increasing its width \( b \). (iii) Once the tendril 'reservoir' is depleted the Rayleigh instability sets in. (iv) The cylinder breaks up into drops; the transient gel de-percolates.](image-url)
8.3 Structural stability and weight-induced rearrangement in the transient gel

Now we consider the effect of gravity on a system-spanning structure where no intrinsic rearrangements are taking place (e.g. $U \gg k_BT$, large particle-solvent density difference $\Delta \rho$ and/or large sample height $h$). In order for collapse to occur not only must the particles go down, the solvent must also go up. Hence two things can support the structure against its own weight; the rigidity of the system-spanning cluster, and the viscous drag of the solvent.

An estimate of weight-induced stress $\sigma_{wt}$ acting on a layer near the base of a transient gel sample of volume fraction $\phi$ and height $h$ is given by

$$\sigma_{wt} = \Delta \rho g h \phi.$$ (8.1)

For our samples this gives $\sigma_{wt} \sim 10\text{ Pa}$. This would seem at odds with our transient gel rheology measurements which place an upper bound on the yield stress $\sigma_y \lesssim 10^{-3}\text{ Pa}$. However we note that the latter is a shear stress measurement, whereas the former is an osmotic-compressional stress. Shear deformation is volume conserving (i.e. does not increase the density of the colloidal structure) and the solvent 'goes with' the structural deformation. Osmotic compression of the gel structure involves an increase in the density of the system-spanning cluster, and the solvent 'moves against' the structural deformation. Hence we can envisage a scenario where a high osmotic-compressional yield stress $\sigma_y^{oc}$ has to be overcome, opening the 'flood gates' to shear flow and the destruction of the gel structure.

8.3.1 Structural stability

The stability (over a certain timescale) of any structure depends essentially on two factors:

(i) The properties of the material(s) comprising the structure; its resistance to deformation against various forces (compressive/tensile, shear) and the type of deformation resulting e.g. elastic, viscoelastic, plastic flow, brittle fracture etc.

(ii) The structural arrangement of the material(s) which determines the distribution of forces.

This is a complex problem. Here we must be content with discussing a few simple ideas concerning the resistance to deformation of the transient gel structure by its own weight.

On the microscopic scale the spherical colloidal particles are the basic building-blocks. Individually they are considered non-deformable. Two particles bonded together by a force such as the depletion or Van der Waals force where there is no preferred bond orientation would exhibit tensile/compressive rigidity but no bending rigidity — fig.8.6(a). Bending rigidity would only result from multiple-bond configurations, as in fig.8.6(b).

Structurally we envisage 'resistance to deformation' as arising from the 'backbones' that percolate the sample cell. Tenuous backbones (fig.8.7(a)) would have little rigidity, and would respond flexibly to deformation. Macroscopically we might see 'plastic' compression of the
structure. Thick backbones (fig.8.7(b)) would be more resistant to deformation. We might expect to see elastic behaviour for small strains. However such a structure could be vulnerable to brittle fracture under large enough forces.

So far we have only considered the structural weight as a 'destructive' force. However it is likely that the deformation of the gel structure could serve to strengthen it. For example, in fig.8.8(a) the fractal tendrils, which contribute mass only and no strength to the structure, are converted to backbones through compression. In fig.8.8(b) a flexible tenuous backbone buckles and forms 'loops', giving it greater rigidity.

We can gain insight into the structural stability of the gel by considering the deformation of a fractal object. The density of a fractal object tends towards zero as its size increases. This leads us to believe that such an object should become 'floppier' as it grows. From the work of Kantor and Webman [74] one can show that the compliance \( C \) (reciprocal of the force constant) of a fractal object scales as \( C \sim R^{3} \), where \( R \) is the fractal size [75]. In the DLCA gel model the cluster radius \( R_{\text{gel}} \) is determined by the sample volume fraction, scaling as \( R_{\text{gel}} \sim \phi^{-1/(3-d)} \) where the fractal dimension \( d \approx 1.8 \) in the high bond energy limit. The deformational stress imposed by the weight of the sample above the cluster is \( \Delta p g \phi \); its product with the compliance goes as \( \sim \phi^{-1.5} \), hence we would expect samples at lower volume fraction to be more susceptible to weight deformation.

Finally we note that deformation/compression of the gel structure might serve to promote the
8.3.2 Hydrodynamics

Hydrodynamic forces exerted by the solvent may play a role in supporting the transient gel structure. In order to ascertain the importance of such forces in maintaining the gel state some kind of estimate of the hydrodynamic resistance to structural collapse is needed.

The gel collapse can be likened to the filtration process, where liquid is driven through a porous medium by a pressure difference. It has been well established by experiment that for low Reynolds number flow through porous media the pressure drop follows Darcy's law [76],

$$\frac{dp}{dz} = -\frac{\eta_s}{k_p} V$$

(8.2)

where $V$ is the uniform liquid velocity upstream of the medium and $\eta_s$ is its viscosity. The constant $k_p$ is called the permeability and dimensionally $k_p \sim p^2$, were $p$ is the characteristic radius of the porous channels.

For our model we assume no structural rigidity so that the weight of the colloidal structure provides the driving pressure. Hence

$$V_{sed} = \frac{\Delta \rho g \phi}{\eta_s} k_p(\{r_c\})$$

(8.3)

where $V_{sed}$ is the sediment interface velocity and $k_p(\{r_c\})$ denotes that the permeability is a function of the arrangement of the colloidal particles $\{r_c\}$.

We need an empirical expression for the permeability $k_p$. We can get a estimate from a commonly used form of the Kozeny-Carman equation [76], which supposes the porous medium to
be composed of a regular arrangement of uniform spheres of radius $a$;

$$k_p = \frac{a^2(e^3)}{45(1 - e)^2}$$  \hspace{1cm} (8.4)

where $e = V_{\text{void}}/V$ is the volume fraction of voids, i.e. $e = 1 - \phi$. For our system, particle radius $a = 300 \text{ nm}$, at a volume fraction of $e = 0.2$ the calculated sediment velocity is $V_{\text{sed}} \sim 5 \text{ nm s}^{-1}$, which is very comparable to the 'slow' sediment velocities $V_s \sim 10 \text{ nm s}^{-1}$ ($0.01 \mu\text{m s}^{-1}$) measured for the transient gel. Hence this estimate, although crude, does not discount hydrodynamic resistance as a significant factor in 'supporting' the gel structure.

