Microscopic view of coexisting gas, liquid and solid colloidal phases formed by the addition of free polymer to polystyrene latex.
Polymers: Their Effect on The Rheology of Concentrated Colloidal Dispersions

by

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A dissertation submitted to the University of London in partial fulfilment of the requirements of the degree of Doctor of Philosophy and of the diploma of Imperial College.

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Preface.

This thesis is a description of the work performed at Chesterford Park, AgrEvo UK Limited, Saffron Walden, Essex and in the Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London, under the supervision of Dr. P.F. Luckham. The material presented here is the original work of the author except where acknowledged. No part of this work has been submitted for a degree at this or any other university.
Dedication.

To my parents.
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I would like to thank Dr. P.F. Luckham for his foresighted guidance, enthusiasm in my discoveries and encouragement throughout my studies.

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Abstract.

In the first part a series of three PEO-PPO-PEO block copolymers, with constant PPO chains (the anchor) and varying PEO chain lengths (the buoy), have been used to investigate the effect of molecular weight of the stabilising polymer on the rheological properties of aqueous polystyrene latices and emulsions.

With the latices, adsorption was Langmuirian and of a high affinity with the area per molecule scaling with the PEO radius of gyration, indicating the chains to be in the form of coils. In contrast, some three times the amount of polymer was adsorbed at the interface of the emulsions and the area per molecule showed little dependence on PEO molecular weight indicating the PEO chains to be in the form of linear rods protruding from the interface to form a "brush."

Dynamic and steady shear measurements were performed as a function of volume fraction. Large latices (400-500 nm) behaved as relatively hard spheres showing little deviation in rheology due to the adsorbed polymers. Conversely, a small latex was much softer in its behaviour and exhibited large deviations which increased with increasing molecular weight of the PEO. Polymer layer thickness increased with molecular weight of the PEO and indicated the coils to be extended from the surface.

For the second part, the effect of nonadsorbing polymers to the above systems has been studied. Addition of hydroxyethylcellulose (HEC) and xanthan resulted in flocculation of the latices by a depletion mechanism. An extensive range of rheological measurements indicated how the floc structure changed with latex volume fraction and molecular weight of nonadsorbing polymer. With both increasing volume fraction of latex at constant polymer molecular weight and increasing polymer molecular weight at constant volume fraction the amount of polymer required to induce flocculation decreased. The small latex showed gas-liquid and gas-solid phase behaviour with increasing HEC content and passed through a three phase coexistence region. The amount of HEC required was sensitive to the adsorbed block copolymer and decreased with increasing molecular weight of the PEO. This corresponded to an increase in the volume concentration of the PEO.
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Introduction.

Polymers are widely used to stabilise colloidal dispersions by modifying the interparticle forces. Their use dates back many thousands of years to the ancient Egyptians and Chinese who stabilised soot particles with natural polymers such as casein, albumin and gum arabic to produce ink\(^1\). Today their use is so widespread that they are an indispensable part of everyday life. Their applications range from synthetic blood to paints and include foods, pharmaceutical and agricultural preparations, lubricants, detergents, inks, glues, cosmetics and ceramics to name but a few.

Colloidal dispersions are often described\(^2\) as being composed of particles with a dimension between 1nm and 1\(\mu\)m, although many practical systems lie just above this range, and describe systems ranging from large molecules to small particles. On account of the small size of the particles, colloidal dispersions have a large surface area in relation to their volume. This area plays a major role in dictating the properties of colloidal dispersions since it usually has a positive free energy which means that the dispersion has a high surface free energy and is thermodynamically unstable with respect to coagulation. Despite this, there are many examples of stable dispersions such as Faraday's gold sol,\(^3\) which alone remains dispersed for decades but flocculates in the presence of electrolyte. However, when stabilised by gelatin, this flocculation of the gold particles in electrolyte is prevented. This illustrates the two mechanisms which act in the stabilisation of colloidal dispersions, namely electrostatic and polymeric or steric. Without the gelatin the gold particles are electrostatically stabilised by a charged layer which, on addition of electrolyte, becomes compressed and allows flocculation of the particles, which is apparent as a colour change from red to blue. When gelatin is added, it adsorbs onto the particles to form a polymeric layer which sterically prevents flocculation of the particles even in electrolyte.

It is this second mechanism that has been studied in this work. As already seen, it has the advantage over electrostatic stabilisation in that it is relatively insensitive to electrolyte and can even work in non-aqueous, low dielectric systems where electrostatic stabilisation fails. It also allows for greater control of the range and magnitude of these stabilisation forces through the thickness, nature and concentration of any adsorbed layers. It can be clearly seen that as the concentration of the dispersion increases, the interaction of the stabilising layers on adjacent particles will have a marked effect on the flow properties of the dispersion. The study of these properties is termed rheology.
Nonadsorbing polymers are also widely used to modify the flow properties of colloidal dispersions where they must perform more than one role, simultaneously and usually in conflict. One example is paint which requires complex rheological properties to allow flow of the paint during application, but prevent it from sagging once applied.\textsuperscript{4,5} Another is the prevention of sedimentation in agricultural suspensions.\textsuperscript{6-8} Suspension concentrates are an important formulation type in the design of crop protection products in which sedimentation has long been recognised as an inherent problem. This, if not controlled by an anti-settling agent, can lead to dilatant sediments which are difficult to redisperse. This can be particularly acute in agricultural suspension concentrates where a balance of properties are required since a suspension needs to be sufficiently viscous to prevent sedimentation and yet also be sufficiently fluid to allow it to be readily emptied and rinsed from its pack, without any residue remaining, in accord with regulatory requirements.

This conflict of interests is often overcome by forming a weak, volume filling, three dimensional network of particles which is sufficiently strong to overcome gravitational stresses and prevent sedimentation. However, upon application of a slightly greater stress, such as encountered when inverting the pack or pouring out the contents, the three dimensional network must be sufficiently weak such that it is able to break down and allow the suspension to flow. Rheologically this corresponds to a "solid" on standing which breaks down to a fluid on application of a stress or shearing, i.e. a plastic material. The three dimensional network of particles is often formed by the flocculation of a dispersion by nonadsorbing polymers such as high molecular weight polysaccharides, e.g. xanthan. With the appearance of new, high potency, active ingredients, modern trends are towards lower concentration suspensions. Here, the sedimentation problem is exacerbated since there is less material available to form a "supporting" network and in order to overcome this problem, greater knowledge of the mechanism by which the different components interact is required.

The aim of this work is to gain a greater understanding of the effect of the various components of suspensions, especially adsorbed stabilising polymers and free nonadsorbed polymers, on their flow properties to enable better products to be designed within shorter timescales.

Model suspensions have been used here to allow various scientific theories to be applied where applicable. The model suspensions are aqueous, monodisperse polystyrene latices and oil in water emulsions, which were both stabilised with a series of ABA block copolymers. Three copolymers were chosen in which the B units were poly(propyleneoxide) and had a constant length while the A units were poly(ethyleneoxide) with different lengths.
In aqueous environments the B blocks are insoluble and adsorb onto the interface, while the soluble A blocks extend out into the medium providing a barrier to flocculation.

In the first part of this thesis, the theory of rheology and interparticle forces are introduced. Then the adsorption of the copolymers with the latices and emulsions is characterised, followed by the rheology of the resulting dispersions. Both steady state shear rate and oscillatory shear measurements are used to study the effect of the adsorbed polymer layer as a function of dispersed phase volume fraction. This is then complimented by the addition of nonadsorbing hydroxyethylcellulose, which is spread over three chapters. In the first, the effect of the nonadsorbing polymer concentration and latex volume fraction is examined, followed by the effect of the molecular weight of the depleting polymer for the second. The third examines the outcome when the molecular weight of the adsorbed stabilising copolymer is varied. The final experimental chapter extends this work to a "real" system in which the rheology and sedimentation of an agricultural insecticide suspended in a solution of nonadsorbing xanthan polymer is studied.
Chapter 1. Rheology.

1.1 General Rheological Principles.

Rheology is the study of the deformation of materials and owes its origins to the work of Hooke\(^9\) and Newton\(^10\) in the 17th century. In general there are two types of rheological measurements that can be performed. Those at large deformations where the structure is broken down and the rheology is governed by the hydrodynamic properties of the system and those at small deformations, in which the structure of the sample is not broken down and the rheology is governed by the interparticle forces/microstructure of the system. In the case of the latter it is necessary to perform measurements at small strains in a sample's linear region where the results obtained do not vary with strain i.e. the linear viscoelastic region.

Experiments may either be performed by applying a known strain or strain rate and measuring the resultant stress transmitted through a sample, or by applying a known stress and measuring the resultant deformation. If a cube of material is sheared from \(abcd\) to \(a'b'c'd'\) (see figure 1.1) then the strain, \(\gamma\), is given by the tangent of the angle, \(\alpha\), and the shear stress, \(\sigma\), is the force per unit area.

\[
\gamma = \tan \alpha = \frac{\Delta X}{Y} \quad (1.1)
\]

\[
\sigma = \frac{F}{A} \quad (1.2)
\]

Figure 1.1 Shear deformation of a material.

1.2 Measurements at Large Deformations.

In this type of rheological experiment a sample is either deformed at a known rate and the resultant stress transmitted through the sample is measured or a known stress is applied to a sample and the rate of deformation is measured. If the shear stress is plotted as a function
of shear rate, \( \dot{\gamma} = \frac{dy}{dt} \), then in both cases four different types of flow can be distinguished. These are illustrated in figure 1.2.

The relationship between stress, strain and time is referred to as the constitutive equation. For Newtonian liquids the shear stress is linearly dependent on the shear rate and the slope of the line is the coefficient of viscosity, \( \eta \):

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

Many liquids and very dilute suspensions show Newtonian behaviour. If the material is plastic, flow only occurs once a certain stress has been exceeded. The term plastic is derived from the Greek word *plastikos* which means "to mould" or "to form". The terminology "plastic" applied to many polymeric materials such as PVC is actually a description of their flow properties; at high temperature and pressure the polymer flows and can be moulded into a form which becomes rigid on cooling. Once flow is obtained its form is Newtonian and it is termed the plastic viscosity, \( \eta_{pl} \), while the limiting stress is termed the yield stress, \( \sigma_y \), which, if introduced into equation (1.3) gives the Bingham model:

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

Shear thinning, which is a decrease in the viscosity with increasing shear rate, is often observed with many concentrated suspensions, emulsions and polymer solutions and is usually
a consequence of the structure of the dispersion changing with the rate of shear. The opposite, shear thickening where the viscosity increases with increasing shear rate can occur for many reasons, the more common being flocculation, comminution and dilatancy. Dilatant flow is usually observed in very concentrated suspensions and is attributed to the fact that as shearing becomes more intense, the structure of the suspension expands or dilates into layers. This type of non-Newtonian behaviour can be described by a power law or Ostwald de Waal model:\textsuperscript{13}

\[ \sigma = k_1 \dot{\gamma}^n \]  

(1.5)

The power index, \( n \), describes the degree of deviation from Newtonian flow while \( k_1 \) is a constant with units of Pa s\(^n\). Values of \( n \) less than 1 correspond to shear thinning, values greater than 1 to shear thickening and a value of 1 to Newtonian flow. If a yield stress is also present then we obtain the Herschel Bulkley model:\textsuperscript{14}

\[ \sigma = \gamma_0 + k_1 \dot{\gamma}^n \]  

(1.6)

Pseudoplastic fluids do not have a yield stress but exhibit Newtonian flow at low and high shear rates with a region of shear thinning at intermediate shear rates. This type of flow requires at least four parameters for its description and can be successfully described by the model due to Cross:\textsuperscript{15}

\[ \eta = \eta_\infty + \frac{\eta_o - \eta_\infty}{1 + k\dot{\gamma}^m} \]  

(1.7)

where \( k \) is a constant with units of time, \( m \) is a dimensionless constant and \( \eta_o \) and \( \eta_\infty \) are the limiting Newtonian viscosities at low and high shear rates respectively.

Time dependent behaviour may also be found, a reversible decrease in viscosity with time under constant shear conditions is termed thixotropy whereas a reversible increase is termed rheopexy. Thixotropic behaviour is observed with gels formed from semi-dilute polymer solutions and dispersions of highly anisotropic and interacting particles such as smectite clays, and when the rate of structural breakdown is slow compared to the time of the experiment. Rheopexy is usually observed at low shear rates with particles that interact attractively.

### 1.3 Measurement at Small Deformations

#### 1.3.1 Viscoelasticity

Upon application of a stress to a material a recoverable elastic deformation instead of viscous flow may be observed. Here the material behaves as an elastic solid and obeys
Hooke's law\(^9\) where the shear modulus, \(G\), is given by the ratio of the shear stress, \(\sigma\), to the strain, \(\gamma\):

\[
G = \frac{\sigma}{\gamma} \quad (1.8)
\]

If a material is neither totally elastic or viscous, but exhibits both types of behaviour it is viscoelastic.

For viscoelastic materials the timescale of the experiment is important and is classified by the ratio of the relaxation time of the sample, \(\tau\), to the experimental time. This ratio was termed the Deborah number, \(D\), by Marcus Reiner\(^{16,17}\) after the prophet Deborah who declared "The mountains flowed before the Lord...". For colloidal dispersions the relaxation time is simply the time taken by a particle to diffuse through a specified distance such as its own diameter. An elastic response is observed when \(D \gg 1\), a viscous response when \(D \ll 1\) while both viscous and elastic (i.e. viscoelastic) responses when \(D \approx 1\). This behaviour is readily illustrated through mechanical analogues composed of either a spring, with shear modulus \(G\), or dashpot of viscosity \(\eta\), with the stress given by Hooke's\(^9\) and Newton's\(^{10}\) laws respectively:

\[
\begin{align*}
\text{Spring} & : \sigma = G \gamma \\
\text{Dashpot} & : \sigma = \eta \dot{\gamma}
\end{align*}
\]

With the spring the energy of deformation, \(E\), is stored while with the dashpot the energy of the deformation is dissipated at the rate given by \(\dot{E} = \frac{dE}{dt}\).

Combining the Hookean spring in series with the Newtonian dashpot gives a Maxwell model.\(^{18}\)

\[
\begin{align*}
\text{Maxwell model} & : \sigma = G \gamma + \eta \dot{\gamma}
\end{align*}
\]

Here the stress is the same in both parts while the strains are additive. This gives the
following constitutive equation where $\dot{\sigma} = \frac{d\sigma}{dt}$:

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \tag{1.9}$$

Over short periods the elasticity, $G$, has a maximum limiting value, $G^\alpha$, while over long periods the viscosity, $\eta$, has a maximum limiting value, $\eta_\infty$. The Maxwell relaxation time, $\tau$, is simply $\eta/G$. Many systems have a range of relaxation times which can be represented by a series of Maxwell models in parallel or by a continuous spectrum of relaxation times, $H(t)$, which represents the spring constant of each element, $G_i$, multiplied by the frequency of its occurrence.

Another model commonly used is the Kelvin or Voight which consists of a Hookean spring in parallel with a Newtonian dashpot.

Another model commonly used is the Kelvin or Voight which consists of a Hookean spring in parallel with a Newtonian dashpot.

![Kelvin or Voight model](image)

This time the strain is the same in both parts and the stresses are additive giving:

$$\sigma = G\dot{\gamma} + \eta \dot{\gamma} \tag{1.10}$$

In this case $\eta/G$ is the retardation time $\tau$. These models are useful for illustrating the response of viscoelastic materials to rheological experiments and can, especially if extended to a combination of several Maxwell or Kelvin units, be used to model the response of real materials.

1.3.2 Stress Relaxation.

In this experiment a strain is rapidly applied and maintained at a constant level while the stress is monitored as a function of time. The stress, at time $t$, divided by the constant strain, gives the relaxation modulus, $G(t)$. For a single Maxwell model, the measured stress decays exponentially and its relaxation time, $\tau$, corresponds to the point at which the relaxation modulus has relaxed to $1/e$ of its limiting value at short timescales, $G^\alpha$. This is
illustrated in figure 1.3 where the top diagram shows how the strain is controlled and the bottom diagram shows how the relaxation modulus behaves for a viscoelastic material.

![Strain and relaxation modulus graphs](https://via.placeholder.com/150)

Figure 1.3 Stress relaxation experiment.

For a single Maxwell model the decay of the relaxation modulus can be described by:\(^{18,19}\)

\[
\frac{dG(t)}{dt} = -\frac{1}{\tau} G(t) \tag{1.11}
\]

where \(1/\tau\) corresponds to a rate constant for the relaxation process. Integrating to find \(G(t)\) at time \(t\) using \(G(t) = G^\infty\) at \(t=0\) gives:

\[
\ln G(t) - \ln G^\infty = \frac{t}{\tau} \tag{1.12}
\]

or:

\[
G(t) = G^\infty \exp\left(-\frac{t}{\tau}\right) \tag{1.13}
\]

while for a continuous range of relaxation times the decay of the relaxation modulus can be described in terms of the relaxation modulus \(H(t)\):

\[
G(t) = \int_0^t H(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \tag{1.14}
\]
A useful way of interpreting stress relaxation data is to integrate the relaxation modulus with respect to time to give a viscosity equivalent to the zero shear viscosity:

\[ \eta_0 = \int_0^\infty G(t) \, dt \]  

This is only valid, however, if the relaxation modulus decays to zero. This means that the sample is not plastic and doesn't possess a yield stress. If the modulus decays to a constant value, then the sample is a plastic solid which has no zero shear viscosity but a yield stress which corresponds to the plateau of the relaxation modulus. It should be born in mind that the timescale of the experiment is important. Barnes has stated that everything flows if you wait long enough and consequently the observed plateau may only be apparent at short times and may, at longer times, eventually relax to zero. In practice it may not be feasible to wait for the relaxation modulus to fully decay and then it becomes necessary to perform the experiment over the timescale of interest. For example, sedimentation of flocculated suspensions is a long timescale process and requires measurements of ca. \(10^4\) to \(10^5\) seconds. However, measurements at longer times become so long that the sedimentation has occurred before the measurement has finished.

1.3.3 Oscillatory Shear.

When a small, sinusoidally varying strain is applied to a sample, a sinusoidal response in the measured stress is obtained. This is illustrated in figure 1.4 where the upper diagram shows how the strain varies and the lower diagram shows how the measured stress responds for a viscoelastic material. The amplitude ratio of the stress to the strain gives the complex modulus, \(G^*\), of the sample. For a Newtonian liquid the maximum stress is obtained when the angular velocity is greatest. This occurs when the cup is in the middle of its oscillation cycle and has a strain of zero. Consequently, the measured stress is 90° out of phase with the applied strain. With a Hookean solid the maximum stress occurs when the strain is greatest (i.e. when a spring is fully stretched) giving a response in phase with the applied strain. For viscoelastic systems intermediate behaviour is observed with a phase lag, \(\delta\), which allows the complex modulus to be separated into its storage/elastic component, \(G'\), and its loss/viscous component, \(G''\), thus:18,19
The storage/elastic modulus is a measure of how much of the applied deformation is stored within the structure of the sample through its deformation. Upon removal of the deformation the stored energy is returned as the sample reverts to its original state. Conversely, the loss/viscous modulus is a measure of how much of the applied deformation is dissipated through flow of the sample. Here the energy has been lost to the system and is not returned on removal of the deformation, the sample is no longer in its original state. Experiments may be performed at one strain as a function of frequency, at one frequency as a function of strain or at one frequency and strain as a function of time.

We can examine the response of a single Maxwell model in this experiment to understand how viscoelastic materials behave. Expressing the variation of the maximum stress, \( \sigma_0 \), and the maximum strain, \( \gamma_0 \), with time using complex notation gives:

\[
\gamma(t) = \gamma_0 e^{i\omega t}, \quad \dot{\gamma}(t) = i \omega \gamma_0 e^{i\omega t} = i \omega \gamma(t)
\]

and

\[
\sigma(t) = \sigma_0 e^{i(\omega t + \phi)}, \quad \dot{\sigma}(t) = i \omega \sigma_0 e^{i(\omega t + \phi)}
\]
substituting these values into the constitutive equation for the Maxwell model (equ. 1.9) gives:

\[ i \omega \gamma_0 = \frac{i \omega \sigma_0 e^{i \theta}}{G} + \frac{\sigma_0 e^{i \theta}}{\eta} \]  
(1.18)

substituting for the complex modulus and rearranging results in:

\[ \frac{G^*}{G} = \frac{i \omega \eta / G}{i \omega \eta / G + 1} \]  
(1.19)

and multiplying both sides by 1-iωτ and using τ=η/G gives:

\[ \frac{G^*}{G} = \frac{i \omega \tau + (\omega \tau)^2}{1 + (\omega \tau)^2} \]  
(1.20)

G' is given by the real part and G'' by the imaginary:

\[ G' = \frac{G(\omega \tau)^2}{1 + (\omega \tau)^2}, \quad G'' = \frac{G \omega \tau}{1 + (\omega \tau)^2} \]  
(1.21)

The response of the Maxwell model is shown below in figure 1.5 where the moduli and viscous response of these equations is plotted as a function of frequency.

Figure 1.5 Response of a Maxwell element to an oscillation experiment performed as a function of frequency.
At low frequency the model is predominantly viscous with $\eta'$ approaching the zero shear viscosity, $\eta_0$, and $G'$ virtually zero. As the frequency increases, $G'$ and $G''$ rise while $\eta'$ falls until they are all equal. Here the phase angle, $\delta = \pi/4$ (i.e. $45^\circ$) and the model has equal viscous and elastic components. This frequency corresponds to the relaxation time of the model.

**1.3.4 Stress Growth.**

A linearly increasing strain (i.e. shear rate) is applied to a sample and the stress is monitored as a function of time. For a Maxwell body the stress initially increases steadily and then plateaus. The time dependent viscosity, $\eta(t)$, is obtained from the ratio of the stress, $\sigma$, to the strain rate, $\dot{\gamma}$. This is illustrated in figure 1.6 where the upper diagram shows the applied strain and the lower diagram shows the response for a viscoelastic material.

![Figure 1.6 Stress growth experiment.](image)

Figure 1.6 Stress growth experiment.

This is essentially a viscometry experiment except that measurements can be made at much lower strains and shear rates, down to $10^{-4} \text{s}$. Such measurements take a long time to perform with this technique, typically of the order of hours. Equivalent results may be obtained from stress relaxation measurements in much shorter times although the precision of these results would generally be poorer.
1.4 Rheology of Colloidal Dispersions.

1.4.1 Dispersed Hard Spheres.

The typical rheological behaviour of moderately concentrated colloidal dispersions is depicted in figure 1.7.²¹ It can be seen that colloidal dispersions are usually pseudoplastic from low to high shear rates and shear thickening at very high shear rates.

![Diagram of viscosity profile](image)

Figure 1.7 Illustration of the viscosity profile of moderately concentrated colloidal suspensions.

There is a Newtonian plateau at low shear rates, the viscosity of which is called the zero shear viscosity, \( \eta_0 \). Here the interparticle forces and Brownian motion dominate the shear forces giving a random or pseudo lattice arrangement of the particles. It is this structure that gives rise to the high viscosity since the particles which must move around each other generate a high resistance to flow. As the shear rate increases the shear forces increase in magnitude and begin to align the particles into layers. This reduces the resistance to flow, i.e. the viscosity. Such structural changes have been observed experimentally by light²² and neutron scattering.²³,²⁴ When all the particles are aligned into planes, the viscosity is again Newtonian and is called the plastic or high shear viscosity, \( \eta_{pl} \). As the shear rate increases to very high shear rates, particles are ejected from their shear planes and "jam" the flow between adjacent planes, resulting in an increase of the resistance to flow, and hence the viscosity. This is more pronounced at high volume fractions. Furthermore, with such high concentrations of particles...
the zero shear viscosity may occur at such low shear rates that it may not be measurable and
the suspension will appear plastic in its behaviour exhibiting a yield stress.

If either the zero shear or plastic relative viscosities ( = viscosity of suspension /
viscosity of medium) are plotted as a function of volume fraction then, the curve shown in
figure 1.8 is obtained.

![Relative Viscosity vs Volume Fraction Graph](image)

Figure 1.8 Change in relative viscosity of suspension with volume fraction.

At low volume fractions the relative viscosity slowly increases from its dilute limit
of one. This is due to the particles disrupting the linear flow of fluid by their presence, which
requires more energy and manifests itself as an increase in the resistance to flow of the
suspension. Higher volume fractions show much greater deviations which are due to multibody
collisions and more complex perturbations to the flow of fluid. At high volume fractions the
viscosity becomes infinite as the particles become so tightly packed that they cannot flow past
each other.

The viscosity of a dilute suspension was first described by Einstein\textsuperscript{25} who calculated
the perturbation of the fluid flow due to a single particle as:

$$\eta_r = \frac{\eta}{\eta_m} = 1 + [\eta] \phi$$

(1.22)

where $\eta_r$, $\eta$, $\eta_m$ and $[\eta]$ are the reduced, suspension, medium and intrinsic viscosities
respectively and $\phi$ is the volume fraction of particles. The intrinsic viscosity is the slope of
the reduced viscosity plotted as a function of volume fraction at infinite dilution. For
uncharged rigid spheres this is equal to 2.5. This is illustrated in figure 1.8 where it can clearly be seen that real suspensions start to deviate from Einstein's result even at low volume fractions of ca. 0.05. In order to overcome this deficiency, Einstein's equation was extended to higher volume fractions by taking into account the perturbations due to two and multibody interactions through the coefficients $k_2$ and $k_3$ respectively:

$$\eta_r = 1 + [\eta] + k_2 \phi^2 + k_3 \phi^3 + \cdots$$  \hspace{1cm} (1.23)

Several values have been calculated for $k_2$ and $k_3$, the accepted values being 7.6\textsuperscript{26} and 37.4\textsuperscript{27}. This extends the agreement between theory and experiment up to volume fractions of 0.15. For higher concentrations theoretical calculation of the viscosity is not possible on account of the complex multibody collisions and empirical relationships are required. Of the several that have appeared, the equation proposed by Krieger and Dougherty\textsuperscript{28} has been quite successful:

$$\eta_r = (1 - \phi / \phi_m)^{-\eta_1} \phi_m$$ \hspace{1cm} (1.24)

where $\phi_m$ is the maximum packing fraction of the suspension which is dependent on the arrangement of the particles. For monodisperse spheres possible arrangements are listed in table 1.1.\textsuperscript{30} Polydisperse samples will have high $\phi_m$ while non-spherical particles will tend to have lower $\phi_m$.

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>$\phi_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic</td>
<td>0.52</td>
</tr>
<tr>
<td>Minimum thermodynamically stable configuration</td>
<td>0.548</td>
</tr>
<tr>
<td>Hexagonally packed sheets just touching</td>
<td>0.605</td>
</tr>
<tr>
<td>Random close packing</td>
<td>0.637</td>
</tr>
<tr>
<td>Body-centred cubic packing</td>
<td>0.68</td>
</tr>
<tr>
<td>Face centred cubic / hexagonal close packed</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 1.1 Maximum packing fractions of suspensions for different packing arrangements.

In their studies of non-aqueous, hard silica suspensions, de Kruif et al.\textsuperscript{31} found values of 0.71 and 2.72 for $\phi_m$ and $[\eta]$ at the high shear viscosity limit and 0.63 and 3.11 at the low shear limit. The high shear value confirms that there is ordering of the particles into some form of close packed sheets which flow over each other. It is not possible for a hexagonally closed packed structure to flow without expansion of the structure and consequently a $\phi_m$ less
than 0.74 is necessary. Expansion of the structure such that the sheets can slide over each other gives a maximum packing fraction of 0.698. The small difference may be due to slight compression of the hard octadecyl stabilising layer. The low shear \( \phi_{m} \) value indicates a random close packing structure which is to be expected when the disordering Brownian forces exceed the shear forces. In both cases, the intrinsic viscosities are higher than the 2.5 calculated by Einstein for perfectly hard spheres which indicate that there is a small additional contribution to the interaction between the particles. This is termed as the "softness" of particles.

### 1.4.2 Effect of Particle Softness.

So far, the discussion on rheology has concentrated on "hard" spheres where there is a sharp boundary between the particle and its suspending medium. Here, the particles do not interact until they touch. However, in practice many systems are "soft" and exhibit an interfacial layer of finite thickness over which the particle gradually ends and the suspending medium begins. In this case the particles begin to interact with each other at large separations. Hard spheres are commonly found with very dense, short steric polymer layers while soft spheres have sparse, extensive steric polymer layers. These are illustrated in figure 1.9.

![Hard Sphere vs. Soft Sphere](image)

Figure 1.9 Illustration of "hard" and "soft" spheres.

A consequence of this is that soft spheres begin to interact with each other at lower concentrations than hard spheres. Jones et al.\(^{32}\) compared the rheology of soft steric stabilised
spheres to that of hard spheres. The softness of the particles was achieved by choosing small particles (54-58nm), bearing a PEO layer of 12 EO units per chain, dispersed in water. The hard spheres consisted of 49nm silica particles coated with a dense layer of stearyl alcohol chains dispersed in a hydrocarbon solvent. In order to account for the effects of the stabilising layers, effective volume fractions were obtained from intrinsic viscosity measurements at low particle concentrations. At volume fractions below \( \phi_m \), the soft spheres exhibited lower viscosities indicating some compression of the steric layer on the soft particles. This was also evident from the maximum packing fraction which was found to increase from 0.63 to 0.66 when changing from hard to soft spheres. Above \( \phi_m \) the suspensions cease to exhibit a low shear Newtonian plateau and are transformed into elastic gels. Here, there are no differences between the flow properties of the two suspensions. However, dynamically the soft spheres have a higher elastic modulus which is due to their different interparticle interaction which contributes to the mechanism by which energy is stored and dissipated.

From deviations in the relative viscosity of a polystyrene latex bearing a grafted layer of PEO (\( M = 2,000 \)), Prestidge and Tadros\(^3\) observed a reduction in the thickness of the stabilising layer from 20.5 to 9.2 nm as the volume fraction was increased from 0.33 to 0.57. Miano et al.\(^4\) examined the effect of changing the molecular weight of the stabilising layer with a series of four nonylphenyl poly(propyleneoxide) poly(ethyleneoxide) polymers which each contained 13 PO units and 27, 48, 79 and 175 EO units. These polymers were adsorbed onto carbon black to form an aqueous colloidal suspension. The hydrophobic nonylphenyl poly(propyleneoxide) blocks adsorbed onto the surface of the particles and acted as an anchor while the hydrophilic poly(ethyleneoxide) chains extended into the water to form a soft steric stabilising layer. On increasing the volume fraction of the carbon particles, the elastic modulus rose when the volume fraction was sufficiently high that the steric layers on adjacent particles began to touch. This volume fraction was dependent on the poly(ethyleneoxide) chain length. The shortest chain rose very sharply at high volume fraction and exhibited hard sphere behaviour. However, the longest chain, 175 EO, not only rose at a much lower volume fraction, but also rose more slowly, illustrating soft sphere behaviour. This was considered to be due to "denting" or compression of the PEO chains. Pingret et al.\(^5\) observed identical effects with these copolymers and polystyrene latices and found that the adsorbed layer thickness increased with the square root of the PEO chain length, indicating that the PEO chains were in the form of coils. Miano et al.\(^6\) also studied carbon black suspensions stabilised with PEO:PPO:PEO block copolymers, including the series used in this work. Here,
the PPO chain acts as the anchor while the two PEO chains extend into the medium forming a stabilising layer. For a central PPO block of 56 units and increasing PEO lengths of 25, 37 and 148 units, steady shear and oscillatory shear measurements revealed adsorbed layer thickness of 6.8, 7.2, 10.7 and 8.8, 9.5, 11.0 nm respectively. This corresponds to an increase in the softness of the particles. However, it is interesting to note that the steady shear thicknesses are lower suggesting that greater compression of the chains occurs under conditions of high shear.

This illustrates how soft spheres are more complex rheologically, due to the compressibility of their stabilising layer and the effect of this on the interparticle forces. Despite this complexity, it is soft spheres which are found in everyday life and these are what we must study in order to understand and predict how real systems function.

1.4.3 Flocculated Suspensions.

The rheology of dispersed suspensions is relatively well understood. However, flocculated systems have received much less attention, probably due to their complexity even though they are encountered widely in industry and everyday life from paints to milkshakes. Flocculated suspensions are formed when the attractive forces exceed the stabilising repulsive forces and are commonly found with clay suspensions and latices with high levels of electrolyte.

From their studies of the settling behaviour of flocculated kaolin suspensions, Michaels and Bolger proposed the floc-aggregate structural model which is illustrated in

Figure 1.10 Floc-aggregate structural model.

Figure 1.10 Floc-aggregate structural model.
Their premise was that the basic flow unit was not the particle but small clusters of particles called "flocs", which include the water enclosed within the cluster. These flocs are assumed to be sufficiently strong to survive moderate amounts of shear such that they retain their identity during processes such as sedimentation. On standing or at very low shear rates, the flocs group into larger clusters, termed "aggregates", which may join together to form a continuous network throughout the suspension. It is this network which results in the plastic flow properties of such suspensions and their resistance to sedimentation.

Firth and Hunte\textsuperscript{38,39} formalised flocculated structures with the development of the "elastic floc model" in which rheological parameters are related to the "openness" of the flocs given by the floc volume ratio, $C_{FP}$, which is the ratio of the floc volume fraction, $\phi_{f}$, to the particle volume fraction, $\phi$. The floc volume fraction is obtained from measurements of the viscosity over a range of shear rates which is interpreted in terms of the Krieger-Dougherty equation (equ. 1.24):

$$\eta_{pl} = \eta_0 (1-\phi/\phi_m)^{-\gamma N_{c}}$$

At high shear rates the aggregates are broken down into elementary flocs, called flocculus, which along with their entrapped fluid govern the viscosity of the suspension. The strength of the coagulation is also expected to govern the compactness of the flocs. As the interparticle attraction weakens, only the more compact flocs are able to withstand the stresses encountered at high shear rates. This was confirmed with coagulated poly(methylmethacrylate) latex particles where $C_{FP}$ decreased linearly with the square of the zeta potential of the particles (i.e. the interparticle attraction falls as the zeta potential rises).

For such systems it is not possible to separate the flocs into individual particles since the strength of flocculation is too high. However, with weakly flocculated suspensions such as found with suspensions containing free polymer, these flocs can be fully dispersed by shearing. Such systems exhibit plastic or pseudo-plastic behaviour and exhibit an extrapolated yield stress similar to the Bingham model (equ. 1.4). In this case the yield stress divided by the total number of particle-particle contacts, $N$, is the energy required to separate two flocculated particles, $E_{sep}$:\textsuperscript{40,41}

$$E_{sep} = \frac{\sigma_y}{N}$$

(1.26)
where:

\[
N = \frac{1}{2} \frac{3\phi n}{4\pi a^3}
\]  

(1.27)

and \( n \) is the average number of contacts per particles. For hexagonal close packing \( n=12 \) while for random close packing \( n \) is reduced to 8. Often the floc structure is relatively open and \( n \) will be lower with a limiting value of 2 which corresponds to a chain. Values between 4 and 8 have been taken as the two extremes.\(^{42}\)

Heath and Tadros\(^{43}\) added free, nonadsorbing, high molecular weight poly(ethyleneoxide) to a sterically stabilised polystyrene latex and observed a sharp rise in the viscosity, yield stress and modulus at a critical free polymer concentration. This corresponded to the formation of an extensive network in the suspension due to flocculation of the particles. Liang, Tadros and Luckham\(^{44-47}\) extended these studies by considering the effect of particle size and free polymer molecular weight with polystyrene latices bearing grafted stabilising layers of poly(ethyleneoxide). Addition of high molecular weight poly(ethyleneoxide) resulted in a linear increase in the yield stress once the critical polymer concentration had been exceeded. Furthermore, the yield stress increased with the latex volume fraction, \( \phi \), and was found to scale to the power of 2.8, i.e. \( \sigma_y = \phi^{2.8} \). The corresponding \( E_{mp} \) values also increased with latex volume fraction suggesting that the number of contacts for each particle is increasing. The elastic modulus rose sharply at the critical polymer concentration but then plateaued. The different trends between these two measurements is due to the fact that the yield stress measures the strength of the attractive forces between the particles while the elastic modulus measures the number of chains permeating through the sample, which appears to be constant for polymer levels above the critical level. This was confirmed by microscopic observation which indicated no great change in the appearance of the floc structure. Decreasing the particle size increased both the elastic modulus and yield stress values in accord with expectations from the greater number of particles available to form chains. Replacing the free polymer with hydroxyethylcellulose (HEC) was similar with the exception that the elastic modulus increased with particle size. This is the opposite from the PEO and was interpreted as a repulsive effect between the grafted PEO layer and the free HEC, which increased as the graft density increased with particle size. This suggests that the softness of particles may also be important with weakly flocculated suspensions.

Van den Temple\(^{48}\) and Strenge and Sonntag\(^{49}\) modelled the elastic modulus in terms of a network composed of chains, in which the stress was transmitted along the chains through the interparticle forces. A consequence of this was that the modulus values depended on the
interparticle forces. However, the model did not predict the strong dependence of the modulus on concentration. Van den Temple subsequently improved the agreement between theory and experiment by modelling the network as preformed aggregates.

Good agreement has also been found by Goodwin et al. who used a statistical mechanical analysis to calculate the particle pair potential and the particle pair distribution function. From this, the elastic modulus as a function of latex volume fraction was calculated.

1.4.4 Scaling of Aggregated Networks.

1.4.4.1 Fractal Aggregates.

Irreversible aggregation of colloidal suspensions can be described by two limiting regimes, diffusion limited and reaction limited. Diffusion limited aggregation occurs when the repulsive force between particles is negligible and consequently the rate of aggregation is limited by the time taken for particles or clusters to encounter each other through diffusion. Reaction limited aggregation occurs when there is a high but not insurmountable barrier to aggregation such that the rate of aggregation is limited by the time taken for particles or clusters to overcome this barrier. Each of these cases leads to a different structure for the aggregate which can be characterised by a fractal dimension, D, which describes how the mass of an aggregate scales with its size thus:

$$\text{mass} \propto \left( \frac{R_s}{a} \right)^D$$  \hspace{1cm} (1.28)

where $R_s$ is the radius of gyration of the aggregate and $a$ is the radius of the individual particles. It should be noted that not all aggregates are fractal; fractals are self similar which means that they have the same "structure" irrespective of the scale from which the fractal is viewed.