One might enquire about the hydrodynamic resistance of a system comprising connected fractal clusters. Following Allain et al. [58] the characteristic pore size $p$ scales as the radius of the clusters $R_{\text{gel}}$. Using the DLCA model of section 5.6.1 (equ.5.12) the permeability $k_p$ of the gel scales as

$$k_p \sim \phi^{-2/(3-d)}$$  \hspace{1cm} (8.5)

where $d$ is the cluster fractal dimension. For high bond energies $d \approx 1.8$, giving $k_p \sim \phi^{-1.7}$. From equation 8.3 the sedimentation velocity scales with $\phi k_p \sim \phi^{-0.7}$. Therefore we would expect the 'slow' sedimentation velocity $V_s$ of a system of 'connected' fractal clusters of negligible stiffness to decrease with increasing volume fraction $\phi$.

**Hydrodynamic rearrangement**

Intriguing images of the weak transient gel collapse have been recently obtained by Starrs [78] using dark-field microscopy. She often observes the growth of a number of 'channels' starting from near the sample base, growing upwards towards the interface during the latency period. It would seem that the channels are associated with solvent flow. The growth of the channels leads to large-scale convective-like flow and disintegration of the gel structure. The typical channel growth speed is $V_{\text{ch}} \sim 1 \text{ cm hr}^{-1}$ ($\sim 1 \mu\text{m s}^{-1}$), whilst the width is $\sim 0.5 \text{ mm}$.

What causes the channels? One could believe this is the result of flow-induced rearrangement. The weight of the transient gel provides the pressure difference $\Delta p g \phi$ and the solvent meanders upwards through the gel structural maze. However the solvent tends to seek the path of least resistance. One can imagine local solvent flows meeting like tributaries meeting at a river as the *preferential path* is sought. On the cluster-scale one can envisage solvent flow 'flattening' tendrils normal to the flow, locally decreasing the hydrodynamic resistance. Particle bonds could be broken in an erosion-like manner.

Alternatively channelling might be a consequence of a fluid-displacement instability. When a high-viscosity fluid is penetrated by a low-viscosity fluid an interfacial instability may be observed known as 'viscous fingering' — the growth of smooth intrusive fingers along the fluid-fluid interface. However if the submissive fluid is viscoelastic the development of the instability depends on the timescale of the intrusive flow $t_{\text{ff}}$ compared with the relaxation time of the viscoelastic fluid $t_{\text{relax}}$. For $t_{\text{relax}}/t_{\text{ff}} \ll 1$ viscous effects dominate; viscous fingering would be observed. However for $t_{\text{relax}}/t_{\text{ff}} \gg 1$ the submissive medium behaves like an elastic solid, and one might expect to observe fracturing rather than fingering. Lemaire et al. [77] observe
such a transition from viscous fingering to viscoelastic fracture in clay suspensions intruded by water. Perhaps the channelling we observe is essentially viscoelastic fracturing of the colloidal aggregates by 'intruding' weight-induced solvent flow. Lemaire et al. estimate \( t_\mathrm{fr} \) from the crack width/velocity ratio. For our channelling this gives \( t_\mathrm{fr} \sim 100 \text{ s} \). We require a much longer structural relaxation time on the \( \sim 1 \text{ mm} \) length scale for the channelling to be viscoelastic fracture. This would be the case if the structural relaxation time on this length scale were comparable to transient gel latency times.

8.3.3 Modelling the effect of weight on the transient gel

So far we have discussed some basic ideas regarding transient-gel structural stability and possible weight-induced rearrangement mechanisms. However we are still far away from predicting the deformational response of a gel structure under its own weight.

However, we can still speculate. Consider a transient gel sample at some point in its intrinsic-rearrangement life-cycle (in the absence of gravity). Let’s ‘stop’ the intrinsic rearranging, suddenly ‘switch on’ gravity, and wait — a rheological thought experiment with osmotic-compressive stress \( \sigma_{\text{wt}}(h) \). As one increases the height \( h \) of the sample, one might observe the following:

![Figure 8.9](image)

**Figure 8.9.** Speculation of the behaviour of a ‘fixed’ transient gel structure (i.e. no intrinsic rearrangement) due to its weight as a function of sample height \( h \). For small heights no collapse is seen, creep deformation only. Increasing sample height results in the gel creeping for a fixed time interval \( \Delta t_{\text{wt}} \) before collapse occurs. Tall enough samples collapse immediately.

1. Small elastic deformation of the gel structure. The gel is unlikely to display elastic behaviour for anything but the smallest strains; therefore we shall treat this situation as negligible weight-induced rearrangement.

2. Creep behaviour. The gel structure undergoes creep compression and continues to do so until the structure becomes close-packed — i.e. weight-induced rearrangement does not lead to collapse.
3. Plastic behaviour. The gel structure creeps for a finite time $\Delta t_{\text{wt}}$, at which point the gel 'yields' and collapses. Such 'plastic flow' behaviour may be exhibited by a power-law fluid (see section 8.6). The creep time $\Delta t_{\text{wt}}$ reduces with increasing sample height.

4. Yield. A sufficiently tall sample collapses immediately under its own weight.

Examples 2 and 4 are just limiting cases of example 3 ($\Delta t_{\text{wt}} = \infty$ and $\Delta t_{\text{wt}} = 0$ respectively). Essentially we are simply saying that, in the absence of intrinsic rearrangement, the weight of a transient gel structure may be responsible for its collapse after some time $\Delta t_{\text{wt}}(h)$, where $\Delta t_{\text{wt}}$ is a decreasing function of sample height $h$.

8.4 The transient gelation picture: intrinsic and weight-induced rearrangement.

We return to the intrinsic rearrangement picture and ask how the stability of the gel changes as intrinsic rearrangement progresses (fig.8.10).

![Figure 8.10. Schematic visualization of the intrinsic rearrangement process in the transient gel, 'strengthening' (1-2) then 'weakening' (3-4) the gel structural stability.](image)

1. Initially the transient gel is a 'close packed' arrangement of fractal-like clusters of radius $R = R_{\text{gel}}$. Structural rigidity/resistance to deformation arises from the 'backbone' branches of width $b$ that percolate the structure. Tendrils are non-percolating branches that contribute mass but no structural rigidity. The characteristic pore size $p$, indicated by the circles, can be thought of as the gaps in between the branches. This would effectively be an average of the larger gaps between the clusters, and the smaller, more numerous gaps between the tendrils.

2. In our picture of intrinsic rearrangement the material from the tendrils is drawn into the backbones, increasing the width $b$, thus converting 'dead weight' into 'supporting material'. The cluster size $R$ remains fixed. Hence initially the structure is becoming 'stronger' (as suggested by our viscosity measurements of section 7.4.3, fig.7.13). The loss of the tendrils increases the characteristic pore size $p$, and hence the permeability $k_p \sim p^2$, resulting in a decrease in hydrodynamic resistance.

3. Once the tendril reservoir is exhausted the cluster size $R$ begins to decrease (i.e. $R < R_{\text{gel}}$).
Hence backbones start breaking, and the structure becomes weaker.

4. Finally the system de-percolates at time $t_{dp}$ and the structure has no rigidity.

The surface-diffusion sintering model suggests a backbone width $b$ gradually increasing with time, whilst the cluster radius $R$ stays fixed at $R_{gel}$ over some time period, then suddenly decreases. Hence gradual backbone thickening might lead to a gradual strengthening of the transient gel. The abrupt breaking of backbones would have a greater effect on the gel structural stability. We might expect a rapid weakening of the transient gel. We envisage a time-dependent (osmotic) compressive yield stress $\sigma_y^{oc}$ for the transient gel in the absence of gravity as in fig.8.11(a).

![Graph](image)

**Figure 8.11.** (a) Speculation of the effect of intrinsic rearrangement on the 'structural strength' of the transient gel. (b) Depercolation time $t_{dp}$ due to intrinsic rearrangement would be some increasing function of bond strength $U$ for fixed volume fraction $\phi$.

The de-percolation time $t_{dp}$, effectively the latency time in the absence of gravity, would be an increasing function of bond strength $U$ (and hence $C_r^{free}$) for a fixed volume fraction $\phi$ — fig.8.11(b). We would expect the de-percolation time to be independent of the sample size and geometry, at least for container dimensions $\gg$ cluster size $R$.

Now we consider transient gel samples of fixed volume fraction $\phi$ and bond strength $U$ on earth. In our simple model the latency time $t_{lat}$ of the transient gel is simply determined by the quickest rearrangement process. This is illustrated in fig.8.12, which combines fig.8.11(a) (with axis swapped) and fig.8.9 to compare the characteristic timescales of intrinsic rearrangement $t_{dp}$ (height independent), and weight-induced rearrangement $\Delta t_{wt}(h)$ (height dependent — here we assume a linear dependence of $\Delta t_{wt}$ on height $h$ for simplicity). The bold line indicates the shortest rearrangement time, and hence the latency time $t_{lat}$ and its dependence on sample height $h$.

As we decrease the height of the sample $h$ we can envisage the sample behaving as follows:

(i) height $h > h_0$; weight-induced stress $\sigma_{wt}(h) \geq$ sample yield stress $\sigma_y^{oc}$. The sample is too tall and collapse occurs immediately — no latency seen.

(ii) $h_0 > h > h_1$; $\Delta t_{wt} < t_{dp}$. Weight causes plastic deformation, the sample creeping for time $\Delta t_{wt}$ before collapsing. Weight-induced rearrangement occurs on a faster timescale than
intrinsic rearrangement; hence observed latency time \( t_{lat} \) is dependent on \( h \) — 'strong' transient gel behaviour. Gravity is the protagonist.

(iii) \( h < h_1; \Delta t_{wt} > t_{dp} \). Here intrinsic rearrangement occurs at a quicker rate than weight-induced rearrangement. Latency time is independent of height, as \( \sigma_{y}^{oc} \) falls off quickly in this regime (rapid weakening). This is 'weak' transient gel behaviour. Gravity is the observer.

(iv) Special case that may be observed for sufficiently small sample heights. We noted that samples may creep under their own weight. Through compression the sample essentially increases its volume fraction \( \phi \), de-percolation time \( t_{dp} \) increasing at a rate which avoids collapse — \( t_{lat} = \infty \).

Hence ideally one might observe both 'weak' and 'strong' behaviour in a single transient gel sample as the height is increased. However this simple model ignores (except in case (iv) above) the coupling between \( t_{dp} \) and \( \Delta t_{wt}(h) \) through (a) the dependency of both on the sample volume fraction \( \phi \), and bond strength \( U \) (b) the effect a continual 'creeping' deformation \( \Delta h(t) \) has on both rearrangement times. Realistically therefore we would expect to see cases (i)(iii)(iv) for a 'weak' transient gel and cases (i)(ii)(iv) for a 'strong' transient gel as the sample height is decreased.

For a samples of fixed height \( h \) and volume fraction \( \phi \) we require the de-percolation time \( t_{dp}(U) \) to increase at a faster rate than \( \Delta t_{wt}(U) \) as bond strength \( U \) is increased in order to account for the 'weak'/'strong' gel crossover observed for \( \phi = 0.30 \) transient gels as polymer concentration \( C_{p}^{free} \) is increased (fig.8.13).
8.5 Transient gel sedimentation results

Here we review the main aspects of our transient gel latency results in the light of the discussion so far.