In the case of reaction limited aggregation, a particle approaching a cluster has time to "explore" all the sites on the cluster before aggregation occurs. This model, which is also called the "chemical model" was first suggested by Eden who found that very dense aggregates were produced, such as illustrated in figure 1.10. Simulation gives a very high fractal dimension of 2.97 in three dimensional space. For diffusion limited aggregation, relatively open structure are found since the particles "stick" on their first contact with the cluster. Witten and Sanders have found from simulation, a much lower fractal dimension of 2.50.
These models only consider the aggregation between particles and clusters. In the real world clusters can also aggregate. Such a model, the cluster-cluster aggregation model (CLCLA), was developed independently by Meakin and Kolb et al. and leads to even more open structure (see figure 1.11) with a fractal dimension of 1.78. Interestingly, the fractal dimension does not depend on the rotation of the clusters since they are incapable of interpenetration at any orientation.

Colloidal systems have been shown experimentally to obey either the slow reaction limited or fast diffusion limited aggregation and furthermore, that these two regimes are universal in colloidal suspensions with fractal dimensions of ca. 2.1 and 1.8 respectively. The latter, DLA, is in remarkable agreement with the diffusion limited cluster-cluster aggregation model and tells us that cluster-cluster aggregation occurs with colloids.

Figure 1.11 Illustration of structures obtained from simulation.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{Illustration of structures obtained from simulation.}
\end{figure}

1.4.4.2 Elasticity of Aggregates.

Dilute suspensions are relatively easy to study by techniques such as light scattering and show good agreement with simulation. Concentrated suspensions are more complex to study since they gel or are opaque to light. Rheology is a powerful tool in such instances. Ball and Brown related the scaling of the elasticity with volume fraction, for flocculated networks, to the fractal dimension through an exponent, $f$:

$$G \propto \phi^f$$

(1.29)
where $G$ is the limiting elastic shear modulus at short timescales which is equal to $G'$ at high frequencies. For diffusion limited aggregation, $f = 3.5$ while for reaction limited aggregation $f = 4.5$. Buscall et al.\textsuperscript{60,61} and Kim and Luckham\textsuperscript{62} have found scalings for $f$ of ca. 4.3 and 4.0 respectively for strongly flocculated aqueous latices. Here, diffusion limited aggregation would be expected leading to relatively open flocs. The higher values indicate that some consolidation of the floc is occurring during formation or during the experiment.

In contrast, Kim and Luckham\textsuperscript{63} have found scalings of 2.4 for a poly(vinylalcohol) stabilised polystyrene latex, flocculated by heating above its flocculation temperature. This corresponds to a very open structure such as formed by a diffusion limited cluster-cluster aggregation mechanism. Sonntag and Russel\textsuperscript{64} also observed a similar value of 2.5 with electrostatically stabilised latices. However, upon aging for up to fifteen weeks, the flocs had become more compact with a scaling of 4.4, in agreement with reaction limited aggregation.

Recently, a scaling analysis by Shih and coworkers,\textsuperscript{65} based on the theory for polymer gels by De Gennes\textsuperscript{66} has been used to relate both the strain limit and modulus of elasticity of a gel to its network structure. The network was considered to consist of closely packed fractal flocs and depending on the relative strength of the interfloc links to the flocs, two types of behaviour can occur. Strong link behaviour occurs when the interfloc links are stronger than the flocs themselves, which exists when the individual flocs are very large, whilst weak link behaviour occurs when the flocs are stronger than the interfloc links and exists with very small flocs.

For the strong link regime:

$$G \propto \phi^{(d-2)\beta(d-D)}$$ \hspace{1cm} (1.30)

and

$$\gamma_0 \propto \phi^{-(1+\beta(d-D))}$$ \hspace{1cm} (1.31)

while for the weak link regime:

$$G \propto \phi^{(d-2\beta(d-D))}$$ \hspace{1cm} (1.32)

and
where $x$ is the backbone fractal dimension of the flocs which is a function of concentration and increases from 1.1 to 1.4 in three dimensional systems as the volume fraction is lowered and $d$ is the Euclidean dimension which is 3.

Taking $D=2.0$ and $x=1.25 \pm 0.15$ for the strong link case gives $G \propto \phi^{4.2+0.15}$ and $\gamma_0 \propto \phi^{-2.25+0.15}$ while changing $D$ to 1.75 for the weak link case gives $G \propto \phi^8$ and $\gamma_0 \propto \phi^8$. The diffusion and reaction limited models do not distinguish between strong and weak link behaviour. However, the reaction limited model scales in an identical fashion to strong link behaviour. For both the strong link and reaction limited regimes, the elasticity scales with $\phi^{4.0-4.5}$ while, for the diffusion limited case, the elasticity scales with $\phi^{3.5}$ and for the weak link regime scales with $\phi^8$. Shih et al. found strong link behaviour for colloidal boehmite alumina gels with $G \propto \phi^{4.1+0.2}$ and $\gamma_0 \propto \phi^{-2.1}$ to $-2.3$. The low scaling found both by Kim and Luckham and by Sonntag and Russel may indicate the presence of weak link behaviour, however, no other reporting of weak link behaviour are known of.

The strong and weak link analysis also predicts that the linear region would shrink as the volume fraction rises for the strong link regime. This is to be expected at low volume fractions where the flocculation favours the formation of large clusters which can then form strong intercluster links. For the weak link regime the linear region increases with increasing volume fraction and is most likely to occur at high volume fractions where small clusters are formed which subsequently form weak inter-cluster links.
Chapter 2. Colloid stability.

2.1 DLVO Theory.

2.1.1 Van der Waals Forces of Attraction.

Many colloidal particles have a tendency to form aggregates through collisions due to their thermal motion. This aggregation is a consequence of attractive forces that exist between colloidal particles, which have their origins in the intermolecular forces of attraction commonly termed "van der Waals forces" after the scientist who investigated their effects on the phase behaviour of fluids.²⁷

Van der Waals forces in non-polar molecules are principally due to the interaction between a temporary dipole on one molecule and the subsequently induced dipole, via the propagation of electromagnetic waves, on a nearby molecule. For this interaction, London⁶⁸ calculated that the interaction energy decreases with the inverse sixth power of the separation between the molecules. De Boer⁶⁹ and Hamaker⁷⁰ calculated the London interparticle forces for colloidal particles by assuming that the intermolecular forces between pairs of molecules could be added together to give the total interaction. For equal spheres of radius a, at centre to centre separation r, their van der Waals energy of interaction, \( G_A \), is:⁷¹

\[
G_A = -\frac{A}{6} \left[ \frac{2a^2}{r^2} \ln \frac{r^2 - 4a^2}{r^2} \right] + \ln \frac{r^2 - 4a^2}{r^2}
\]

The Hamaker constant, \( A \), for a material of type 1 interacting with itself through a vacuum is given by:⁷²

\[
A_{11} = \pi^2 q^2 \lambda
\]

where \( q \) is the number of atoms per unit volume and \( \lambda \) is the interaction parameter (=3/4 h νₐ αₚ, h is Planck's constant, νₐ is the dispersion frequency and αₚ is the static polarizability).

For a material of type 1 interacting with itself through a medium of type 2, the Hamaker constant can be calculated from:

\[
A_{12} = A_{11} + A_{22} - 2A_{12}
\]

If it assumed that:

\[
A_{12} = (A_{11} A_{22})^{\frac{1}{2}}
\]
then:

\[ A_{121} = \frac{1}{2} \left( A_{11}^2 - A_{22}^2 \right) \]  

(2.5)

where \( A_{11} \), \( A_{22} \) and \( A_{12} \) refer to the Hamaker constants for particle-particle, medium-medium and particle-medium interactions in a vacuum respectively. Hamaker constants have been determined for a wide range of materials and range from \( 2.5 \times 10^{-20} \) J for alkanes to \( 1.89 \times 10^{-20} \) J for sapphire when dispersed in an aqueous medium.

2.1.2 Electrostatic Stabilisation.

Colloidal particles immersed in ionic solutions are almost always charged. This charge can arise from:

a) differences in the affinities of two phases for an electron such as observed at the mercury - aqueous electrolyte solution interface.

b) differences in the thermodynamic potential between a lattice ion in the solid and in solution such as an iodide ion in silver iodide.

c) ionisation of surface groups such as sulphates or carboxylic acids on the surface of a latex particle.

d) replacement of an atom in a crystal lattice by one of a different valency such as in the isomorphous substitution of \( \text{Si}^+ \) by \( \text{Al}^{3+} \) in clay particles.

e) adsorption of ionised surface active agents at the interface.

As a consequence of this charge, ions of opposite charge in the nearby solution (counter-ions) are attracted to the interface by Coulombic forces while they also migrate toward the bulk solution on account of their thermal motion and likewise, ions of the same charge (co-ions) are repulsed. This results in an excess of counter-ions and a deficiency of co-ions in the solution near the particle where the difference in ion concentration and the surface electrical potential decreases exponentially with distance from the particle surface. This region is called the electrical double layer or diffuse double layer when the ions show a diffuse distribution.
as typically found with colloidal dispersions in ionic solutions. The theory for such diffuse double layers was developed by Gouy and Chapman and describes the change in potential, \( \psi \), with distance, \( x \), for flat plates as:

\[
\psi = \frac{2kT}{ze} \ln \left[ \frac{1 + \gamma \exp(-\kappa x)}{1 - \gamma \exp(-\kappa x)} \right]
\]  

(2.6)

where

\[
\gamma = \frac{\exp \left[ \frac{ze\psi_o}{2kT} \right]}{1 + \exp \left[ \frac{ze\psi_o}{2kT} \right]}
\]

(2.7)

and

\[
\kappa = \left( \frac{2e^2 z^2 n_o}{\varepsilon_o \varepsilon \kappa T} \right)^{\frac{1}{2}}
\]

(2.8)

where \( \psi_o \) is the surface potential, \( k \) the Boltzmann constant, \( T \) the absolute temperature, \( z \) the ion's charge, \( e \) the elementary charge, \( n_o \) the concentration of ions in solution, \( \varepsilon_o \) the vacuum permittivity, \( \varepsilon \) the relative permittivity and \( \kappa \) the Debye-Huckel parameter.

The Debye-Huckel parameter, \( \kappa \), has dimensions of \( 1/\text{length} \) and the distance \( 1/\kappa \) is referred to as the thickness of the double layer. This corresponds to the distance over which the potential has decreased to \( 1/e \) of its value at the surface. It can be seen that the thickness of this layer decreases as the electrolyte concentration or valency is increased and for a \( 10^{-3} \) molar solution of NaCl equals 9.61 nm. Increasing the electrolyte to \( 10^{-2} \) molar reduces the layer thickness to 3.04 nm. The dimensionless parameter \( \kappa a \), where \( a \) is the radius of the particle is a measure of the "sphericity" of the double layer. If \( \kappa a > 100 \) the double layer is much thinner than the particle and may be considered planar relative to the particle surface, while if \( \kappa a < 0.1 \) the double layer is much thicker than the particle and may be considered to be spherical around a point charge.

The charge density at the surface of the adsorbed layer, \( \sigma_o \), may be obtained by assuming that the double layer as a whole must be neutral, giving:
Experimentally the charge of particles may be determined by particle electrophoresis, or by conductometric titration. When two identically charged surfaces approach each other the overlap of the electric double layers results in a repulsive force from an increase in the free energy of the system. This can only be determined exactly by numerical integration. However, for two equivalent spheres with a constant potential, surface separation, h, and relatively small double layers ($\kappa a > 10$) the energy of interaction, $G_R$, is approximately:

$$G_R = \frac{4\pi \varepsilon_0 \varepsilon_a a^2 \Psi_0^2}{H + 2a} \exp(-\kappa h)$$

while for relatively large double layers ($\kappa a < 3$):

$$G_R = \frac{2\pi \varepsilon_0 \varepsilon_a \Psi_0}{2kT} \ln[1 + \exp(-\kappa h)]$$

In the Derjaguin, Landau, Verwey, Overbeek (DLVO) theory the stability of colloidal particles depends on the total energy of interaction, $G_T$, which is obtained from the sum of the van der Waals forces of attraction and the electrostatic repulsive forces thus:

$$G_T = G_A + G_R$$

Since $G_R$ varies exponentially with distance and $G_A$ varies inversely with the square of the distance, $G_A$ dominates at short and large distances while $G_R$ dominates at intermediate distances. This is illustrated in figure 2.1 where it can be seen that as particles approach each other they first encounter a shallow minimum in potential energy called the secondary minimum. If this is greater than a few kT weak reversible flocculation of the particles may occur. Next the approaching particles encounter a maximum in potential energy called the primary maximum. If this barrier is greater than 5-10 kT, the approach of the particles is halted and the particles remain dispersed or weakly flocculated. However, if the particles overcome this barrier they encounter a deep minimum in potential energy called the primary minimum which results in their irreversible coagulation. The height of the primary maximum and secondary minimum are sensitive to the magnitude of the diffuse electrical double layer which can be readily controlled by the nature and concentration of the counter-ions.
Interestingly, evidence has recently arisen to support claims that electrostatic forces can also exhibit long range attractive forces. Latices with extensive double layers were observed to form ordered regions and more importantly, areas or "voids" free of any particles were also observed which implies that the particles are experiencing long range attractive forces. At the observed ranges the forces could only arise from the electrical double layers which, according to Sugami can also exhibit attractive forces at these long distances.

2.2 Stabilisation by Polymers.

2.2.1 Adsorption of Polymers.

In their simplest form, polymers are composed of several identical repeating units, called monomers, to form a chain which is termed a homopolymer. In order to stabilise a dispersion the polymer chains must adsorb onto the surface of the particles. However, part of the polymer must also extend from the surface into the medium to provide a polymer layer which prevents the close approach of two particles and their subsequent agglomeration. In aqueous systems this can be achieved with polystyrene latices and poly(ethylene oxide), PEO, which is soluble in the water but also adsorbs onto the surface of the latex particles due to an attraction between the ether oxygens in the PEO and the charged sulphate (and carboxylate) groups on the surface of the particles. This can lead to adsorption of the polymer as a "train" at low coverage. At higher concentrations of polymer, "loops" and "tails" are formed (see figure 2.2). It is these which are necessary for a polymer to stabilise particles against agglomeration.
A far more effective way of increasing the number of tails while maintaining strong adsorption on the surface of the particles, which are taken to be hydrophobic here, is to introduce a second monomer into the homopolymer to produce a copolymer. For strong adsorption to occur the second monomer must be strongly attracted to the particle surface, which is often achieved by choosing the second monomer to be insoluble in the medium, such that it "precipitates" from solution to form a strong anchor on the particle surface. The arrangement of the two monomers within the copolymer is important too. They can either be arranged throughout the train: AABABAABBBABB to give a random copolymer or in units: AAAAAABBBBBBB giving a block copolymer. Random copolymers tend to favour the formation of loops with their multiple anchoring points while block copolymers form tails. The tails from the block copolymer form a much more clearly defined polymer layer, often called a steric layer, than the loops and tails from the random copolymer. This is illustrated in figure 2.3.

With block copolymers, a second stabilising chain may be added to the anchor giving a tri-block copolymer. In this work, copolymers of this kind have been used. This idea can be taken even further by adding several stabilising chains along the length of the anchoring...
chain to give a "comb" block copolymer, or by changing the chemistry of each of the blocks such that there are three chemically distinct monomers. The properties of these copolymers can be readily tailored to a wide variety of uses by varying both the molecular weight and chemical nature of homopolymer components.

There are many ways of characterising copolymers such as molecular weight and solubility. One particularly simple and eloquent method, for aqueous systems, is to categorise polymers in terms of the balance between their hydrophobicity and hydrophilicity, termed their HLB. This is a scale which starts at 0 for completely hydrophobic polymers and ends at 20 for completely hydrophilic nonionic polymers. Low values (<6) have limited solubility in water and tend to be good for emulsifying water in oil. Intermediate values (8-10) are effective for wetting while high values (12-16) are effective detergents and oil in water emulsifiers.

2.2.2 Thermodynamic Considerations.

2.2.2.1 Thermodynamics of Polymer Stabilised Colloids.

As two sterically stabilised particles approach each other, their change in free energy at constant temperature and pressure can be described in terms of the enthalpy, H, and entropy, S, of the system:

$$\Delta G_p = \Delta H_p - T \Delta S_p$$  \hspace{1cm} (2.13)

where T is the absolute temperature. If the free energy remains negative as the particles approach, then flocculation will occur. Consequently, the energy of interaction is the free energy of flocculation, which is indicated by the subscript $F$.

There are four ways in which the enthalpy and entropy can control the stability of particles. Firstly, both can be positive so that the enthalpy favours stabilisation while the entropy promotes flocculation. If the enthalpy term outweighs the entropy term, then the particles are stable and the stabilisation is enthalpic. Conversely, if both are negative and the entropy term is greater than the enthalpy term, then the stabilisation is entropic. Now, if the enthalpy term is positive and the entropy term negative, both contribute to a positive value of the free energy and the stabilisation is combined enthalpic-entropic stabilisation. The opposite, negative enthalpy and positive entropy, results in flocculation of the particles.

If the stabilisation is enthalpic, then it can be seen from equation 2.13 that raising the temperature increases the contribution from the entropy until a point is reached whereby the entropy term exceeds the enthalpy term and flocculation occurs. Thus flocculation on heating
is indicative of enthalpic stabilisation and the temperature at which flocculation occurs is called the upper critical flocculation temperature (UCFT). Likewise, entropic stabilisation fails when the temperature is lowered to a point where the enthalpy term exceeds the entropy term. Here, flocculation occurs at the lower critical flocculation temperature (LCFT) which indicates the presence of entropic stabilisation. Combined enthalpic-entropic stabilisation is stable both on heating and cooling and shows neither a LCFT or UCFT. This is summarised in table 2.1.

<table>
<thead>
<tr>
<th>( \Delta H_f )</th>
<th>( \Delta S_f )</th>
<th>( \Delta G_f )</th>
<th>Stabilisation</th>
<th>Flocculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+</td>
<td>+ (( \Delta H_f &gt; T\Delta S_f ))</td>
<td>enthalpic</td>
<td>on heating</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>+ (T( \Delta S_f &gt; \Delta H_f ))</td>
<td>entropic</td>
<td>on cooling</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>+</td>
<td>combined</td>
<td>stable</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>-</td>
<td>none</td>
<td>flocculated</td>
</tr>
</tbody>
</table>

Table 2.1 Entropic and enthalpic contributions to the free energy of flocculation of two particles.

Aqueous PEO stabilises dispersions enthalpically,\(^\text{86}\) which show flocculation on heating. However, replacing the water with methanol converts the stabilisation to entropic.\(^\text{87}\) Combined enthalpic-entropic stabilisation is achieved with water-methanol mixtures. This illustrates the importance of the medium. In contrast many non-aqueous dispersions are also entropically stabilised.

This macroscopic approach gives us little information on the microscopic processes which are responsible for steric repulsion. In order to obtain more information here, specific models are required which relate the structure of the stabilising layer to the interaction energy between particles.

### 2.2.2.2 Flory-Huggins Theory of Polymer Solution Thermodynamics.

In the early 1940's, Flory and Huggins\(^\text{88-92}\) developed a method for calculating the free energy of mixing polymer and solvent, \( \Delta G_M \), by treating the enthalpy, \( H \), and entropy, \( S \), contributions separately where:

\[
\Delta G_M = \Delta H_M - T \Delta S_M
\]  

(2.14)

A mean field lattice model was used to calculate the configurational entropy of mixing \( n_1 \) solvent molecules and \( n_2 \) polymer chains from the number of conformations available to a three dimensional train to give:
\[ \Delta S_M = -k (n_1 \ln \phi_1 + n_2 \ln \phi_2) \]

where \( \phi_1 \) and \( \phi_2 \) are the volume fraction of solvent and polymer respectively and \( k \) is the Boltzmann constant.

The enthalpy is obtained by considering the mixing of solvent (1) and polymer (2) as a chemical reaction:

\[ 1 - 1 + 2 - 2 \rightarrow 2 (1 - 2) \]

and calculating the corresponding change in internal energy from breaking 1-1 and 2-2 contacts and forming two 1-2 contacts. If there is no change in volume, the change in internal energy is equal to the change in enthalpy to give the following enthalpy of mixing:

\[ \Delta H_M = n_1 \phi_2 \chi kT \]

where \( \chi \) is the dimensionless Flory-Huggins interaction parameter, which is the difference in energy between a solvent molecule immersed in pure polymer and pure solvent. This is a central key component in the thermodynamics of polymer solutions and will be encountered later.

Substituting equations 2.15 and 2.16 into 2.14 gives:

\[ \Delta G_M = kT (n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi) \]

\[ \text{--- entropic ---} + \text{enthalpic} \]

where the free energy of mixing is composed of two entropic terms and one enthalpic term. If we examine this result we can see that the first term inside the brackets is the dominant entropic term since the number of polymer molecules, \( n_2 \), is always small due to the high molecular weight of polymers. This means that the entropic driving force for mixing of polymer and solution is the additional space available to solvent molecules when the polymer domains become available.

A virial expansion for the osmotic pressure, \( \Pi \), of a polymer solution of concentration \( c_2 \) is:
\[
\frac{\Pi}{c_2} = RT\left( B_1 + B_2c_2 + B_3c_2^2 + \ldots \right)
\]  \hspace{1cm} (2.18)

where the first virial term, \(B_1\), equals 1/molecular weight of the polymer and is the van't Hoff expression for the osmotic pressure at infinite dilution. The second virial coefficient, \(B_2\), accounts for two-body interactions between polymer molecules and is given by:

\[
B_2 = \frac{\Phi^2}{v_1^0} \left( \frac{1}{2} - \chi \right)
\]  \hspace{1cm} (2.19)

where \(v_1^0\) is the solvent molar volume. This coefficient becomes zero when \(\chi = \frac{1}{2}\) and the polymer coil adopts its unperturbed configuration. This point is called the theta (\(\Theta\)) point and corresponds to the situation where the polymer segments have an equal preference for polymer or solvent contacts. Values of \(\chi\) less than 0.5 correspond to good solvent conditions where the polymer chain expands and its segments have a greater preference for solvent molecules, while \(\chi\) values less than 0.5 correspond to poor solvency where the polymer chain contracts and its segments prefer polymer contacts over solvent contacts. These changes in the size of polymer chains are not accounted for in the Flory-Huggins theory and can lead to errors for \(\chi\) values significantly different from \(\frac{1}{2}\).

This concept of solvency is fundamental to the understanding of steric stabilisation of colloidal particles. Higher terms in the virial expansion are usually sufficiently small to be neglected.

2.2.3 Microscopic Theories.
2.2.3.1 High polymer coverage.

When polymeric layers on adjacent particles overlap there are two main contributions to the free energy of the system from the interaction\(^9^3\). Firstly there is the contribution due to mixing of the polymers, called \(G_{\text{mix}}\), which arises from a change in the solvent-polymer segment interaction. In the overlap region the concentration of polymer chains rises leading to a reduction in the chemical potential of the solvent relative to the solvent in the bulk. To redress this imbalance, solvent in the bulk solution rushes in and forces the particles apart. For flat plates Napper\(^9^4\) has given the following relationship:
Where $v_p$ and $v_s$ are the molar volumes of the polymer and solvent respectively, $\chi$ is the Flory interaction parameter and $R_{mix}(h)$ is a geometric function which depends on the adsorbed polymer profile. It can clearly be seen that when $\chi=1/2$ (i.e. when the polymer is in a 0 solvent where the chains have an equal preference for polymer or solvent contacts) there is no interaction from mixing of the polymers ($G_{mix}=0$). If $\chi<1/2$ the polymer chains are in a good solvent and repulsion of the particles occurs ($G_{mix}>0$) while if $\chi>1/2$ the polymer chains are in a poor solvent and an attraction between the particles occurs ($G_{mix}<0$). Experimentally $\chi$ can be changed by varying the temperature, composition or electrolyte level of the continuous phase.

Secondly there is an elastic contribution, $G_e$, which arises from the loss in conformational entropy of the polymer chains in the overlap region. For this interaction Napper has given:

$$G_e = 2kT \frac{v_s^2}{v_p} \Gamma^2 \left(\frac{1}{2} - \chi \right) R_{mix}(h)$$  \hspace{1cm} (2.20)

Where $\Gamma$ is the number of adsorbed chains per unit area and, $\Omega(h)$ and $\Omega(\infty)$ are the number of conformations available to the adsorbed chain at $h=h$ and $h=\infty$ respectively. $G_e$ is always positive and results in a repulsive force between approaching particles.

In the absence of electrostatic forces the total free energy of the system, $G_T$, is given by the sum of the mixing and elastic terms along with the van der Waals attractive term, $G_A$, described in section 2.1.1:

$$G_T = G_{mix} + G_e + G_A$$  \hspace{1cm} (2.22)

This is illustrated in figure 2.4 for two approaching surfaces bearing anchored chains in a good solvent ($\chi<1/2$). At separations greater than the thickness of the two polymer layers (i.e. $h>2\delta$) the layers do not interact and the particles are attracted towards each other by the van der Waals forces. However, when the polymer layers touch at $h=2\delta$ a strong repulsive force is encountered which prevents further approach of the particles. Just before this barrier a minimum in free energy can be seen. If this is of the order of a few $kT$ then weak flocculation of the particles occurs. The depth of this minimum can be controlled through the thickness of the adsorbed polymer layer which, in principle, allows precise control of the strength of any desired flocculation.
Steric and electrostatic stabilisation mechanisms exhibit very different interaction profiles with distance from the surface. Steric stabilisation can provide a relatively hard, sharp, short range and incompressible profile which almost approximates to hard sphere behaviour where the interaction profile is composed of a vertical barrier. In contrast, electrostatic stabilisation generally gives a much softer, diffuse, long range and compressible profile. These two mechanisms can give very different rheological properties with suspensions and illustrate how suspensions stabilised sterically can exist at higher volume fractions.

![Diagram of steric stabilisation](image)

Figure 2.4 Illustration of steric stabilisation for adsorbed polymer layers in a good solvent ($\chi<1/2$) at high and low surface coverage for intersurface separation, $h$.

### 2.2.3.2 Low polymer coverage.

At low surface coverage of polymer, bare patches on the surface of particles exist and it is possible for the same polymer chain to adsorb onto two adjacent particles. If such bridging of particles occurs by polymer molecules then the particles are held in this configuration and said to be flocculated. This is termed bridging floculation, for which Napper has given the following expression for parallel flat plates:

$$G_{ab} = 2kT\Gamma r\chi_s \Delta \rho(h)$$

(2.23)

Where $r$ is the number of segments in a polymer chain, $\chi_s$ is the net surface-segment interaction parameter which describes the affinity of the polymer chains for adsorption on the surface and $\Delta \rho(h)$ is the change in $\rho$, the bound segment fraction, as $h$ decreases. This last
term is usually positive and results in an attractive interaction, i.e. $G_{ad}<0$. This is illustrated in figure 2.4 where at separations of the thickness of one polymer layer ($h=\delta$) there is a dominant attractive force which results in a relatively deep minimum in free energy. At closer separations the elastic and mixing terms dominate the attractive adsorption and van der Waals forces. Hence, in order to avoid any flocculation by bridging of polymers it is necessary to have a full coverage of polymer.

2.3 Self Consistent Field Models (SCF).

Scheutjens and Fleer\textsuperscript{95,96} developed a general theory for polymer adsorption using a quasi-crystalline lattice model. The model consisted of a series of layers adjacent to a surface. Each layer is composed of an array of sites which either contain a solvent molecule or polymer segment and is illustrated in figure 2.5. The configuration of each polymer segment is generated randomly by computer from a step-weighted walk in a potential field. This potential field arises from the concentration gradient of the molecules with increasing distance from the surface which, in turn, are dependent on the potential field, resulting in a self-consistent structure. Polymer segment-solvent interactions are described by the Flory-Huggins parameter, $\chi$, while surface-segment interactions are described by a differential adsorption energy parameter, $\chi_s$. The partition function for the polymer near an interface is evaluated from which other measurable quantities can be obtained, including the segment density profiles for trains, loops and tails, the adsorbed amount and surface coverage.

![Scheutjens-Fleer lattice model](image)

Figure 2.5 Scheutjens-Fleer lattice model.

For homopolymers, the segment density decayed exponentially from the surface at small distances but decayed more slowly at large distances. This was due to the existence of loops at small distances and tails at large distances, indicating the high degree of segments...
in the form of tails. It is these tails which form the exterior of the polymer layer which governs the thickness of this layer and the interaction between polymer coated particles. In such situations, the root mean square thickness of the polymer layer was proportional to the square root of the chain length and that the length of the tails are typically 15% of the length of the polymer. Adjusting the model to describe the interaction between two surfaces revealed attraction due to polymer bridging at low surface coverage. However, at high coverage repulsion was found, except for the case of poor solvents. High molecular weight polymers were more effective stabilisers which was due to their greater ability to adsorb resulting in higher surface coverages.

Evers et al. extended the model to the adsorption of block copolymers by modelling two types of segment. "Anchor" segments were attracted to the surface while "buoy" segments had no affinity for the surface. This is illustrated in figure 2.6. With A-B copolymers, the anchor block formed a flat profile on the surface and the buoy block extended away from the surface in a manner similar to grafted chains. The hydrodynamic thickness of this layer was typically 10-30% of the buoy block. At high surface coverages, the extension of the buoy chain depended strongly on the solvent quality. Triblock copolymers with an anchor at either end, i.e. A-B-A, formed dangling tails with sticky ends as opposed to a loop anchored at either end.

Comparison of A-B diblocks with B-A-B triblocks revealed that both exhibited similar adsorption and stabilisation behaviour. For equivalent buoy blocks, the diblock gives thicker adsorbed layers. Furthermore, an optimum A:B block ratio exists for diblock copolymers, at which adsorption and particle stabilisation are at a maximum.

![Figure 2.6 Lattice model for block copolymers.](image_url)
2.4 Scaling Models.

Scaling models are relatively new tools for describing the properties of polymers at interfaces. Such models tend to ignore the precursor numerical factors and concentrate on the power or scaling exponents of relationships to give relatively simple correlations between properties. Many of the recent advances in this area are due to the efforts of de Gennes and his co-workers. Scaling analyses are applicable for semi-dilute polymers such that polymer chains overlap. An important parameter is the correlation length, $\xi$, which corresponds to the range over which any structure exists.

De Gennes' modelled layers of weakly adsorbed homopolymers onto a solid surface and predicted that the structure of adsorbed layers is nearly independent of the bulk polymer concentration, is self similar and is strongly universal when the strength of adsorption is not too large. Furthermore, most of the monomers are within a narrow layer adjacent to the surface with a thickness of the order of the size of the monomers. The effective hydrodynamic thickness is controlled by the longest loops and scales like the polymer coil size in solution. When two such surfaces interact, there is an attraction in both good and bad solvents when the polymer chains are allowed to exchange with the bulk. However, with no desorption, repulsion was found for good solvents which decreased like $h^2$ at large separations and $h^{5/3}$ at small separations.

Grafted polymer layers were different and exhibited two regimes, unstretched and stretched depending on the graft chain density. At high graft density ($\phi>\sigma$) the chains were stretched with a length proportional to the molecular weight of the polymer. Conversely, at lower coverage, the chains were unstretched with the layer thickness equivalent to the coil size in solution. In practice it is difficult to achieve sufficiently high grafting densities that the chains are in the stretched regime. However, such densities may be achieved with block copolymers adsorbed at an interface between two immiscible solvents, such as with emulsions.

Alexander modelled such a system comprised of polar headed polymers adsorbed at an interface between two immiscible liquids. Here the chain was soluble in one liquid while the polar head was soluble in the other. A further interfacial property was also included whereby the polymer chain was also weakly attracted to the interface, which is probably a realistic situation in many real systems. As for the grafted layer, two regimes were predicted, a high density regime in which the polymer chains are confined in narrow cylinders and a low density regime in which the thickness scales as the differential adsorption energy of the monomers to the $-2/3$. 
The adsorption of copolymers, composed of an anchor block and a buoy block, onto a solid plane was modelled by Marques et al.\textsuperscript{104} At very dilute copolymer concentrations a point was predicted where adsorption first occurs. The concentration for this adsorption depended on the spreading power and the van der Waals attraction between the anchor and the surface. At higher polymer concentrations, micellisation occurs in the solution and adsorption is in equilibrium with this state. Here there are two adsorption regimes which depend on the copolymer asymmetry ratio, $\beta$, which is the ratio of the sizes of the buoy and anchor blocks. The buoy dominated regime exists when $\beta \approx 1$. In this case the adsorption is governed by the elastic stretching energy of the buoys, which are not fully extended. The van der Waals-buoy dominated regime occurs when $\beta \gg 1$. Here the structure of the adsorbed layer is governed by a balance of the van der Waals attraction of the anchor to the surface and the elastic stretching of buoy and the adsorbed layer thickness increases approximately linearly with the molecular weight of the buoy.

Ligoure\textsuperscript{105} modelled the adsorption of surfactant micelles and predicted the existence of a critical surface micelle concentration, $c_{\text{smc}}$, which was different from the solution critical micelle concentration, $c_{\text{cmc}}$. For wetting contact angles less than 51° the $c_{\text{smc}} < c_{\text{cmc}}$ while for contact angles greater than 51° the $c_{\text{smc}} > c_{\text{cmc}}$ and for too high $c_{\text{cmc}}$'s surface micelles will not form. Two domains were also predicted for surface micelles in which they were either small and polydisperse in size or large and monodisperse.

2.5 Depletion Flocculation.

2.5.1 Mechanism of Flocculation.

When a polymer solution is added to a stable, dispersed suspension, flocculation may occur. We have seen previously (section 2.2.1) that this may arise from the bridging of a mutually adsorbed polymer molecule between two particles. However, if the polymer does not adsorb onto the surface of the dispersed phase, flocculation may still occur on account of the difference in the free polymer concentration in the bulk and the region between two approaching particles, which will be devoid of polymer.

Flocculation of suspensions by polymers was first observed in the early twentieth century by Traube\textsuperscript{106} in 1925 who reported the creaming of natural rubber latex when mixed with water soluble polymers. Subsequently, Bondy\textsuperscript{107} showed that with the use of sodium alginate as the creaming agent, the flocculation could be reversed on dilution to give a dispersed system again and furthermore, that the same suspension could be reflocculated and dispersed repeatably. Monoghan and White\textsuperscript{108} observed that gelatin agglomerated erythrocytes
even though the gelatin was not apparently adsorbed onto the cells. Several hypotheses were put forward to explain these agglomeration effects; partial dehydration of the stabilising layers by the addition of the hydrophilic polymer, bridging of the particles by a loose polymer network and "gluing" of the rubber latex particles together by an unknown component forming a viscous envelope around each particle. The true cause of this flocculation was first recognised in 1954 by Asakura and Oosawa. Polymers in solution exert an osmotic pressure and consequently a particle suspended within this medium will experience this pressure equally over its surface (see figure 2.7a). However, when two particles approach one another, say on account of their thermal motion, polymer molecules will be squeezed from the region between the particles on geometrical grounds (see figure 2.7b). The remaining solvent in this region has a lower osmotic pressure relative to the bulk, which results in an imbalance in the pressure over the surface of the particles which thus forces the particles together. Consequently, it can be seen that the strength of the attractive force is proportional to the osmotic pressure of the polymer solution in the bulk and that the range of this force of the order of the size of the free polymer coil.

A more rigorous analysis is required to understand how the free polymer affects the interparticle forces. Firstly, surrounding each particle is a layer which is devoid of free polymer on account that free polymer chains are entropically disfavoured from approaching the surface (in the absence of favourable energies of adsorption) due to their loss of configurational entropy by the space possessed by the impenetrable particles. This layer is termed the depletion layer which usually has a thickness comparable to the diameter of the free polymer coil, \(d_{\text{coil}}\). Secondly, a polymer in a good solvent will readily dissolve and disperse throughout the solvent volume to minimise its free energy. Reversing this process is thus unfavourable and requires energy.
Figure 2.8 Free polymer segment volume fraction profile between two approaching surfaces.

Now we can consider what happens as two particles approach each other from a large separation. The change in the free polymer concentration with decreasing separation, $h$, is illustrated in figure 2.8. For separation greater than twice the size of the free polymer coils, $d_{\text{coil}}$, (a) the surfaces are separated by a region in which the polymer volume fraction, $\phi_p$, is equal to that of the bulk. Closer approach of the particles squeezes out solution at the bulk concentration and consequently there is no change in energy and no force on the particles. However, as the separation is reduced a point is reached (b) where the depletion layers first meet. Here the polymer concentration at the midpoint just reaches its bulk value. Closer approach of the particles pushes free polymer out from between their surfaces (c) leading to a lower polymer concentration in this region. This decreases the uniformity of the polymer coils distributed throughout the system which is energetically unfavoured and results in a repulsive force between the particles. When the separation is of the order of twice the diameter of the free polymer coils, there is only solvent remaining between the particles. Now, closer approach of the particles (d) mixes pure solvent with the bulk polymer solution surrounding the particles. This decreases the free energy of the system and results in an attractive force between the particles.

This change in the free energy of the interaction, $G$, due to depletion of free polymer between two approaching particles is shown in figure 2.9. The repulsive barrier, if sufficiently high, can result in stabilisation of the particles against flocculation. However, in order to prevent flocculation a barrier of ca. 20 kT is necessary while, for flocculation to occur a well of only a few kT is required. Consequently, at low polymer concentrations flocculation rather than stabilisation occurs, while at much higher polymer concentration stabilisation can be achieved. In practice, for not too large spherical particles i.e. in the "colloidal" range, the repulsive force is negligible and can, to a first approximation, be neglected.
Figure 2.9 Illustration of the change in free energy of interaction due to depletion between two approaching particles.

In reality, the free polymer coils are not ideal and as the free polymer concentration increases, the polymer deforms and is forced into gaps smaller than its free solution size. This reduces the separation between particles at which the attraction occurs until a point is reached whereby this gap is so small that there is no longer any attraction and the particles remain dispersed. The thickness of the depletion layer is of the order of the size of the free polymer coils and is called $\Delta$. This is a measure of the range of the attractive component of the depletion force.