**Strong/weak transient gel behaviour**

Two distinct types of transient gel behaviour were observed; 'weak' transient gels, where latency time is independent of sample height, and 'strong' gels, where latency time is markedly reduced as the height of the sample is increased. It is noted however that this categorization is based on the observations of just three samples: \( \phi = 0.20, C_p^{\text{free}} = 7.22 \text{ mg cm}^{-3} \) and \( \phi = 0.30, C_p^{\text{free}} = 5.84 \text{ mg cm}^{-3} \) (weak); \( \phi = 0.30, C_p^{\text{free}} = 7.02 \text{ mg cm}^{-3} \) (strong). The difference in behaviour is explained (in section 8.4) as a consequence of crossover from intrinsically-led collapse (height independent) to weight-led collapse (height dependent). Intrinsic rearrangement could be driven by the surface tension of the colloidal gel structure or by thermal bond-breaking leading to de-percolation. Weight-induced rearrangement is considered as the consequence of the gel structure being unable to support its mass i.e. the structure simply 'breaking' under its own weight or compression of the structure driving de-percolating solvent flow.

The de-percolation time \( t_{dp}(U) \) is required to increase at a faster rate than \( \Delta t_{wt}(U) \) as bond strength \( U \) is increased in order to account for the 'weak'/'strong' gel crossover observed for \( \phi = 0.30 \) transient gels as polymer concentration \( C_p^{\text{free}} \) is increased (fig.8.13).
CHAPTER 8. DISCUSSION OF TRANSIENT GEL LATENCY AND COLLAPSE

Dependency of latency time on volume fraction and polymer concentration

The latency time shows a strong dependence on both polymer concentration and volume fraction. For samples in square cross-section cuvettes (1 cm²) and similar height (∼ 2 cm) an exponential-like or power law dependence of the latency time $t_{lat}$ on polymer concentration $C_p$ was observed for 'moderate' volume fractions $\phi = 0.20, 0.30$. For $\phi = 0.20$ an increase in free polymer from $C_p^{\text{free}} = 6.6$ to 10.5 mg cm⁻³ (bond strength $U \approx 7 - 12k_BT$) resulted in an increase in latency time from 1 to 10 hours. For $\phi = 0.30$ an increase in free polymer from $C_p^{\text{free}} = 5.9$ to 7.4 mg cm⁻³ (bond strength $U \approx 6.5 - 8k_BT$) resulted in an increase in latency time from 3 to 30 hours. For weak gels (intrinsically-led collapse) the rearrangement timescale and hence latency time would be related to the Boltzmann distribution $\exp(-U/k_BT)$ if thermal rearrangement were the dominant mechanism; hence an exponential-like dependency of $t_{lat}$ on $C_p^{\text{free}}$. For strong gels (weight-led collapse) we would expect the structural 'rigidity' to increase as the bonds connecting the particles were increased in strength (via $C_p^{\text{free}}$), but the dependency is not obvious.

The strong volume fraction dependence is highlighted by considering the latency times of samples with similar bond strengths $U \approx 6k_BT$ (i.e. $C_p^{\text{free}} = 5.8$ mg cm⁻³) at different volume fractions displayed in table 8.1. The increase of latency time $t_{lat}$ with volume fraction $\phi$ is essentially a consequence of the reduction in free volume (i.e. particle 'elbow room') in the system as $\phi$ is increased. An intrinsically-led collapse results from the rearrangement of a gravitationally-stable aggregate configuration (a gel) to one that is unstable. For a system with large free volume (low $\phi$) there are many more unstable aggregate configurations than stable ones, hence the rearrangement time from stable to unstable is short (low $t_{lat}$). As the volume fraction is increased however the number of stable aggregate configurations increases rapidly. Conversely there are fewer unstable ones, hence the latency time rapidly increases. Reduction in free volume would similarly affect the time required for a weight-lead collapse. Any rigidity in the system results from the rigidity of the colloidal particles (the basic building-blocks). It follows that the more comparable the average structural void size is to particle size, the more rigid the structure becomes, increasing the weight-led latency time. We also note that both hydrodynamic resistance and structural rigidity of a fractal cluster increase as the cluster size $R$ decreases, which according to our DLCA gel model occurs as the volume fraction is increased.

Table 8.1. Comparison of latency time as a function of volume fraction for a constant bond strength $U \approx 6k_BT$.

<table>
<thead>
<tr>
<th>Volume fraction $\phi$</th>
<th>Latency time $t_{lat}$ (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>0.30</td>
<td>$\approx 4$</td>
</tr>
<tr>
<td>0.40</td>
<td>$\approx 50$</td>
</tr>
</tbody>
</table>

Sample geometry

There are two results regarding sample geometry that so far have not been accounted for. The first is the 'critical-width dependence' of the latency time observed for a strong gel in a
cylindrical container. The result may be an artifact of varying 'container quality', e.g. wall smoothness (optical-quality sample cells gave high $t_{lat}$, whereas a measuring cylinder and cheap sample jar gave low $t_{lat}$). Alternatively the 'rigidity' of the transient gel may suffer appreciably if the structure width/height ratio becomes too large (low $t_{lat}$ samples were wider than they were tall).

A clear reduction in latency time of a weak gel in a cylindrical container was also observed. I can offer no convincing explanation regarding this result and it remains a thorn in my side. Either (i) it is a result of human error or (ii) it is telling us something important.

**Visual observations of the weak transient gel**

Three points are worth noting regarding visual observations of the latency period and collapse of a weak transient gel (section 6.5.2).

1. Early coarsening at the top of the sample. Visually the first change in the sample is the appearance of a coarse texture, *but only at the top of the colloidal sediment (specifically in the corners)*, *not evenly throughout the bulk*. We have to bear in mind that visual observations are only of the top half of the sample plane adjacent to the front face of the surface cell. However Pirie [62], visually studying the structural collapse of a transient gel sample observed small-scale vortices, marking the collapse of the gel structure *occurring first at the top of the sample*. Similarly the 'frozen' small-angle ring collapsed at the top of the sample before the bottom [54]. Starrs' dark-field microscopy (DFM) images [78] (suitable for detecting inhomogeneities in samples showing very little contrast) show 'large-scale intensity fluctuations' forming in patches under the corners of the meniscus before rapid sedimentation begins. Glasrud et al. [79] studied the settling behaviour of iron oxide 'needles' suspended in mineral oil. The sedimentation behaviour also shows a latency period followed by collapse. They note that 'horizontal cracks' appear first at the top of the sample. Why inhomogeneities are first seen at the top of samples is not clear. A meniscus effect would appear plausible; however no change in latency time was seen for a (nearly) full weak gel sample. The lack of material weight above this region of the sample is probably significant.