2.5.2 Theoretical Models.
2.5.2.1 Hard Spheres.

Asakura and Oosawa's model (AO) was based on a statistical thermodynamical approach assuming the free polymer to be spherical, rigid and non-adsorbing. The osmotic pressure of the free polymer was simply calculated from the van't Hoff formula which assumes the polymer to be ideal, while the potential energy of the interaction was proportional to the overlap volume of the depletion layers giving:

$$G_{\text{dep}} = -(3/2) \phi_p \beta x^2$$ (2.24)

where $\phi_p$ is the volume concentration of the free polymer which is $4\pi N_2^3 / 3\nu$, $N_2$ is the total number of molecules in volume $\nu$, of solution, $\beta = a / \Delta$ and $x = [\Delta - (h/2)] / \Delta$ which obeys $0 < x < 1$. When flocculated, $h = 0$ and $x = 1$.

Several developments followed. Sieglafl" included the second virial coefficient in the expression for the osmotic pressure which takes account of the non-ideality of the free polymer. De Hek and Vrij$^{114}$ and Sperry$^{115}$ obtained similar expressions to the AO model from geometrical arguments. All these models are relatively easy to apply but assume that the free polymer coils behave as hard spheres whereas, in reality, the coils are quite flexible and
deform to some degree when compressed between two particles, thus weakening the attractive depletion interaction.

In order to account for this, Fleer, Scheutjens and Vincent\textsuperscript{116} modelled the effect of a flexible coil on the interaction between two flat plates using a mean field approach to derive the so named FSV model for the change in free energy due to depletion:

\[
G_{\text{dep}} = \frac{\mu_{1} - \mu_{1}^{0}}{\nu_{1}} \frac{2\pi}{3} (\Delta - \frac{1}{2} h)^2 (3a + 2\Delta + \frac{1}{2} h)
\]

where $\mu_{1}$ and $\mu_{1}^{0}$ are the chemical potentials of pure solvent and of solvent at the bulk polymer volume fraction respectively and $\nu_{1}$ is the molar volume of the solvent. Flocculation results in contact where $h=0$, giving:

\[
G_{\text{min}} = 2\pi a \frac{\mu_{1} - \mu_{1}^{0}}{\nu_{1}} \Delta^2 (1 + \frac{2\Delta}{3a})
\]

The quantity $\mu_{1} - \mu_{1}^{0}$ is the free energy change on moving a solvent molecule from pure solvent to polymer solution. This is negative and promotes flocculation. Dividing this by the molar volume of the solvent gives the osmotic pressure difference between pure solvent and the bulk polymer solution: $-(\mu_{1} - \mu_{1}^{0})/\nu_{1}$. Multiplying this by the volume of the depletion zone between two particles yields equations 2.25 and 2.26.

In order to account for the softness of the free polymer coils, the following approximate analytical expression for $\Delta$ as a function of free polymer concentration, $\phi_{p}$, was derived for polymer solutions close to the $\theta$ point:

\[
\sin^2 \frac{\pi f \Delta}{2a f + 1} = \frac{2}{r} - \ln(1 - \phi_{p}) - 2 \chi \phi_{p}
\]

with $r$ the number of statistical segments per polymer chain and $f$ the effective length of the polymer segment. For polymer concentrations below the coil overlap value, $\phi_{o}$, the depletion layer thickness was constant and similar to $R_{g}$. Above this concentration, $\Delta$ dropped sharply and began to converge for all molecular weights, $M$, of free polymer. This is illustrated in figure 2.10.
Figure 2.10 Variation of $\Delta$ with concentration for free polymers of molecular weight, $M$, according to Fleer et al.$^{116}$

Vincent$^{117}$ subsequently remodelled the expression for $\Delta$ by assuming that elastic compression of the free polymer chains occurred at the surface as a result of the osmotic pressure of the bulk free polymer solution to give:

$$\frac{\Delta}{\Delta_0^2} - \frac{1}{\Delta} = \frac{1}{2} \left( \frac{V_1}{\phi_p} \right) \left[ \ln(1-\phi_p) + \phi_p(1-\frac{1}{r}) + \chi \phi_p^2 \right]$$

(2.28)

where $\Delta_0$ is the depletion thickness as $\phi_p$ tends to zero, $V_1$ is the molecular volume of a polymer chain which is equal to $M / N_A \rho$ in which $N_A$ is Avogadro's number and $\rho$ the density of the bulk polymer. In this case a continually decreasing value was found for $\Delta$, even below the coil overlap concentration.

De Gennes$^{118,119}$ used a scaling analysis to also model the interaction of a flexible coil and equated the depletion layer thickness to the correlation length, $\xi$, which depended on the bulk free polymer concentration and corresponded to $R_g$ at low concentrations. The range of the attractive depletion force is $\pi \xi^2$ and, at separations less than $\pi \xi$, the force of attraction, $F$, between two spheres where $a \gg \xi$ is:

$$F \propto \frac{a kT}{\xi^3} (\pi \xi - h)$$

(2.29)

and their free energy of interaction, $G$, is:

$$G \propto -\frac{a kT}{\xi^3} (\pi \xi - h)^2$$

(2.30)

When $h=0$, this gives an attractive force of:
The concentration of the polymer adjacent to the wall, $c_o$, scaled to the bulk polymer concentration, $c$, with a power of 2.25 (i.e. $c_o \propto c^{2.25}$) and the concentration gradient in the depletion layer increasing distance from the wall, $z$, scales as $z^{0.1}$.

The following interesting points can be deduced from these models. Increasing the free polymer concentration causes the osmotic pressure, $\Pi$, to rise but the depletion layer thickness, $\Delta$, to fall. At very low free polymer concentrations $\Delta$ is high but $\Pi$ is very low and flocculation is unlikely. Increasing the free polymer concentration leads to flocculation that is due to a high $\Delta$, although both an osmotic pressure and depletion layer are required for flocculation to occur. At high free polymer concentrations $\Delta$ is low and $\Pi$ is high. The flocculation is now due to $\Pi$ and not $\Delta$. At even higher polymer concentrations restabilisation of the particles occurs because $\Delta$ is so thin that it cannot be compensated for by the very high $\Pi$. This restabilisation is called depletion stabilisation.

### 2.5.2.2 Soft Steric Stabilised Spheres.

Further developments have considered the effect of a steric stabilising layer on the surface of the particles. The presence of such a layer complicates the depletion interaction since some penetration of this layer by the free polymer coils will occur, which will change the thickness of the depletion layer. In a good solvent, polymer-solvent contacts will be preferred energetically over polymer-polymer contacts. This results in an osmotic repulsion between the steric layer and the free polymer coils. Penetration of the coil polymer segments into the steric layer will result in a loss of configurational entropy within both the coil and layer polymer chains, which leads to an elastic repulsion between the two. The distance the coils can penetrate steric layers will depend on these osmotic and elastic terms. Experimentally, the depletion interaction will depend on the density of the stabilising layer and the degree of solvency of the steric layers and free polymer coils.

Feigin and Napper\textsuperscript{220} coupled a rotational isomeric state (RIS) scheme, in which the conformations of polymer chains are realistically determined from true bond angles and bond rotations, with a Monte Carlo (MC) simulation to predict the nature of the depletion layer. From this, the free energy required to form these layers was calculated using the Flory-Huggins theory, introduced in section 2.2.2.2. However, this model is only applicable in $\Theta$ solvents where the polymer chains are free to interpenetrate the steric layer.
Vincent, Luckham and Waite\textsuperscript{121} calculated the depletion interaction from the difference between the free energy of mixing of two steric stabilising layers overlapped with each other and two steric layers overlapped with free polymer coils. This model is applicable to the limited cases where the depletion layer is buried within the steric layer.

Vincent, Edwards, Emmett and Jones\textsuperscript{122} modified the FSV model by considering the distance, $p$, the free polymer coils penetrate the steric stabilising layer of thickness, $\delta$. The effective depletion layer thickness is then $\Delta+\delta-p$. Incorporating this into equation (2.26) gives the VEEJ model:

$$G_{dep} = 2\pi a \left( \frac{\mu_1 - \mu_0}{v_1} \right) \left( \Delta + \delta - p - \frac{h}{2} \right)^2 \quad (2.32)$$

where $h$ is now the separation between the two particle core surfaces. Assuming that closest approach occurs when the steric layers on adjacent particles touch, i.e. $h=2\delta$, equation 2.31 becomes:

$$G_{dep} = 2\pi a \left( \frac{\mu_1 - \mu_0}{v_1} \right) (\Delta - p)^2 \quad (2.33)$$

In order to calculate $p$ it is necessary to know the profile of the steric layer normal to the particle surface. Four different profiles were examined: uniform, linear, pseudohomopolymer and pseudotails. Of these only pseudotails fitted grafted chains which resulted in the following expression for $p$:

$$p^2 (2\delta - p) = \frac{-(\mu_1 - \mu_0) \delta^2 \Delta}{kT(1-2\chi) \phi_p \phi_p^a} \quad (2.34)$$

where $\phi_p^a$ is the polymer volume fraction of the adsorbed stabilising layer which is given by:

$$\phi_p^a(z) = \phi_p^o \left( 1 + \frac{2z}{\delta} - \frac{3z^2}{\delta^2} \right) \quad (2.35)$$

for distance from the surface, $z$, and $\phi_p^a$ is the mean adsorbed polymer volume fraction. Similar behaviour was also obtained from the simpler uniform profile:
\[ p = \frac{-(\mu_1 - \mu_1^0) \Delta}{kT(1 - 2\chi) \phi_p \phi} \]  

(2.36)

Jones and Vincent\textsuperscript{123} extended this model to allow for compression of the attached stabilising chains by the free polymer chains in solution. This was accomplished by replacing the \( \delta \) term in equation 2.31 with \( \delta - q \) where \( q \) is the distance the steric layer collapses. This model is applicable to suspensions where the steric stabilising polymer and the free polymer are chemically different and incompatible.

Scheutjens and Fleet\textsuperscript{124} applied their self consistent field model to the depletion of nonadsorbing polymer between two flat plates. At low polymer concentrations and for a fixed plate separation, the concentration in the gap was much lower than in the bulk. Increasing the bulk polymer solution concentration reduced the difference in the concentration between the bulk and the gap, until at very high polymer levels the two were nearly equal, illustrating how the depletion layer thickness decreases as the free polymer concentration increases. This was due to the freedom of the polymer chains decreasing as the number of chains increases.

Van Lent, Israels, Scheutjens and Fleet\textsuperscript{125} subsequently applied this model to flat plates containing a terminally attached steric layer and immersed in a solution of free polymer. Their findings showed that for hard plates the attraction was purely osmotic while if a steric layer was present, conformational changes within this layer also contributed to the interaction. A minimum occurred in the strength of the attraction at very low surface coverage (<1%), with maximum attraction occurring at zero and full coverage. These two extremes of coverage correspond to the hard sphere case while the presence of a polymer layer at low coverage corresponds to soft spheres. The strength of the attraction could also be reduced by lengthening the stabilising chains in the steric layer or by reducing the size of the free polymer chains. Decreasing the miscibility of the free polymer and the steric layer increased the depletion layer thickness and resulted in a large increase in the strength of the attraction.

2.5.3 Phase Separation / Depletion Experiments.

The first experimental studies were with non-aqueous systems. Sieglaff\textsuperscript{113} observed phase separation with polystyrene (PS) / divinylbenzene microgels dispersed in toluene once a critical concentration of free PS was achieved. The samples interestingly separated into a clear upper layer and a grainy / turbid lower layer separated by a sharp interface.

Clarke and Vincent\textsuperscript{126} extended these studies with ethylbenzene / n-butylformamide microgels of 500 and 1100nm diameter flocculated with PS of 1.8 x10\(^3\) to 2 x10\(^6\) molecular
weight. Their results implied that larger particles were more readily flocculated. Other work on silica particles containing grafted PS in ethylbenzene\textsuperscript{127} confirmed this and also found that flocculation was more readily induced with higher molecular weights of free polymer. Another interesting observation was that the stability of particles increased with increasing coverage of the stabilising layer.

In their studies of similar systems, de Hek and Vrij\textsuperscript{114,128,129} observed the critical polymer concentration for flocculation to fall as the molecular weight of the free polymer rose. However, if the stabilising layer of stearyl alcohol was replaced by polyisobutene then the dependence of the critical polymer concentration on the free polymer molecular weight was much stronger. The critical free polymer concentration for flocculation was also found to decrease as the volume fraction of the silica particles increased.

Studies on non-aqueous systems have revealed much information on how depletion flocculation depends on the concentration and molecular weight of the free polymer, size and concentration of the dispersed phase and even the nature of the steric stabilising layer on the particles. However, studies with aqueous systems are more scattered.

The first conclusive demonstration that free polymer can flocculate aqueous dispersions was presented by Li-in-on and Vincent,\textsuperscript{130} with polystyrene latices stabilised with a grafted PEO chain and flocculated by free PEO. This was further elaborated by Vincent and his co-workers\textsuperscript{131,132} who found evidence for depletion stabilisation at high polymer concentrations. Sperry and his co-workers\textsuperscript{115,133,134} in their studies of electrostatically or sterically stabilised latices flocculated with hydroxyethylcellulose (HEC) have shown that aqueous systems are similar to non-aqueous systems. Increasing the molecular weight of the free polymer decreased the quantity of polymer required to flocculate the latex. Furthermore, with the latex particles stabilised with sodium dodecylsulphate (SDS), the amount of free polymer required was also greater than for particles stabilised with Triton X-405, an octylphenylethoxylate containing 40 moles of ethylene oxide.\textsuperscript{135} This illustrates the importance of the nature of the stabilising layer of particles.

2.5.4 The Liquid Phase.

By varying the molecular weight of the depleting polymer it is also possible to change the range of the attractive force. Gast \textit{et al.}\textsuperscript{136,137} and Vincent \textit{et al.}\textsuperscript{138} have modelled this phase behaviour by summing the depletion and interparticle forces between the particles and calculating the phase boundaries from perturbation theories. When the particles are large relative to the size of the depleting polymer (i.e. a > 3R\textsubscript{p}), then gas, gas coexisting with solid
and solid phases are predicted. This is depicted in figure 2.11(a) and has been confirmed experimentally both for electrostatic and steric stabilised suspensions.

When the depleting polymer is greater than one third of the size of the particles, a liquid phase is also predicted. Sperry has vividly illustrated with photomicrographs how the morphology of a suspension can change in agreement with the theories of Gast et al. and Vincent et al. For low free polymer concentrations and small particle sizes, gas + liquid phases were observed. Increasing either the particle size or polymer concentration resulted in a transition from the gas + liquid to gas + solid phases. Vincent found two critical particle volume fractions for non-aqueous silica dispersions, \( \phi_{\text{min}} \) and \( \phi_{\text{max}} \). For \( \phi < \phi_{\text{min}} \) gas + solid phases occur, for \( \phi_{\text{min}} < \phi < \phi_{\text{max}} \) gas + liquid phases exist, while for \( \phi > \phi_{\text{max}} \) liquid and solid phases.

![Figure 2.11](image-url) Illustration of predicted phase behaviour for colloidal suspensions in free polymer, (a) \( a > 3R_g \), (b) \( a < 3R_g \).

### 2.5.5 Multiphase Coexistence.

Recently, Lekkerkerker et al. have introduced the partitioning of the free polymer between the phases into a model and found that, along with the liquid phase, a three phase coexistence region should also exist when the phases are presented in terms of the polymer concentration in the sample. This is illustrated in figure 2.11(b). If one chooses a fixed particle volume fraction and slowly increases the concentration of the free polymer, then fluid, g+1,
g+i+s and g+s phases are predicted in turn. Some preliminary evidence for these phases has been put forward recently. Leal Calderon et al.\textsuperscript{140} produced phase diagrams for aqueous latices flocculated by hydroxyethylcellulose which included a three phase region. Pusey et al.\textsuperscript{141} also observed similar phase diagrams for non-aqueous dispersions which were in reasonable agreement to the theory of Lekkerkerker et al.
Chapter 3. Experimental.

3.1 Preparation of Colloidal Dispersions.

3.1.1 Latex Preparation.

For these studies polystyrene latices were prepared using the surfactant free aqueous dispersion polymerisation technique developed by Goodwin et al.,[142,143] which is capable of producing highly monodisperse polystyrene particles, electrostatically stabilised by sulphate and carboxylate groups on the surface of the particles.

The latex polymerisations were performed in a 5 dm³, three necked, Pyrex flask which had been fitted with baffles to ensure adequate agitation. The three necks contained a nitrogen gas inlet, a stainless steel paddle stirrer and a water cooled reflux condenser. The flask was immersed in a thermostatted water bath which allowed the reaction temperature to be controlled to within 1°C. The flask was charged with 3.8 dm³ of distilled water, warmed to 75°C, purged with nitrogen (B.O.C. white spot), charged with 404 g of freshly distilled styrene (B.D.H. GPR grade), 3.75 g of potassium persulphate (Aldrich ACS reagent 99+%%) dissolved in 100 g of water and washed through with 100 g of water. The flask was maintained at 75°C for 20 hours and allowed to cool to room temperature. The resulting latex was filtered through washed glass wool (Fisons low lead grade) and dialysed against distilled water using well boiled visking tubing (Gallenkamp) for several weeks, by which time the conductivity had dropped to 10⁻⁵ S cm⁻¹. This procedure produced the large polystyrene latices A, B and C. To achieve a smaller size, latex D was prepared at 95°C with the addition of 0.134% w/w sodium dodecylbenzenesulphonate (Na dbs) to 3.275% w/w styrene and 0.121% w/w potassium persulphate. These conditions are summarised in table 3.1.

<table>
<thead>
<tr>
<th>latex</th>
<th>styrene %w/w</th>
<th>K₂S₂O₈ %w/w</th>
<th>Na dbs %w/w</th>
<th>temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A,B,C</td>
<td>9.17</td>
<td>0.085</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>D</td>
<td>3.275</td>
<td>0.121</td>
<td>0.134</td>
<td>95</td>
</tr>
</tbody>
</table>

Table 3.1 Conditions for synthesis of latices.

The latex volume fractions were calculated from the weight lost on drying to constant weight at 80°C. Corrections were made for any polymer and electrolyte present and the density of polystyrene was taken as 1050 Kgm⁻³.
3.1.2 Emulsions.

Emulsions are thermodynamically unstable dispersions of one immiscible phase within another. They do not form spontaneously and require energy for their formation, such as that provided by a high shear mixer. Also, in order to prevent coalescence of the droplets some form of interfacial barrier between the two phases is required, such as surfactants, to yield a metastable dispersion.

Oil in water (O/W) emulsions of hexadecane stabilised with P103, P105 or F108 were prepared at a φ of 0.7 by adding 54% w/v hexadecane (oil phase) at a controlled rate to 1% w/v of copolymer in 29% w/v of 0.01 molar sodium chloride (aqueous phase) with high shear agitation (Silverson homogeniser). These are summarised in table 3.2.

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Polymer</th>
<th>Polymer %w/v</th>
<th>Hexadecane %w/v</th>
<th>0.01 M NaCl %w/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>P103</td>
<td>1</td>
<td>54</td>
<td>29</td>
</tr>
<tr>
<td>B</td>
<td>P105</td>
<td>1</td>
<td>54</td>
<td>29</td>
</tr>
<tr>
<td>C</td>
<td>F108</td>
<td>1</td>
<td>54</td>
<td>29</td>
</tr>
<tr>
<td>D</td>
<td>P105</td>
<td>7.3</td>
<td>43.8</td>
<td>35.6</td>
</tr>
</tbody>
</table>

Table 3.2 Composition of hexadecane emulsions.

It was necessary to prepare emulsions at such a high volume fraction since only then is the emulsion's viscosity sufficiently high to allow high shear forces to develop within the head of the mixer, which are necessary for complete comminution of the dispersed phase. The agitation was maintained until a near constant droplet size was achieved (typically 24 minutes) after which the emulsions had attained a temperature of 50 - 60°C. During emulsification care was taken to ensure that the emulsions receive sufficient and similar amounts of mixing since the droplet size of an emulsion also depends on the intensity and duration of the applied agitation.

The emulsions A, B and C were purified by dialysis against 0.01M NaCl at 20°C for four weeks, after which no significant changes in droplet size had occurred, indicating the emulsions to have a high degree of metastability. The emulsions were maintained at a temperature of 20°C to avoid crystallisation of hexadecane which has a freezing point of 17°C. It was subsequently found that the emulsion droplets were stable against crystallisation down to temperatures of ca. 2°C. This is consistent with homogeneous crystallisation of hexadecane whereby it no longer has sufficient energy to maintain the liquid state and
spontaneously crystallises. This is in contrast to heterogeneous crystallisation whereby particulate impurities act as nuclei for crystallisation once the system is below its freezing point. This illustrates the high purity of these emulsions by the absence of any particulate material which would cause crystallisation as soon as the temperature drops below 17°C. Such supercooling of emulsions has also been found with similar systems\textsuperscript{144} and with water in oil emulsions.\textsuperscript{145} By changing the polymer content, emulsions of different sizes were also prepared.

Optical microscopy revealed that there were no multiple emulsion droplets and that these emulsions were substantially more polydisperse than the latices. The volume fractions of the emulsions were calculated from their densities, which were measured with a Paar Scientific DMA35 density meter.

3.1.3 Agrochemical Suspensions.

Clofentezine (3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine), a high melting crystalline acaricide, was used in its technical grade. Synperonic PE/P105, an ABA block copolymer, and Polyfon H (Westvaco), a sulphonated lignin polyelectrolyte were used as wetters and dispersants for the clofentezine. Fat Black HBO1 (Hoechst) is an insoluble dye which was incorporated to prevent any increase in the size of the clofentezine particles by Ostwald ripening. This process is driven by the high interfacial energy of dispersions. Smaller particles have a higher surface area and hence energy than larger particles. In order to minimise this energy, the smaller particles preferentially dissolve and these dissolved molecules subsequently redeposit on the larger crystals. The dye is believed to prevent this growth by adsorbing strongly onto the particle surface where it prevents solution and redeposition of the dispersed phase molecules. Kelzan (Kelco) is a commercial grade of xanthan and is used as a rheological modifier to control sedimentation in suspension concentrates. Proxel XL2 (Zeneca) is a preservative which was used to prevent the microbial degradation of xanthan. Distilled water was used for all preparations and all other materials were of analytical grade.

A suspension of clofentezine was prepared by bead milling (Eiger 250ml Motormill) a slurry of clofentezine (50 %w/w) and Fat Black HBO1 (0.1 %w/w) in a solution of 0.5 %w/w of the Synperonic copolymer and 0.15 %w/w of the sulphonated lignin in 0.01 molar sodium chloride. The resulting suspension had a volume median diameter of 1.96 μm as determined by laser diffraction using a Malvern Instruments Mastersizer. The suspension was then diluted to the required concentrations with 0.01 molar sodium chloride and xanthan,
which was prepared as a 2% gel in 0.01 molar sodium chloride preserved with Proxel XL2 at 3%.

Sedimentation of the samples was studied at room temperature in 50ml glass measuring cylinders with an internal diameter of 21mm. The height of the boundary between the sedimenting magenta suspension and the black supernatant (solutions of Polyfon H have a black colour) was measured at various times over a period of 2 years.

3.2 Polymers.

3.2.1 Stabilising Copolymers.

Three polyethylene oxide - polypropylene oxide block copolymers, Synperonic PE/P103, P105 and F108 were supplied by ICI Chemicals and Polymers and used as received. These polymers are ABA block copolymers where A=PEO and B=PPO; and have the following structure:

\[
\begin{align*}
H-(OCH_2CH_2)_n(OCH_2CH_2)_m(OCH_2CH_2)_n-OH \\
\end{align*}
\]

They are part of a range of polymers in which both the PEO and PPO chain lengths are varied systematically to give a vast range of surfactants in which one of many parameters may be varied. In this work a series was selected in which the B block has a constant chain length of 56 units while the length of the A block increases from 39 units for P103 to 74 and 258 units for P105 and F108 respectively. With aqueous dispersions the hydrophobic PPO is strongly adsorbed onto the surface while the hydrophilic PEO extends into the medium providing a barrier to flocculation. These polymers were characterised by gel permeation chromatography (GPC) and NMR(H1 and C13). The results along with the manufacturers details are summarised in table 3.3.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M.Wt.</th>
<th>%EO(w/w)</th>
<th>GPC results</th>
<th>NMR results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
<td>Mw</td>
</tr>
<tr>
<td>P103</td>
<td>4950</td>
<td>30</td>
<td>5680</td>
<td>7580</td>
</tr>
<tr>
<td>P105</td>
<td>6500</td>
<td>50</td>
<td>7160</td>
<td>9690</td>
</tr>
<tr>
<td>F108</td>
<td>14600</td>
<td>80</td>
<td>11400</td>
<td>15800</td>
</tr>
</tbody>
</table>

GPC measurements were made in THF against PS as a standard.
NMR measurements were made in deuterated DMSO.

Table 3.3 Properties of Synperonic PE copolymers.
3.2.2 Non-Stabilising Polymers.

Xanthan, an extracellular polysaccharide produced by the microorganism *Xanthomonas campestris*, and five different molecular weight grades of hydroxyethylcellulose (HEC) were obtained from Kelco and Aqualon respectively with the Kelzan and Natrosol trade names. For this work these polymers were prepared as 1-2% aqueous gels and dialysed against water for several weeks, by which time the conductivity had dropped to \(10^{-5}\) S cm\(^{-1}\). Formaldehyde was added at 0.1% to prevent microbial degradation.

3.2.3 Preparation of Suspensions in Non-Stabilising Polymer Gels.

Samples were prepared by mixing PEO-PPO-PEO stabilised latices with an aqueous HEC gel to the required volume fraction and polymer concentration. A magnetic stirrer was used to ensure that the samples were thoroughly mixed and homogeneous without causing aeration of the samples. For all samples the electrolyte concentration (NaCl) was 0.01M and the pH maintained at 7.0 ± 0.5.

3.3 Characterisation of Dispersions.

All measurements were performed in 0.001-0.010 molar sodium or potassium chloride solution and are summarised in tables 3.4 and 3.5 (latex D flocculated in 0.01 molar electrolyte).

<table>
<thead>
<tr>
<th>Latex</th>
<th>Diameter (z average) / nm</th>
<th>Polydispersity</th>
<th>Zeta potential / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>429 ± 10</td>
<td>1.29 ± 0.30</td>
<td>-38 ± 11</td>
</tr>
<tr>
<td>B</td>
<td>499 ± 10</td>
<td>0.086</td>
<td>-52.5 ± 11</td>
</tr>
<tr>
<td>C</td>
<td>424 ± 10</td>
<td></td>
<td>-36 ± 15</td>
</tr>
<tr>
<td>D</td>
<td>67 ± 2</td>
<td>0.06 ± 0.06</td>
<td>-40 ± 16 or 1.6</td>
</tr>
</tbody>
</table>

Table 3.4 Particle size (PCS) and surface potential of polystyrene latices.

3.3.1 Particle Sizing by Photon Correlation Spectroscopy.

Photon correlation spectroscopy (PCS) is highly suited to measuring the particle size of dispersed, spherical submicron particles. The PCS technique works by directing a monochromatic, coherent light source (i.e. laser) into a dispersion and measuring the intensity of the scattered light. The light scattered from all the particles will interfere either constructively or destructively, depending on the separation between the particles. Over very short times (ca. µs-ns) the particles will not have moved and the intensity will remain
constant. However, at longer times diffusion will occur resulting in a change in the interference and intensity. This change is interpreted in terms of a correlation function which is a measure of the intensity at increasing times compared to its initial value. At very short times before diffusion has occurred there is complete correlation, while at long times after diffusion, there is no correlation. The time over which the particles lose their correlation yields a value for their diffusion coefficient, $D$. From this the particle radius, $a$, is calculated using the Stokes'-Einstein equation:

$$a = \frac{kT}{6\pi \eta D}$$  \hspace{1cm} (3.1)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature and $\eta$ is the viscosity of the continuous phase. The results, obtained with a Malvern Instruments Autosizer IIc are shown in table 3.4.

3.3.2 Microelectrophoresis.

The surface potential of the latex particles was determined from particle electrophoresis measurements made with either Coulter Electronics Delsa 440 or Brookhaven Zetaplas instruments. The technique of microelectrophoresis operates by applying an electric field to a dilute suspension of particles and measuring their resultant velocity through the doppler frequency shift of a monochromatic light beam by the moving particles. The electrical potential at the surface of the particles is called the zeta potential, $\zeta$, and for this work was calculated from the Smoluchowski equation:

$$\zeta = \frac{v\eta}{E\varepsilon_0}$$  \hspace{1cm} (3.2)

Where $v$ is the velocity of the particles and $E$ is the strength of the applied electric field. It should be noted that the Smoluchowski equation is only accurate for high values of $\kappa a > 100$ (for these measurements $\kappa a$ is approximately 17 for the larger latices and 3 for the small latex) and consequently these calculated zeta potentials will underestimate the true potential by some 10% for the large particles and some 20% for the small particles. The measurements were made in 1 mM NaCl solution at neutral pH and are shown in table 3.4.

3.3.3 Particle Sizing by Laser Diffraction.

As particles approach the top of the colloidal size range, ca. 1\mu m, their thermal motion rapidly decreases to the point where there is insufficient doppler broadening for size
measurement by PCS. However, with this size range, particles give angular variations in the intensity of the scattered light. This measurement of the angular dependence of scattered laser light is called laser diffraction and is capable of measuring particle sizes from 0.1 to 600\(\mu\)m. For larger particles greater than ca. 4\(\mu\)m the scattering is relatively simple and does not depend on the optical properties of the particles or medium.\(^{148}\) For smaller particles the scattering of light is more complex and depends strongly on the optical properties of the particles and medium. In this case the particle size distribution is calculated from Mie theory\(^{149}\) and requires two optical parameters of the dispersion to characterise its optical properties; the refractive index difference between the particles and the medium, and the absorbance of the dispersed phase. For these measurements a Malvern Instruments Mastersizer was used with values of 1.490 and 0.03 for the emulsions and values of 1.75 and 0.1 for the clofentezine suspension respectively for the refractive index and absorbance. The clofentezine suspension and hexadecane emulsion droplet sizes after dialysis are tabulated in table 3.5.

<table>
<thead>
<tr>
<th>System</th>
<th>Polymer</th>
<th>Volume mean diameter ((\mu)m)</th>
<th>Sauter mean diameter ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion A</td>
<td>P103</td>
<td>2.69 ± 1.08</td>
<td>2.22 ± 0.92</td>
</tr>
<tr>
<td>Emulsion B</td>
<td>P105</td>
<td>2.36 ± 0.89</td>
<td>2.08 ± 0.77</td>
</tr>
<tr>
<td>Emulsion C</td>
<td>F108</td>
<td>2.96 ± 1.08</td>
<td>2.63 ± 0.93</td>
</tr>
<tr>
<td>Clofentezine suspension</td>
<td>P105/Polyfon H</td>
<td>1.96 ± 1.57</td>
<td>1.18 ± 0.96</td>
</tr>
</tbody>
</table>

Table 3.5 Diameter of hexadecane emulsions and clofentezine suspension as determined by laser diffraction.

3.3.4 Microscopy.

Observations were performed with an Olympus BHS optical microscope fitted for either brightfield or Normarski Differential Interference Contrast (DIC) analysis. Under ordinary brightfield observation, objects immersed within a medium of similar refractive index are virtually invisible. Using DIC allows such objects to be clearly viewed since this technique is very sensitive to refractive index changes and is ideally suited to the study of multiphase systems. The basis of the technique involves splitting a coherent ray of plane polarised light into two, and applying a lateral shift to one with a Wollaston prism, so that the rays pass through a sample at slightly different positions. This shift is then reversed and the rays are recombined with a second prism. If the sample contains an object of a different refractive index, and if one of the rays of light passes through a different thickness of the object, say due to its curvature, then it will take a longer or shorter time for this ray to pass through the
sample and consequently, when the rays are recombined, they will be out of phase and there will be an interference shift observable as a colour change. Therefore, this technique visualises changes in the thickness of objects and results in a three dimensional relief like image. The amount of interference increases with the rate of change in the thickness of the object under observation, such that when viewed, emulsion droplets will show the greatest interference at their edges and virtually none at their centres.

3.4 Other Materials and Apparatus.

The water used in this work was de-ionised and distilled. All other materials were used as received. Glassware and other apparatus were thoroughly cleaned and rinsed in distilled water and acetone before use.

3.5 Copolymer Adsorption Isotherms.

3.5.1 Latices.

Adsorption isotherms were determined so that the required coverage of polymer may be adsorbed onto the particles surface. These were determined photometrically for the PEO-PPO block copolymers on polystyrene latices by the methods of either Attio and Rubio\textsuperscript{150} or Baleux and Champetier.\textsuperscript{151}

Samples containing 9.2 to 2.2 mg/cm$^3$ of particles and from 8 to 800 mg/cm$^3$ of polymer were equilibrated for at least 24 hours at 20°C and centrifuged (10,000 to 28,000 rpm for 30 min. at 20°C). The supernatant was removed and analysed by one of the two methods.

In the first method 1 ml tannic acid solution (1% w/w) followed by 1 ml NaCl solution (2M) were added to 5 ml of the supernatant and shaken. After a specific period of time to allow for stabilisation (between 30 and 90 minutes depending on the number of samples) the absorbance was measured at 360nm and 440nm in a Perkin-Elmer lambda 5 UV/VIS spectrophotometer.

In the second method 1 ml of an aqueous solution containing 5 g/l potassium iodide and 2.5 g/l iodine was added to 5 ml of the supernatant and shaken. After 15 minutes the absorbance of the samples was measured as before at 500nm.

The concentration of polymer was determined from calibration curves covering the range 2-32 mg/l. Samples that exceeded this range were measured by dilution. The two methods were of similar accuracy but the second was found to be simpler experimentally.
3.5.2 Emulsions.

The amount of copolymer adsorbed at the water/hexadecane interface was determined by centrifugally creaming the emulsions at low g, separating the clear aqueous phase from the base of the centrifuge tube (by carefully cutting off the tube base) and measuring the copolymer residue remaining in this phase after drying to constant weight at 80°C.

3.6 Rheological Measurements.

A Bohlin VOR rheometer (Bohlin Instruments, Cirencester, U.K.), fitted with either double gap (DG24/27) or concentric cylinder (C25 or C14) geometries, was used for all measurements. The instrument operates by applying a controlled strain to the outer "cup" and measuring the resultant slight deflection of the inner "spindle" against interchangeable torsion bars. Corrections are made for the compliance of the torsion bars by the processing software supplied with the instrument. A thin layer of silicone fluid (Dow Corning 200/20cs) was applied to the sample to prevent evaporation.

In the continuous shear experiments, a constant rate of strain, \( \dot{\gamma} \) (\( = \text{d}y/\text{d}t \)), was applied to the outer cylinder and the stress, \( \sigma \), transmitted through the sample to the inner cylinder monitored. By varying the strain rate from \( 10^3 \) to \( 10^3 \text{ s}^{-1} \) flow curves may be obtained for each system. The yield stress was determined by fitting the linear portion of the shear stress \( (\sigma) \) - strain rate \( (\dot{\gamma}) \) flow curve, which was typically at strain rates from \( 10^2 \) to \( 1.4 \times 10^3 \text{ s}^{-1} \), to the Bingham model (equ. 1.4).

In oscillatory shear experiments, the response stress, \( \sigma_0 \), of the material to a sinusoidally varying strain of known amplitude, \( \gamma_0 \), is monitored. The stress is also a sinusoidally varying function, but for a viscoelastic material it is shifted out of phase from the strain by an amount, \( \delta \), the phase angle. From the amplitudes of stress and strain and the shift in phase angle, the complex modulus, \( G^* \), storage (or elastic) modulus, \( G' \), and the loss modulus, \( G'' \) may be determined. Colloidal dispersions exhibit an amplitude dependence in their response to an oscillatory shear. However, at low amplitudes a linear response is obtained. Therefore a strain sweep, where the applied strain at a frequency of 0.5 Hz is gradually increased, was performed for each dispersion to ensure operation in the linear viscoelastic region. From this we obtain the critical strain, \( \gamma_c \), which is a measure of the extent of the linear viscoelastic region and was defined in this work as the intercept of two linear lines drawn through the elastic modulus, \( G' \), in the linear plateau region and in the region of structure breakdown beyond the linear region from a lin-log plot of \( G' \) against strain. This typically corresponded to a strain at which \( G' \) had decreased by some 5-10% of its value in
the linear region. The frequency dependence of these moduli was examined by applying a sinusoidal strain within the linear viscoelastic region over the frequency range $10^{-3}$ to 10 Hz.

By their very nature, the viscoelastic properties of flocculated suspensions can be sensitive to their shear history. In this work we have observed such sensitivity and consequently the following experimental procedure was followed. Firstly, a strain sweep was performed (0.5 Hz) to a high strain of 0.2 where the flocculated structure is broken down. The reformation of the floc network was then monitored for 10 minutes at a frequency of 0.5 Hz within the linear viscoelastic region, during which only a slight rise was observed in the moduli indicating that once broken down, the floc network reforms rapidly; i.e. within a few seconds. Frequency sweep experiments were then performed which typically showed that the moduli had decreased by some 10\% to their values prior to the strain sweep, indicating some change in the network. These are the values presented in this work. Shearing (up to $1.4 \times 10^3$ s) also affected the values, the critical strain and $G'$ generally increased while $G''$ decreased.
Chapter 4. Copolymer Adsorption Results.

4.1 Introduction.

In chapter 2 it was shown how copolymers adsorbed at an interface of a dispersion are important for providing a repulsive steric layer to prevent agglomeration. However, it is not sufficient to add a copolymer to a suspension since, if partial coverage of the particles is achieved, then bridging flocculation may occur, while if excess copolymer is added, then depletion flocculation may occur. For stabilisation, the optimum amount of copolymer is that which gives full coverage on the particle surface. In this chapter, the adsorption of three Synperonic PEO-PPO-PEO block copolymers onto polystyrene latex particles and at the water-hexadecane interface is studied.

4.2 Adsorption onto Latices.

The adsorption isotherms of P103, P105 and F108 on both large and small latices are given in figures 4.1a to d and the plateau values presented in table 4.1. Identical results were obtained with and without electrolyte (0.01 M NaCl). The adsorption is Langmuirian and of a high affinity indicating that the copolymer molecules adsorb strongly in a monolayer on the surface of the latex particles. These results are in accord with previous measurements on similar systems. For example Baker et al. have determined an adsorption plateau of 1.35 mg m$^{-2}$ for P105 and F108 whilst Kayes and Rawlings have found the adsorption to be 1.1 mg m$^{-2}$ for F108.