2. Channels. 'Channels' or 'fingers' of motion, associated with solvent flow were observed originating from the bottom half of the sample and growing upwards. This 'channelling' has been most spectacularly observed by Starrs [78] using DFM and appears to play an important role in transient gel collapse. The channelling phenomenon might be (i) weight-induced solvent flow or (ii) release of built-up weight-induced stresses via cracking (buckled sediment interface prior to collapse indicating 'stored stresses').

3. Vulnerability to shear. Once convective-like flow begins much of the gel structure is rapidly destroyed. The vulnerability of the transient gel structure to shear flow is discussed in section 8.6.
8.6 Transient gel rheology results

The results presented in chapter 7 show that the rheological behaviour of colloid-polymer transient gels is fascinating and complex. Here we discuss these results in the context of the transient gel collapse.

We began the rheological investigation of the transient gel with the speculation that it may exhibit a detectable yield stress. A yield stress was not observed for the transient gel within experimental limit. Our results place an upper bound of \( \sigma_y \approx 10^{-3} \text{ N m}^{-2} \) on the yield stress (if it exists). This finding is in agreement with the work of de Rooij et al. [80]. They investigated the elastic behaviour of weakly-aggregating polystyrene latex dispersions \( (U \approx 4 - 10k_BT, \phi = 0.02 - 0.30) \) via creep and oscillatory measurements. Their homemade creep rheometer was capable of applying very small stresses \( (\sim 10^{-3} \text{ Pa}) \) and of measuring very small angular displacements \( (\sim 10^{-6} \text{ radians}) \). Their measurements indicated the absence of a yield stress or equilibrium storage modulus for all samples.

The viscosity of the transient gel mixture was found to be strongly dependent on shear stress at low shear rates \( (1 \lesssim Pe \lesssim 10^{-4}) \), increasing by 2 orders of magnitude \( (10^{-1} - 1000 \text{ cp}) \) over a magnitude in shear stress \( (0.1 - 0.01 \text{ N m}^{-2}) \) i.e. power-law fluid behaviour. The strong shear-thinning exhibited by the transient gel can lead to 'yield-like' action in its sedimentation behaviour without recourse to a yield stress (see below). At higher shear rates \( (Pe \gtrsim 1) \) the flow curve is Bingham-like, tending towards a plastic viscosity \( \eta_p \approx 17 \text{ cp} \).

We measured the effect of polymer concentration \( C_p \) on shear stress at two very different rates of shear; the 'benchmark' stress \( \sigma_{\text{min}} \) at \( Pe \approx 10^{-4} \), and the 'plastic' stress \( \sigma_{\text{pl}} \) at \( Pe \approx 1 \). For comparison the estimate of the shear rates of the macroscopic flow observed during collapse is \( Pe \approx 10^{-3} \). Although both showed a linear trend, the effect of increase in polymer concentration on the shear stress was much greater at lower shear rates — an increase of a factor of \( \approx 16 \) in \( \sigma_{\text{min}} \) compared with \( \approx 2 \) in \( \sigma_{\text{pl}} \) over \( C_p^{\text{free}} = 5.5 - 7.8 \text{ mg cm}^{-3} \). This is not surprising.

At high rates of shear the samples would act like a hard sphere suspension \( (\phi = 0.30) \), the 'background' solvent viscosity equivalent to the viscosity of the polymer solution; hence their viscosities become similar. At lower shear rates however aggregation competes with shear flow destruction; larger clusters appear and the change in colloidal structure greatly increases the viscosity. Samples with higher polymer concentrations have greater interparticle bond strengths, leading to more rigid and ramified clusters occupying a greater 'hydodynamic' volume and leading to greater differences in viscosity between samples of different polymer concentrations.

The strong dependency of the sample viscosity on time at low rates of shear \( (Pe \approx 10^{-4}) \) for samples with higher polymer concentrations can be understood as the result of structural change occurring within the sample. Conversely we can take this as an indication of the strong dependence of viscosity on the colloidal mesostructure.

We now consider our rheological measurements in relation to the transient gel collapse, and try to show that the 'yield-like' action shown during the collapse can be understood as a consequence of the shear-thinning nature of the colloid-polymer mixture. Looking at the weak transient gel images presented in chapter 6 we noted local large scale \( (\sim 0.1 \text{ mm}) \) 'coarsening' occurring at the top of the sediment bulk during the latency period. This coarsening is equated with density...
variation (i.e. clusters and voids) in the sediment. We can model this situation by envisaging a large compact cluster surrounded by an essentially 'homogeneous' gel structure, $\phi = 0.20$ say. The large compact cluster has a greater average density than the rest of the sample, $\phi \approx 0.50$ say. We model the surrounding transient gel sample as a very viscous fluid. The viscosity of a 'weak' gel at Peclet number $Pe \approx 10^{-4}$ is $\sim 1000$ cp. In view of the large variations in viscosity already observed it is not unreasonable to assign a value for the initial 'unperturbed' viscosity of the transient gel two magnitudes greater i.e. $\eta \sim 100,000$ cp. We imagine the dense cluster, of radius $R$, sedimenting very slowly through the very viscous transient gel. The sedimentation velocity $V$ of the large cluster is of order

$$V \sim \frac{2\Delta \rho \Delta \phi R^2}{9\eta} \quad (8.6)$$

where $\Delta \rho$ is the particle-solvent density difference and $\Delta \phi$ is the cluster-sample average volume fraction difference. As the cluster slowly moves it effectively shears the sample surrounding it, at a rate

$$\dot{\gamma} \sim \frac{V}{R} \quad (8.7)$$

However the transient gel viscosity is a function of shear rate; i.e. the sample surrounding the cluster shear thins, over a timescale $\Delta t \sim \gamma^{-1}$ say, to a lower viscosity $\eta$ given by

$$\eta \sim \psi^{-1/N} \gamma^{(N-1/N)} \quad (8.8)$$

from the power-law fluid flow curve equation 7.3, with $N = 3$ and $\psi \approx 1000$. The lower viscosity $\eta$ now results in a greater sedimentation velocity $V$ for the cluster, which continues to shear thin the sample surrounding it and so on.