<table>
<thead>
<tr>
<th>Latex</th>
<th>P103</th>
<th>P105</th>
<th>F108</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex A</td>
<td>1.25 ± 0.2 [0.25]</td>
<td>1.25 ± 0.2 [0.19]</td>
<td>1.55 ± 0.2 [0.11]</td>
</tr>
<tr>
<td>Latex B</td>
<td>1.35 ± 0.2 [0.21]</td>
<td>1.85 ± 0.2 [0.13]</td>
<td></td>
</tr>
<tr>
<td>Latex D</td>
<td>1.1 ± 0.2 [0.22]</td>
<td>1.0 ± 0.2 [0.15]</td>
<td>1.4 ± 0.2 [0.096]</td>
</tr>
<tr>
<td>Emulsions A,B,C</td>
<td>4.0 ± 0.4 [0.81]</td>
<td>2.8 ± 0.4 [0.43]</td>
<td>4.0 ± 0.4 [0.27]</td>
</tr>
</tbody>
</table>

Table 4.1 Plateau adsorption values (mg m$^{-2}$ and [μmol m$^{-2}$]) for Synperonic PE copolymers.
Figure 4.1 Latex adsorption isotherms, (a) to (d) mg/m$^2$, (e) and (f) μmol/m$^2$. For (a), (e) and (f): P103 (■), P105 (●) and F108 (▲).
A better way of expressing these data is to represent the amount adsorbed, \( \Gamma \), in mol m\(^{-2}\) as is shown in figures 4.1e and f and also in table 4.1. In this case there is a systematic decrease in \( \Gamma \) with increases of molecular weight of the EO chain. In other words the area occupied per molecule tends to increase with increase of the EO chain length. This implies that the amount of adsorption is governed by the size of the PEO chain rather than the anchoring PPO chain, which is constant in these experiments. Direct evidence for this may be obtained from a plot of the area per molecule versus \( n \) (where \( n \) is the number of EO units per PEO chain) (figure 4.2). The linearity of the plot shows that the adsorption is dependent on the radius of gyration of the PEO (the radius of gyration is proportional to \( n^{1/3} \) in a \( \Theta \) solvent). Similar results have recently been obtained on carbon black dispersions with the same surfactants.\(^{36}\) Extrapolating to \( n=0 \) from P103 and P105 gives an area of 4.5±0.5 nm\(^2\) (\( R_g^2=1.2 \) nm\(^2\)) for 56 PO units on the large latices. This figure is in remarkable agreement to 4.48 nm\(^2\) found by Kayes and Rawlings\(^{154} \) and is smaller than the value for PPO in a good solvent (\( R_g^2=17.2 \) nm\(^2\) for 56 units\(^{155} \)) as expected for a polymer chain in a poor solvent (water/PEO). Considering this information allows us to build up a picture of the polymers on the surface of the particles. The most probable is of a compact disc of PPO sitting on the surface of the polystyrene.

![Figure 4.2](image-url)
Calculating the area we would expect for PEO chains in a good solvent from:

\[ R_g = \left( \frac{C_n n^2}{6} \right)^{1/2} \]  

(4.1)

gives 8.9, 17 and 60 nm\(^2\) for P103, P105 and F108 respectively. The area for P103 is in fair agreement with the experimental value of 6.6 nm\(^2\). However, for P105 and F108 we find much higher values than the experimental results of 8-11 and 13-17.5 nm\(^2\) respectively. We can obtain an insight into this discrepancy by considering the relative size of the PPO and PEO chains. This is illustrated diagrammatically in figure 4.3 with the PPO drawn as a compact coil and a circle showing the size of the PEO chain according to its \(R_g\) value. For the P103, the size of the PPO and PEO are the same and consequently the two PEO chains are held sufficiently apart so that their areas touch but do not overlap. Here we would expect close agreement between the experimental areas found at full coverage and the areas calculated from \(R_g\), as indeed we do find. However, for P105 and F108 the size of the PEO coils is considerably larger than the PPO coil, which consequently, must hold the two PEO chains close together such that their expected volumes overlap and occupy a smaller area. The areas obtained when considering this overlap are shown in table 4.2. Although the expected area per molecule is reduced for P105 and F108, it is still considerably larger than the experimental

![Figure 4.3 Scaled plan view of copolymers adsorbed onto latices.](image)
values. Therefore, the PEO chains must either overlap considerably with adjacent PEO chains on neighbouring molecules or extend further from the surface.

<table>
<thead>
<tr>
<th>copolymer</th>
<th>plateau adsorption</th>
<th>$R_z$ calculation</th>
<th>overlap removed (fig. 4.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P103</td>
<td>7</td>
<td>8.9</td>
<td>8.9</td>
</tr>
<tr>
<td>P105</td>
<td>9</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>F108</td>
<td>16</td>
<td>60</td>
<td>44</td>
</tr>
</tbody>
</table>

Table 4.2 Comparison of experimental and calculated areas per molecule ($\text{nm}^2$).

An indication as to which of the two situations occurs can be obtained from the plot of area per molecule vs. n EO (figure 4.2). For true coils the area, A, is simply the equation for the area of a circle with the radius given by the radius of gyration: $\pi R_g^2$. Substituting equation 4.1 into this expression for the area with $C_o=4$ and $l=0.3$ gives $A=0.2n$. Therefore, from a plot of A against n, we would expect a slope of 0.2. For a brush of linear chains normal to the surface, the area is the same regardless of the length of the chain and would give a horizontal line with a slope of zero.

The latex results have a slope of 0.1 which tells us that both are happening and the PEO coils are extended from the surface of the particles. So, from knowledge of the adsorbed copolymer areas we know that the PPO is in the form of a tight coil which constrains the PEO chains into an extended coil conformation normal from the surface. However, we do not know the amount of extension of the PEO coils. To overcome this we need information about the thickness of the polymers normal to the surface, which we can obtain from rheological measurements and will be discussed in chapter 5.

4.3 Adsorption at the Emulsion Interface.

The droplet size was found to be similar for the three copolymers and decreased linearly with increasing level of copolymer when the droplet diameter was plotted against the polymer concentration on a log-log basis (see figure 4.4). This is an interesting result which tells us that the droplet size of an emulsion depends not on the number of molecules of surfactant but on its mass. Also, it is the amount of surfactant relative to the oil phase and not the surfactant concentration in the aqueous phase which governs the size of the droplets.
Figure 4.4 Change in Sauter mean diameter of hexadecane emulsions for P103 (○), P105 (○) and F108 (△). Polymer concentration is relative to the oil phase.

The adsorbed amount of copolymer found at the water/hexadecane interface is shown in table 4.1. It is immediately apparent that the quantities are much greater than for the latices. Why is 2-3 times more polymer required to stabilise an emulsion droplet than a latex particle? The reason for this is most interesting since it gives us further insight into the factors relevant to the adsorption of these copolymers.

The areas per molecule are shown in figure 4.2 using the volume mean diameters given in table 3.6. Firstly, extrapolation of the P103 and P105 results to zero EO content gives an area of virtually zero for the PPO. This is very different to the value of 4.5±0.5 nm$^2$ for 56 PO units on the large latices and tells us that the PPO must extend into the hexadecane phase as a loop and furthermore, that this loop must be highly extended in order for the occupied area at the interface to be small. This is reasonable since PPO is miscible with hexadecane. The slope of the curve is also reduced indicating that the PEO chains are more elongated than with the latices (recall that chains rigidly extended from the surface in the form of a brush have a slope of zero while spherical coils have a slope of 0.2). This is necessary for tighter packing of the copolymer molecules at the emulsion interface. With the emulsions, the PPO loop appears to be adsorbed strongly leading to the high interfacial concentration which in turn causes lateral compression of the PEO coils forcing them into a more highly extended configuration. This is evident from the slope of the areas in figure 4.2 which shows that the PEO chains have very little effect on the adsorbed amount.
Surprisingly, only ca 45% of the copolymers is found at the droplet interface, with the remainder in solution in the aqueous phase, yet reducing the amount of copolymer during emulsification results in larger droplets instead of less free copolymer in solution. This is most unusual since any free copolymer would be expected to stabilise oil droplets during emulsification. Even more surprising is the absence of any change in the droplet size after dialysis where the free copolymer in solution would be removed. This suggests that the copolymer molecules are not only strongly adsorbed at the emulsion interface but are also permanently fixed there. This is in contrast to latex systems where such polymers are known to desorb and readсорb dynamically.

What can we conclude from the polymer adsorption on latices and emulsions? According to polymer statistics, the PEO exists as a spherical coil in a good solvent, as we have here. This becomes laterally compressed into an elongated coil extending away from the interface by either high levels of adsorption of adjacent copolymers or intramolecular compression of one PEO coil by the second PEO coil, which are constrained by the relatively small size of the PPO coil. Therefore, the PPO - substrate interaction is greater than the loss of configurational entropy on constraining a PEO coil and that the PPO - substrate interaction is greater with the emulsion than the latex systems. Adsorption continues until the loss of configurational entropy of the PEO coils balances the favourable substrate interaction. This behaviour at the emulsion droplet interface appears to agree with the high density/stretched regimes predicted from scaling analysis by Alexander$^{103}$ and de Gennes$^{102}$ (see section 2.4). To quantify the degree of extension of the PEO coils from the surface, measurements of the thickness of the adsorbed copolymer layer are required. Such studies are presented in the following chapter.
Chapter 5. Rheology of Dispersed Systems.

5.1 Introduction.

In this chapter, the effect of the steric layer on the rheology of latices and emulsions is studied. Two sizes of latex are examined, 4-500 nm where the steric layer is relatively thin compared to the size of the particles and 67 nm where the layer is proportionally much thicker. Comparison is also made with emulsion droplets in which it was found in chapter 4 that the steric layer is more densely packed.

5.2 Steady Shear Measurements.

5.2.1 Large latices.

The shear stress as a function of shear rates for latex A stabilised with F108, at several volume fractions, \( \phi \), is shown in figure 5.1. At low \( \phi \) the behaviour is virtually Newtonian (i.e. stress \( \propto \) shear rate, slope equals one). As \( \phi \) increases the shear stress begins to diverge from Newtonian to pseudoplastic flow with the appearance of a region of shear thinning at intermediate shear rates with Newtonian flow at high and low shear rates. Here we are observing a change from a disordered random arrangement of the latex particles at low shear to an ordered, layered arrangement at high shear. The greater stress at low shear arises...
from the high resistance to flow experienced by the particles as they try to pass each other, which is considerably reduced at high shear where the "sheets" of particles glide over each other. At even higher $\phi$ the low shear Newtonian plateau is no longer visible and the flow becomes plastic with an apparent yield stress. Similar data were obtained for the other copolymers.

Figure 5.2 High shear relative viscosity data for large latices: A+P103 ( ), A+P105 (O), A&B+F108 (s), C without polymer (•) and K-Dougherty equ (line).

The data for all of the copolymers is plotted in figure 5.2 in which the relative viscosity, $\eta_r$, at high shear rates ($\eta_r = \eta_{pl}/\eta_s$ where $\eta_s$ = viscosity of solvent) as a function of particle volume fraction, $\phi$, is shown. The results are those to be expected for a concentrated dispersion, namely a gradual followed by a rapid increase in $\eta_r$ with increase in $\phi$. For comparison the solid curve shows the theoretical curve for a hard sphere dispersion, calculated using the Krieger-Dougherty equation (equation 1.24) as introduced in chapter 1:

$$\eta_r = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-\phi_{max}\cdot[\eta]}$$  \hspace{1cm} (5.1)

where $[\eta]$ is the intrinsic viscosity that is equal to 2.5 for hard spheres and $\phi_{max}$ is the maximum packing fraction. Krieger$^{156}$ and de Kruijf $et\ al.$$^{157}$ have reported experimental values of 2.71 and 0.708 respectively. Figure 5.2 reveals two main points. Firstly that the Krieger-
Dougherty equation is underestimating the relative viscosity of the material, particularly at high solid content fractions. This is not too surprising as the true volume fraction of the particles (in terms of the hydrodynamics) should include the volume of the adsorbed polymer layer in addition to the volume of the particle itself. Furthermore, the relative viscosity of the F108 stabilised dispersion is somewhat higher than the P105 and P103 stabilised samples. This implies that the polymer layer is appreciable and that F108 produces thicker adsorbed layers. Indeed, one can use the Krieger-Dougherty equation to estimate the effective volume fraction and hence adsorbed layer thickness for these systems. However, this analysis with Krieger’s hard sphere values give unrealistically thick adsorbed layers and so, to provide a true baseline for the effect of the adsorbed polymer layers, an effective hard sphere system was prepared by adding sufficient electrolyte to latex C, without an adsorbed polymer layer, to compress the repulsive, diffuse electrical double layer such that it almost balances the attractive van der Waals forces. The high and low shear limiting viscosities are plotted in figure 5.3.

Up to a $\phi$ of ca. 0.2 the relative viscosities are the same. Above this value the high shear viscosity rises less rapidly, illustrating how the ordering of particles into sheets significantly reduces the resistance to flow of the latex. A plot of $1/\eta_{r}^{1/2}$ against $\phi$ gave a linear relationship up to $\phi=0.4$ with a maximum packing fraction, $\phi_m$, of 0.670±0.01. From the differences between latex C and the polymer stabilised latices one can estimate the thickness of the adsorbed polymer layer.
5.2.2 Small Latex.

A similar treatment can be applied to the smaller latex, D. Here, because of its smaller size, the particles have a much faster diffusion time and consequently the latex only exhibits a low shear viscosity plateau within the experimental range. This can be seen in the flow curves shown in figure 5.4 where the Newtonian plateaus (the regions with a slope of one) are clearly visible and much more apparent than for the large latex results shown in figure 5.1.

![Graph](image)

Figure 5.4 Shear stress verses shear rate data for latex D (67nm) stabilised with F108 at several volume fractions: top to bottom, 0.325, 0.284, 0.246, 0.245, 0.238, 0.171.

Thus, in figure 5.5, the relative low shear viscosity of latex D, bearing adsorbed layers of the three different copolymers is presented. The results are strikingly different from the large latex shown in figure 5.2. As before, the F108 produces the greatest deviation and the P103 the least. These results support the previous conclusion that the F108 produces the thickest layers and P103 the thinnest. This is what would be expected with the molecular weight increasing from P103 to F108. However, what is most surprising is the magnitude of these deviations from the Krieger-Dougherty equation for the small latex compared to the large latex results. Even greater deviations were found for bare latex particles in 1mM electrolyte indicating very extensive electrical double layers, while reducing the P103 coverage from full to one twelfth produces less deviation in the viscosity implying that a reduction in the thickness of the steric polymer layer occurs.
For this latex it was not possible to measure an effective hard sphere system by adding sufficient electrolyte to suppress the electrical double layer since the latex flocculated in 0.01 M electrolyte, as shown by PCS. So, for a baseline, the low shear viscosity data for latex C was used. A plot of $1/\eta_r$ vs. $\phi$ gave a $\phi_m$ of 0.60 ± 0.02. For hard sphere systems Krieger\textsuperscript{15d} has reported a slightly higher $\phi_{\text{max}}$ of 0.632 and an $[\eta]$ of 3.13. Interestingly, hexagonally packed sheets of particles have a $\phi_{\text{max}}$ of 0.605 while random close packing has a $\phi_m$ of 0.637 (see table 1.1). This implies that the latex has an ordered rather than a random structure.

The adsorbed layer thickness for both the large and small particles can be obtained from the maximum packing fraction using:

$$\phi' = \phi (1 + \delta/a)^3$$

(5.2)

where $\phi$ and $\phi'$ are the maximum volume fractions of the latices with and without the adsorbed polymer layers. The results are shown in table 5.1.

Firstly, it can be seen that as the molecular weight of the PEO increases the adsorbed layer thickness increases, as one would expect. Furthermore, the data for the two latices are similar with the smaller latex having a thicker apparent adsorbed layer. This is not what one would expect from geometrical arguments but we must recall that the adsorbed layer thickness...
for the large particles were calculated from the high shear limiting viscosity whilst the smaller particles were calculated from the low shear viscosity. Thus comparison may not be appropriate, as at high shear rates the thickness of polymer layers is known to decrease.\textsuperscript{33,44} Furthermore, reducing the amount of P103 adsorbed on the small latex, D, by 1/12 only reduces the adsorbed layer thickness marginally.

| System (latex + polymer) | Steady shear measurements |  |
|-------------------------|---------------------------|  |
|                         | Zero shear viscosity      | Plastic viscosity |
| A + P103                | 3.8 ± 2                   |  |
| A + P105                | 5.7 ± 1                   |  |
| A + F108                | 8.9 ± 1                   |  |
| B + F108                | 13.4 ± 2                  |  |
| D + P103/12             | 4.9 ± 1                   |  |
| D + P103                | 5.5 ± 1                   |  |
| D + P105                | 6.5 ± 1                   |  |
| D + F108                | 9.4 ± 0.5                 |  |

Table 5.1 Steric polymer layer thicknesses (nm) from relative viscosity measurements.

5.3 Polymer Coverage.

The effect of polymer coverage was further investigated with F108 adsorbed onto latex B (499nm) at full, two thirds and one third coverage. The polymers were adsorbed at low latex volume fraction, \textit{ca.} 0.1, and slowly concentrated by compression of dialysis tubing. Shear rate sweeps were performed from which the high shear plastic viscosities are plotted in figure 5.6.

At full coverage, the latex viscosity increased as expected with increasing latex volume fraction. At two thirds coverage the behaviour was identical up to a volume fraction of 0.42. Above this value the latex flocculated to form a thick, unmeasurable solid. This was also observed for the latex at one third coverage above volume fractions of 0.31. Below this volume fraction the latex was fluid but exhibited higher viscosities than the latex at full coverage. Evidently, the latex is beginning to flocculate here but full flocculation is not achieved until higher volume fractions. Increasing the coverage of F108 raises the volume fraction at which flocculation occurs. Furthermore, the "partially" flocculated latex at one third coverage exhibited shear thickening after prolonger shearing at high shear rates, while dilution of the fully flocculated samples did not readily lead to their redispersion. This is consistent
with a bridging mechanism which is quite possible for a polymer of this high a molecular weight and may also be the reason for the P103 not flocculating latex A at one twelfth coverage, its size being too small to bridge between two latex particles.

Figure 5.6 Relative viscosity for latex B with F108 at full (□), 2/3 (●) and 1/3 (▲) coverage of polymer.
5.4 Dynamic Results.

5.4.1 Latices.

Typical oscillatory shear results for latex B (499nm) stabilised with F108 are shown in figure 5.7. At low $\phi$, 0.370 (a), the suspensions have very low moduli values and are fluids with the loss modulus, $G''$, greater than the storage modulus, $G'$, at all frequencies. As $\phi$ is increased slightly to 0.403 (b) the adsorbed polymer layers on adjacent particles begin to interact repulsively on account of the loss of configurational entropy and/or increase in the enthalpy of mixing of the PEO chains. This results in an increase in the moduli and $G'$ rising above $G''$ at high frequencies, where the particles do not have time to relax from the applied deformation and hence store the energy elastically. Here the sample is viscoelastic, showing

![Figure 5.7](image-url)

Figure 5.7 Elastic (●) and viscous (○) moduli as a function of frequency for latex B stabilised with F108. Volume fractions (a) 0.370, (b) 0.403 and (c) 0.437.
both fluid like and gel like behaviour. At higher $\phi$, 0.437 (c), the system is predominantly elastic with $G'$ dominating $G''$ at all frequencies.