For our system $\Delta \rho \approx 0.3 \, g \, cm^{-3}$, and we estimate $\Delta \phi \sim 0.3$. If we base our model on the images of section 6.5.2, we envisage a large cluster or density inhomogeneity of $R \sim 0.1$ mm i.e. $\sim 100$ particles across. The sedimentation velocity and position of the cluster are displayed in figs.8.14(a) and (b). A sharp transition is seen from a slow sedimentation velocity $V_{cl} \approx 0.02 \, \mu m \, s^{-1}$ to a much higher velocity $V_{cl} \approx 0.8 \, \mu m \, s^{-1}$, resulting in the 'yield-like' motion of the cluster. Local flow would then result in a 'knock on' effect which would soon destroy the entire gel structure.

For strong transient gel samples we noted that the latency period strongly decreased as the height of the sample was increased. It would seem likely therefore that the sample's own weight hastens the collapse, perhaps effectively shearing the sample. Hence we might draw parallels between this behaviour and the observed reduction in latency of a very strong transient gel under a small but constant shear force $\sigma_c$.

Finally we note the strong increase and decrease in viscosity $(5000 - 50,000$ cp and back) during the latency period of a very strong transient gel subjected to a small constant shear stress $(\sim 0.01 \, N \, m^{-2})$. The decrease coincides with the transient gel collapse. We must be
aware that the probing stress we use to measure the viscous response of the gel is altering its behaviour. However it is tempting to see this large increase and decrease of viscosity as evidence that the transient gel structure is strengthening and then weakening during latency (even in the absence of external shear forces), and that the weakening leads to transient gel collapse.

8.7 Other systems exhibiting ‘delayed sedimentation’

A summary of other systems exhibiting delayed sedimentation is displayed in tables 8.2 and 8.3 for completeness. It is evident that delayed sedimentation occurs in a wide variety of systems over a broad range of concentrations. Latency periods range vastly from as little as minutes to as much as a year.

Ideally comparison of these systems and their behaviour would give insight into the physics of delayed sedimentation. However it is noted that, with the exception of this study and perhaps that of Partridge, none of the systems is well characterised.
CHAPTER 8. DISCUSSION OF TRANSIENT GEL LATENCY AND COLLAPSE

<table>
<thead>
<tr>
<th>Authors</th>
<th>This study</th>
<th>Robbins et al. [81]</th>
<th>Glasrud et al. [79]</th>
</tr>
</thead>
<tbody>
<tr>
<td>system</td>
<td>PMMA spheres dispersed cis-decalin</td>
<td>oil dispersed in water (emulsion)</td>
<td>iron oxide needles dispersed in heavy mineral oil</td>
</tr>
<tr>
<td>particle size and polydispersity</td>
<td>radius $a \approx 300$ nm $\sim 5%$</td>
<td>$a \approx 750$ nm $&gt; 100%$</td>
<td>length $\approx 500$ nm, width $\approx 100$ nm ?</td>
</tr>
<tr>
<td>continuous phase viscosity $\eta_s$ (cp)</td>
<td>3</td>
<td>10 — 4000 (inc. polymer)</td>
<td>135</td>
</tr>
<tr>
<td>particle-solvent density difference $\Delta \rho$ (g cm$^{-3}$)</td>
<td>0.3</td>
<td>0.3 — 0.4 (creaming)</td>
<td>3.6</td>
</tr>
<tr>
<td>particle interaction</td>
<td>depletion force (polystyrene)</td>
<td>depletion force (hydroxyethyl cellulose)</td>
<td>Van der Waals? and ferromagnetic</td>
</tr>
<tr>
<td>interaction range $\delta$</td>
<td>$\approx 0.06a$</td>
<td>$\approx 0.09a$</td>
<td>?</td>
</tr>
<tr>
<td>typical bond energies $U (k_B T)$</td>
<td>5 — 10</td>
<td>40 — 500</td>
<td>?</td>
</tr>
<tr>
<td>typical volume fractions $\phi$</td>
<td>0.20 — 0.30</td>
<td>$\approx 0.2$</td>
<td>0.01 — 0.10</td>
</tr>
<tr>
<td>typical latency times $t_{lat}$</td>
<td>1 — 30 hrs</td>
<td>1 — 50 hrs</td>
<td>$\sim$ hours — $\approx$ 1 year (!)</td>
</tr>
<tr>
<td>typical ‘slow’ sedimentation velocities $V_s$ ($\mu$m s$^{-1}$)</td>
<td>$\sim 0.01$</td>
<td>$\sim 0.1$</td>
<td>$\sim 0.01$</td>
</tr>
<tr>
<td>typical ‘collapse’ velocities $V_{cs}$ ($\mu$m s$^{-1}$)</td>
<td>$\sim 1$</td>
<td>$\sim 1 — \sim 0.1$</td>
<td>$\sim 1 — \sim 0.001$</td>
</tr>
<tr>
<td>typical final sediment volume fractions $\phi_{fin}$</td>
<td>0.3 — 0.5</td>
<td>$\approx 0.4$</td>
<td>0.02 — 0.1</td>
</tr>
<tr>
<td>container shape dependence observed?</td>
<td>yes</td>
<td>yes [82]</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 8.2. Summary of systems exhibiting delayed sedimentation.

8.8 Ideas for future work

It would be desirable to have (i) experimental proof that intrinsic rearrangement leads to gel de-percolation and (ii) an estimate of the dependency of $t_{dp}$ on $\phi$ and $C_p^{free}$. The only earth-bound method involves density matching the particles and solvent. Detection of gelation would be by observation of a ‘frozen’ small-angle light scattering ring. For small enough $\phi$, $C_p^{free}$ one would hope eventually to see discrete compact clusters.

Measurement of the minimum height for ‘immediate’ collapse $h_0$ for samples of various $\phi$, $C_p^{free}$ would give insight into the dependency of gravitational stability of the early-time gel structure, as all collapses must be weight-induced.

A closer look at the height dependency of the transient gel might be revealing. One might examine a sample of height $\approx 4$ cm that exhibits a long latency time, $t_{lat} \approx 1$ day say. One could then vary the height over a significant range ($1 — 10$ cm say) and hope to observe large
### Table 8.3. Summary of systems exhibiting delayed sedimentation.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Partridge [83]</th>
<th>Allain et al. [58]</th>
</tr>
</thead>
<tbody>
<tr>
<td>system</td>
<td>polystyrene latex spheres dispersed in water</td>
<td>calcium carbonate spheres dispersed in water</td>
</tr>
<tr>
<td>particle size and</td>
<td>radius $a \approx 500,700,1000$ nm</td>
<td>$a \approx 70$ nm</td>
</tr>
<tr>
<td>polydispersity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>continuous phase</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>viscosity $\eta_s$ (cp)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>particle-solvent density</td>
<td>$\sim 0.05$</td>
<td>1.7</td>
</tr>
<tr>
<td>difference $\Delta \rho$</td>
<td>$\rho$ (g cm$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>interaction</td>
<td>Van der Waals</td>
<td>Van der Waals</td>
</tr>
<tr>
<td>interaction range $\delta$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>typical bond energies</td>
<td>$7 - 15$</td>
<td>?</td>
</tr>
<tr>
<td>$U (k_BT)$</td>
<td>0.10 — 0.30</td>
<td>0.003 — 0.007</td>
</tr>
<tr>
<td>typical volume fractions</td>
<td>0.5 — 5 hrs</td>
<td>$\sim 10 - 30$ mins</td>
</tr>
<tr>
<td>typical latency times</td>
<td></td>
<td>($\phi \geq 0.008$ shows no collapse)</td>
</tr>
<tr>
<td>$t_{lat}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>typical 'slow'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sedimentation velocities</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_s$ ($\mu$m s$^{-1}$)</td>
<td>$\sim 0.008$</td>
<td>1 — 0.1 (0.01)</td>
</tr>
<tr>
<td>typical 'collapse'</td>
<td></td>
<td></td>
</tr>
<tr>
<td>velocities $V_{rs}$</td>
<td></td>
<td>$\sim 100$</td>
</tr>
<tr>
<td>typical final</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sediment volume fractions</td>
<td>$0.40 - 0.45$</td>
<td>?</td>
</tr>
<tr>
<td>$\phi_{fn}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>container shape</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>dependence observed?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Latency time variations.

Systems using smaller $\phi$ and 'very high' polymer concentrations (i.e. greater than the overlap polymer volume fraction $\phi_p^* \sim 1$) could show some very interesting behaviour. At the other end of the spectrum investigation of high volume fraction transient gels (i.e. $\phi > 0.3$) with latency times of $\sim$ weeks would give us a better measure of the dependency of latency period on particle concentration.
Chapter 9

Conclusion

As was noted at the beginning of this thesis, this work is essentially just a collection of observations and measurements motivated by some simple questions. Although many of these questions remain unanswered it is hoped that this work will provide some kind of foundation for further study and understanding.

It is noted that this study benefits from the well-characterised systems used; i.e. sterically-stabilized PMMA nearly-monodisperse ‘hard’ spheres, and ‘small’ monodisperse polystyrene coils. The ‘model’ nature of both the hard-sphere suspension and the colloid-polymer mixture enables useful comparison with theory. It is also clear that the Zimm-Crothers viscometer is a valuable tool for investigating the rheology of colloidal systems in the low-shear regime.

Low-shear viscosity of a hard sphere suspension

The low-shear limit relative viscosity $\eta^0$ of nearly-monodisperse sterically stabilized PMMA spheres dispersed in cis-decalin, a hard-sphere suspension, was found to be $\approx 50$ at the hard sphere freezing concentration $\phi_f = 0.494$. This, as well as the general volume fraction dependence (referenced to the freezing concentration) of the low-shear relative viscosity, was found to be significantly different to previous measurements on hard-sphere suspensions. However, two previous data sets were brought into agreement with our measurements by a simple scaling of volume fractions in each case.

Delayed sedimentation of colloid-polymer transient gels

We observe a shift in the transient gelation line $C_p^t(\phi)$ to higher volume fraction $\phi$ when comparing the nonequilibrium diagram of our system with that with a similar system of smaller particle size ($a = 301$ nm compared with 240 nm). Qualitatively this shift is understood as a consequence of the greater influence of gravity on our system on cluster sedimentation, requiring higher polymer concentration $C_p$ (i.e. higher bond strength) at the same volume fraction $\phi$ for gelation to occur.
The latency time $t_{\text{lat}}$ shows a strong dependence on both free polymer concentration $C_p^{\text{free}}$ and volume fraction $\phi$. For samples in square cross-section cuvettes (1 cm$^2$) and similar height ($\approx$ 2 cm) an exponential-like or power law dependence of the latency time on polymer concentration was observed for 'moderate' volume fractions $\phi = 0.20, 0.30$.

Two distinct types of transient gel behaviour are observed; 'weak' transient gels (lower polymer concentrations and latency times), where latency time is independent of sample height, and 'strong' transient gels (higher polymer concentrations and latency times), where latency time is markedly reduced as the height of the sample is increased. Thermal rearrangement of the gel structure leading to cluster compactification and sedimentation is suggested as the prime cause of 'weak' gel collapse. For the 'strong' transient gel it is proposed that the weight of the gel structure hastens its own destruction before significant thermal rearrangement occurs.

The average volume fraction $\phi_{\text{fin}}$ of the metastable sediment (resultant sediment after the collapse and rapid sedimentation of the transient gel) was found to decrease with polymer concentration and increase with total sample volume fraction.

**Low-shear rheology of colloid-polymer transient gels**

A yield stress is not observed for the transient gel within experimental limit. Our results place an upper bound of $\sigma_y \sim 10^{-3}$ N m$^{-2}$ on the yield stress (if it exists).

The viscosity of the transient gel mixture is found to be strongly dependent on shear stress at low shear rates ($1 \geq Pe \geq 10^{-4}$), increasing by 2 orders of magnitude ($10 - 1000$ cp) over a magnitude in shear stress ($0.1 - 0.01$ N m$^{-2}$) i.e. power-law fluid behaviour. It is suggested that the strong shear-thinning exhibited by the transient gel leads to the 'yield-like' action observed at the gel collapse. At higher shear rates ($Pe \geq 1$) the flow curve is Bingham-like, tending towards a plastic viscosity $\eta_{\text{pl}} \approx 17$ cp. Comparative stresses at different shear rates ($Pe \approx 10^{-4}$ and $Pe \approx 1$) both display a linear polymer concentration dependence.

A strong increase and decrease in viscosity ($5000 - 50,000$ cp and back) during the latency period of a very strong (very high polymer concentration) transient gel subjected to a small constant shear stress ($\sim 0.01$ N m$^{-2}$) is observed. The decrease coincides with the transient gel collapse. It is suggested that the transient gel structure is strengthening and then weakening during latency even in the absence of shearing forces.
Appendix

Effect of unknown particle density on volume fraction

Here we estimate the resultant uncertainty in calculated volume fraction of a sterically-stabilized 'hard' sphere suspension diluted from a calibrated stock suspension due to the uncertainty in particle density.

Ideally the volume fraction of our 'stock' suspension, containing mass $m_i^0$ liquid and $m_p^0$ of PMMA particles is

$$\phi_{\text{stock}} = \frac{\left(\frac{m_i^0}{\rho_p}\right)}{\left(\frac{m_i^0}{\rho_p}\right) + \left(\frac{m_p^0}{\rho_l}\right)} = \frac{1}{1 + \left(\frac{m_i^0}{m_p^0}\right) \frac{\rho_l}{\rho_p}}$$

where $\rho_l$ is the density of the solvent, $\rho_p$ is the estimated particle density (in our case the density of 'bulk' PMMA) and $x = \rho_p/\rho_l$.

Adding liquid $m_i$ to the stock gives the sample volume fraction

$$\phi = \frac{1}{1 + \left(\frac{m_i^0 + m_i}{m_p^0}\right) \frac{\rho_l}{\rho_p}}.$$

However, possible solvent imbibition by the particles would change the sample volume fraction. Say a particle takes up a fraction $\alpha$ of its own mass in liquid i.e. effective mass of particles $= m_p^0(1 + \alpha)$. The sample volume fraction becomes

$$\phi \rightarrow \phi_{\text{imb}} = \frac{\left(\frac{m_i^0}{\rho_p}\right) + \left(\frac{\alpha m_i^0}{\rho_l}\right)}{\left(\frac{m_i^0}{\rho_p}\right) + \left(\frac{m_i^0 + m_i}{\rho_l}\right)} = (1 + \alpha x)\phi$$

The stock suspension would be similarly affected by particle solvent imbibition.
Let us assume that the initial stock is standardised e.g. $\phi_{stock} = \phi_0 = 0.494$. Taking into account particle solvent imbibition we now have

$$\phi_0 = (1 + \alpha x) \frac{1}{1 + \left(\frac{m_p^0}{m_p} \right) x};$$

adding or subtracting solvent mass $m_l$ gives the sample volume fraction

$$\phi = (1 + \alpha x) \frac{1}{1 + \left(\frac{m_p^0 + m_l}{m_p} \right) x}$$

Now the fractional difference of the stock and sample volume fractions is

$$\frac{\phi - \phi_0}{\phi_0} = -\left(\frac{m_l}{m_p^0}\right) \frac{x}{1 + \left(\frac{m_p^0 + m_l}{m_p} \right) x}$$

Differentiating with respect to the particle/solvent density ratio gives

$$\frac{d}{dz} \left(\frac{\phi - \phi_0}{\phi_0}\right) = -\left(\frac{m_l}{m_p^0}\right) \frac{1}{z} \left[1 + \left(\frac{m_p^0 + m_l}{m_p} \right) x\right]^2$$

$$= -\left(\frac{\phi - \phi_0}{\phi_0}\right) \frac{1}{z} \frac{1}{1 + \left(\frac{m_p^0 + m_l}{m_p} \right) x}$$

$$= \left(\frac{\phi - \phi_0}{\phi_0}\right) \frac{1}{z} \frac{1}{1 + \left(\frac{m_p^0 + m_l}{m_p} \right) x}$$

$$= \left(\frac{\phi - \phi_0}{\phi_0}\right) \frac{\phi}{(1 + \alpha x)^x}$$
Hence

\[ d\phi = (\phi - \phi_0) \frac{\phi}{(1 + \alpha x)} \frac{dx}{x} \]

so that the fractional uncertainty in particle/solvent density \( x \) gives us the fractional uncertainty in volume fraction \( \phi \)

\[ \frac{d\phi}{\phi} = \frac{\phi - \phi_0}{(1 + \alpha x)} \frac{dx}{x} \]

For small \( \phi \)

\[ \frac{d\phi}{\phi} \approx \frac{-\phi_0}{(1 + \alpha x)} \frac{dx}{x} \ll \frac{dx}{x} \]

For \( \phi \sim \phi_0 \)

\[ \frac{d\phi}{\phi} \ll \frac{dx}{x} \]
Bibliography


[29] A. Einstein, Ann.Physik 19 289 (1906) (see also ibid. 34 591 (1911)).


[40] P. N. Pusey, private communication.


Great sentence said by Mike Evans during a discussion on transient gel collapse.

good sentence said by W. C. K. Poon.


M. Cates and R. M. Evans, private communication.


L. Starrs, Direct Observation of Colloid-Polymer Gels, unpublished (1997).


M. M. Robbins to W. C. K. Poon, private communication.

Publications

Concentration dependence of the low-shear viscosity of suspensions of hard-sphere colloids

Dynamics of concentrated colloidal suspensions

Viscosity and structural relaxation in concentrated hard-sphere colloids

Viscosity and structural relaxation in suspensions of hard-sphere colloids