The change in these moduli at a fixed frequency as a function of $\phi$ is shown in figure 5.8 where the sharpness of the transition from a viscous fluid to an elastic gel can clearly be seen. In the viscous fluid phase region the moduli show little dependence on $\phi$, but when $\phi=0.37$, $G'$ rises sharply and continues rising steadily as $\phi$ increases further and the particles become more tightly packed. However, $G''$ does not begin to rise sharply until $\phi=0.48$. This lag between the elastic and viscous moduli encompasses the viscoelastic phase as the latex gradually becomes more elastic and less viscous in its behaviour. The point where the two moduli are equal has been termed the transition point and corresponds to the relaxation time at the chosen frequency ($\delta = 45^\circ$).

![Figure 5.8 Elastic (●) and viscous (○) moduli as a function of volume fraction for latex B stabilised with F108.](image)

The change in $G'$ for the large latices, A and B, with $\phi$ is shown in figure 5.9. In contrast to the steady shear results, no differences are visible between the different polymers and indeed the hard sphere system, latex C without polymer in 0.01 M NaCl, is also very similar to the data for the polymer coated latices. Thus the polymer coated particles appear to behave as hard spheres too.

The data for the small latex, D, is shown in figure 5.10. Here, as for the large latex, viscous behaviour is also seen at low $\phi$ and as $\phi$ increases to ca. 0.25, $G'$ rises sharply over three decades and then, in contrast to the large latex results, plateaus again. In addition, when $G'$ rises sharply, a change in the turbidity of the sample occurs, which changes from an
opaque white fluid to a straw coloured gel (figure 5.11). This has not been observed before with soft, steric stabilised systems and suggests that a phase change from a disordered suspension to an ordered lattice or glass is occurring. This then brings into question other results in which this rise in $G'$ has been attributed to compression of stabilising layers rather than a phase change. Furthermore, the plateauing of $G'$ at higher $\phi$ is a direct measure of the

Figure 5.9 Elastic modulus verses volume fraction for large latices: A+P103 (□), A+P105 (○), A&B+F108 (△) and C without polymer (◆).

Figure 5.10 Elastic modulus verses volume fraction for latex D stabilised with P103 (−), P105 (○), F108 (△), P103/12 (⊙) and without polymer (+).
compression of the adsorbed polymer layers. Scattering experiments are currently being performed to elucidate the structure of these systems.

Figure 5.11 Turbidity change observed with latex D. Volume fractions (L-R) are: 0.127, 0.283, 0.388. Latex stabilised with P103.

As with the steady shear experiments the effect of the molecular weight of the stabilising polymer is clearly visible with the high molecular weight polymers producing high elastic moduli gels. Increasing the PEO chain length decreases the $\phi$ at which $G'$ rises sharply while decreasing the coverage of P103 to 1/12 increases the $\phi$ of this transition. This can be seen more clearly if the moduli are plotted as a function of separation between the latex particle surfaces (see figure 5.12). The electrical double layer of the bare latex in 1mM NaCl is by far the most extensive, extending some 20 nm from the surface by this measurement. This value is somewhat larger than that given by $1/\kappa$ in equation 2.8, which is commonly taken as the range of such electrical layers. This shows us that oscillation measurements are very sensitive to the furthest regions of the electrical layers. At the higher electrolyte concentration of 10 mMolar any such electrical layers are not expected to be significant due to a reduction in $1/\kappa$ to 3nm and also to the screening of the charge on the particle surface by the adsorbed copolymer layer. Indeed, adsorption of the polymers in 1mM electrolyte reduced the potential at the surface of shear from -50 mv to -5 mv, thereby effectively eliminating any electrical double layer. Thus steric stabilisation is the sole barrier left against
flocculation. The range of the adsorbed copolymer layers extend some 9-10 nm from the surface of the particles with thicker layers from the higher molecular weight polymers, P105 and F108. Reducing the coverage of P103 from full to 1/12 coverage reduces the range of the interaction also from 9 to 6 nm. Taking the adsorbed polymer layer thickness to be the point where \( G' \) plateaus after rising sharply gives the values in table 5.2.

5.4.2 Emulsions.

As for the latices, the elastic modulus for P103, P105 and F108 stabilised emulsions, A, B and C, is plotted in figure 5.13 as a function of the phase volume of the oil. For all three polymers the modulus is low until a phase volume of \( ca. \) 0.65 is reached where a rapid increase in the modulus is noted. Again there is a molecular weight effect with the modulus of the lower molecular weight material increasing at a higher volume fraction. The rapid increase of modulus occurs over a relatively narrow range of phase volume, \( ca. \) 0.05, and a high modulus plateau seems to be reached. These data show a much sharper increase in modulus than the large latex particles. This is to be expected if we recall from chapter 4 that there is some 2-3 times more copolymer at the interface than with the latices, forming a harder, less penetrable layer.
Figure 5.13 Elastic modulus verses volume fraction for hexadecane emulsions: P103 (□), P105 (○) and F108 (△).

Qualitatively these data seem very similar to those for the small latex except the transition from a low to a high modulus value occurs at considerably higher volume fraction. Thus it appears as though there is a phase transition (crystallisation) occurring at around 0.65 phase volume. At the high modulus plateau it is possible that either the polymer layers, or the emulsion droplets, or both, are deforming. Experiments to determine this by examining the rheological properties of emulsions where the oil phase had crystallised were unsuccessful due to flocculation of the droplets on solidification. However, microscopic examination of the concentrated emulsions at high φ appeared to show deformation of the droplets. If we also consider the difference in G' between the small latex, D, and the emulsions we find that the latices plateau at 2-3000 Pa while the emulsions plateau at ca 1000 Pa. This may not appear to be a great difference but when we consider that the emulsions have some 2-3 times the concentration of copolymer at the interface we would then expect a greater resistance to compression of the EO chains with a corresponding plateau value in excess of 3000 Pa for rigid droplets. From this it appears fair to conclude that the plateauing at high φ is due to deformation of the droplets rather than compression of the EO stabilising chains.
5.5 Polymer Layer Thickness.

5.5.1 PCS Measurements.

Particle size measurements were performed to provide an independent value of the hydrodynamic thickness of the adsorbed polymer layers. The size of latex D, with and without the adsorbed polymers was measured in the plateau region of the adsorption isotherms. The electrolyte (1mM KCl) was the maximum level which could be used without flocculation of the bare, electrostatically stabilised latex. The thickness of the polymer layers, \( \delta \), was calculated from the difference in size between the latex with and without the adsorbed polymer and the results are tabulated in table 5.2.

5.5.2 Rheological Measurements.

The values of the adsorbed layer thickness, \( \delta \), obtained from the steady shear measurements are also listed in table 5.2. All the results show a systematic increase in delta with EO chain length and are plotted in figure 5.14. The rheology results scale with \( n \text{EO}^{1/2} \) (recall \( R_g \propto n^{1/2} \) from equation 4.1) showing the EO chains to be arranged as elongated coils which extend from the surface rather than linear chains (which would scale with \( n \text{EO} \)). For a true coil we would expect a thickness of up to \( 2R_g \). It can be seen that all the experimental values are greater than this indicating the coils to be extended from the surface.

<table>
<thead>
<tr>
<th>System (latex + polymer)</th>
<th>Steady shear measurements</th>
<th>Oscillation</th>
<th>PCS</th>
<th>( 2R_g )</th>
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<td>Zero shear vis.</td>
<td>Plastic vis.</td>
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<td>A + P103</td>
<td>3.8 ± 2</td>
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</tr>
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<td>B + F108</td>
<td>13.4 ± 2</td>
<td></td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>D + P103/12</td>
<td>4.9 ± 1</td>
<td>5.9 ± 1</td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>D + P103</td>
<td>5.5 ± 1</td>
<td>8.9 ± 0.5</td>
<td>10.5 ± 2</td>
<td>1.8</td>
</tr>
<tr>
<td>D + P105</td>
<td>6.5 ± 1</td>
<td>9.3 ± 0.5</td>
<td>12.5 ± 2</td>
<td>2.2</td>
</tr>
<tr>
<td>D + F108</td>
<td>9.4 ± 0.5</td>
<td>10.3 ± 0.5</td>
<td>13.5 ± 2</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 5.2 Adsorbed layer thickness of polymers (nm) from rheological measurements, PCS and calculated radii of gyration.

Decreasing the coverage of P103 from full to 1/12 on latex D results in a reduction of the adsorbed layer thickness which is greatest with the oscillation results. At 1/12 coverage, adsorption of isolated, individual polymer molecules on the surface should lead to a greater
reduction of the adsorbed layer thickness than seen here. This suggests that the polymer molecules adsorb as aggregates or micelles where lateral compression of the PEO coils is maintained conserving their extended configuration. This also explains the greater reduction in thickness observed with the oscillation results. Here, the latex is sufficiently concentrated such that the particles are locked by their neighbours and where the steric layer encounters gaps in the neighbouring particle's layers, closer approach will occur. However, the zero shear viscosity results are obtained at lower volume fractions where the particles are free to rotate on account of their thermal energy. Here, the particles will see a time averaged steric layer which has a thickness equal to the thickness of the polymer aggregates and consequently, shows less of a reduction in the adsorbed layer thickness. This is also confirmed by the identical relative viscosities found for latex B (499nm) in section 5.3 with F108 adsorbed at full and two thirds coverage.

Interestingly, the high shear hydrodynamic thickness results for the large latex, A, agree closely with the low shear values for the small latex, D. This is surprising since the first is a measure of the hydrodynamic thickness while the latter is a measure of the range of the interparticle and Brownian forces. Furthermore, the low shear thickness values differ from the oscillation thickness for the same system. This is unexpected since they are both a measure
of the range of the interparticle/Brownian forces and should therefore be comparable. Even
greater values for $\delta$ are obtained from the PCS measurements as would be expected since the
hydrodynamic thickness is believed to be sensitive to the distal regions of the adsorbed
copolymer.

Miano et al.\textsuperscript{36} have performed similar experiments with P104 (32:56:32), P105 and
F108 on carbon black and obtained adsorbed layer thickness values from both the steady shear
and oscillation results which agree very favourably with our results, even down to the
differences observed between the low shear and oscillation results.

From neutron scattering experiments Cosgrove et al.\textsuperscript{158} have reported volume fraction
profiles for two similar PEO-PPO-PEO block copolymers containing 32:56:32 and 140:56:140
monomer units adsorbed onto D-polystyrene latex. Cut off values for the adsorbed layer
thickness were 9 and 18 nm respectively. Although thicker, these show scaling similar to the
steady shear data with a slightly greater dependence on PEO chain length. Hydrodynamic
layer thicknesses for a wide range of PEO-PPO-PEO copolymers, including P104, P105 and
F108, adsorbed onto PS latex (56 nm) have been determined from PCS and ultracentrifugation
measurements by Killmann et al.\textsuperscript{159} The values obtained, ca. 3.0, 3.8 and 9.3 respectively are
generally lower and also show a slightly greater dependence on PEO chain length, being
proportional to $M_w,\text{PEO}^{0.55}$.

These differences may be due to the nature of the surface of the latex particles. Latex
B has a greater surface potential than the others which corresponds to both an increase in the
amount of F108 adsorbed and the adsorbed layer thickness. The increase in charged surface
sites responsible for the greater potential here would encourage adsorption of the PEO chains
through the ether oxygen, as observed by Killmann et al. with silica suspensions where the
polar silica surface caused considerable adsorption of the PEO chains.

At a planar water-hexane interface, neutron scattering experiments with 100:65:100
gave considerably extended PEO chains, approximately 25% of their maximum extended
length. Here the adsorbed amount was ca. 3 mg m$^{-2}$ \textsuperscript{160-162} which is comparable to the
emulsions studied here. At this concentration considerable extension of the PEO chains is
observed supporting the picture from the adsorption data of the polymers forming a brush at
the emulsion interfaces.

The adsorption measurements presented in chapter 4 indicated that the PEO chains
were extended from the surface of the particles. From the rheological results obtained, the
degree of extension has now been quantified. This information can now be combined to give
a picture of the polymer molecules on the surface of the latex particles. It is also possible to
postulate the conformation of these polymers at the emulsion droplet interface. However, information on the thickness of the polymer layer is not available. This is illustrated in figure 5.15.

![Diagram of polymer conformation](image)

**Figure 5.15** Scaled illustration of the conformation of Synperonic PE copolymers adsorbed onto latex particles and emulsion droplets.

### 5.6 Summary of Adsorption and Rheological Results of Dispersed Systems.

All the polymers were found to be Langmuirian and adsorb strongly onto the latices. The adsorbed amount was sufficiently low for the PEO chains to exist as coils which were extended from the surface. However, the copolymers were some three times more densely packed at the oil-water emulsion interface with the PPO extending into the oil core of the
droplet. Here, the polymers were much more like a brush with only a slight dependence on area with length of the PEO chain.

Rheologically, the large latex (429nm) behaved as a hard sphere system in oscillatory shear, showing no differences between the three polymers. However, differences were seen under steady shear at the high shear rate limit. Much larger differences were seen with the small 67nm latex. In each case, the deviation from a hard sphere increased with molecular weight of the stabilising polymer. From these differences, the thickness of each of the adsorbed layers was obtained. These increased with molecular weight and were in the region of 2-3 times 2Rg, but considerably less than the extended chain length, consistent with the picture of extended coils.

Under oscillatory shear, the small latex gave almost an S shaped profile for G' while the large latex increased linearly. This appears to be evidence for compression of the adsorbed polymer layer at high volume fractions and is a feature of the softness of the particles. A corresponding change in the appearance of the latex occurred, from opaque to translucent, as the volume fraction increased over the point where G' rose sharply. This suggests that some phase change may be occurring with the particles. Emulsions gave similar shaped curves, however, in this case the second plateau appeared to be due to deformation of the droplets rather than compression of the PEO chains, which at the high levels of adsorption found here, would be very hard.

6.1 Introduction.

In this and the following three chapters the effect of nonadsorbing polymers on the rheology of colloidal suspensions is examined. The addition of nonadsorbing polymers to suspensions can result in the flocculation of suspensions through a depletion mechanism as introduced in chapter 2. Such polymers are often added to aqueous suspensions as a means of suspending the dispersed phase and preventing the formation of hard, dilatant sediments which are difficult to resuspend. In this chapter, the effect of the depleting polymer concentration and latex volume fraction is examined with a 424nm latex (C), stabilised with an adsorbed PEO-PPO-PEO layer of Synperonic PE/P105 and flocculated with hydroxyethylcellulose of 300,000 molecular weight (HEC G). This is compared with an emulsion where the stabilising layer is more densely packed. Then in chapters 7 and 8 the effect of the molecular weight of both the free polymer and steric stabilising layer are studied. These are all factors which affect the flow properties of suspensions and can be adjusted to control the properties of suspensions. These are complimented by chapter 9 where the rheology and sedimentation properties of a "real" agricultural suspension are examined. This chapter begins by introducing what rheological measurements of flocculated systems actually mean.

6.2 A Rheological Picture of Flocculated Suspensions.

The rheology of dispersed suspensions was introduced in chapter 1 and is relatively well understood. However, flocculated systems have received much less attention, probably due to their complexity even though they are encountered widely in industry and everyday life from paints to foods.

So what information can we obtain from rheological measurements on such systems? Individually, the numerous types of measurements yield only limited information, yet when combined provide a far more vivid picture of the flocculated structure.

6.2.1 Measurements at Large Deformations.

The first measurements described in chapter 1 were those made at large deformations, namely steady shear where the shear stress is measured at several shear rates to give a flow
curve. For dispersed systems these are usually Newtonian or pseudoplastic while, for flocculated systems, plastic flow is obtained. This means that without shear the particles are flocculated and form a three dimensional network. When sheared this network must break down in order for the sample to flow. Thus the flocculated particles are effectively being pulled apart and the stress required for flow is a measure of the strength of the flocculation. This is illustrated in figure 6.1. Fitting the data to a suitable model such as the Bingham (equation 1.4) allows a yield stress to be extracted. From this, the number of particles and the number of contacts per particle, the energy of separation, $E_{sep}$ can be calculated (chapter 1, section 1.4.3). This is a measure of the depth of the minimum of the interparticle pair potential, $G_{min}$ which can be compared to calculated values from the theories discussed in chapter 2, section 2.5.2.

![Figure 6.1 Illustration of the application of a large steady shear to a flocculated suspension.](image)

### 6.2.2 Measurements at Small Deformations.

In contrast to the steady shear measurements, where the structure is broken down, these measurements are made at very small deformations in the linear viscoelastic region where, in principle, there is no breakdown of the structure. Such measurements are invaluable for studying flocculated suspensions since they provide information on the elasticity of samples which, although viscoelastic, are usually predominantly elastic.

#### 6.2.2.1 Oscillatory shear.

In order for a perturbation to be transmitted elastically through a sample the network of flocculated particles must form a continuous chain right across the sample. It then follows that as the number of chains increases, more of the deforming stress is transmitted through the sample. This is illustrated in figure 6.2a where the small number of chains on the left
would only transmit a small proportion of the deforming stress through the sample, resulting in a low elastic modulus, $G'$, while the greater number of chains on the right would transmit a larger proportion of the deforming stress leading to a higher $G'$. So the elastic modulus is a measure of the "connectivity" of particles within a flocculated suspension.

![Diagram](image)

Figure 6.2 Illustration of how the elastic modulus, $G'$, and critical strain, $\gamma_c$, depend on the structure of the flocculated network.

In the linear viscoelastic region, which is usually at small strains, the elastic modulus and loss modulus are constant and do not vary with strain. However, if the amplitude of the oscillations is gradually increased, a point is reached where the flocculated structure begins to break down and the elastic modulus falls sharply. This point is termed the critical strain, $\gamma_c$. If we consider our chain model again, the critical strain corresponds to the point where the chain breaks. A chain capable of a small extension will have a smaller critical strain than a chain capable of a large extension. This is illustrated in figure 6.2b where the capacity of a chain to extend increases from left to right. So the critical strain is a measure of the "tortuosity" of the floc structure within a flocculated suspension.

Performing these measurements over a range of frequencies can also reveal information about the lifetime of these flocculated structures. Unfortunately, oscillation measurements can only probe short timescales, \(ca. 10^3\) Hz, relative to the lifetime of floc structures and other measurement techniques such as stress relaxation are necessary to probe longer timescale processes.

6.2.2.2 Stress Relaxation.

This is a very powerful technique for probing long timescale processes relatively rapidly. For example this technique can probe to \(10^3\) s in the same time that an oscillation experiment can probe to \(10^2\) s. When a permanent strain within the linear viscoelastic region is applied to a flocculated suspension, the measured stress can only relax through diffusion
of the individual floc units or rearrangement of the shape of the floc units. Of the two, the latter is less likely on account that it requires the breaking of a greater number of particle contacts. So the stress relaxation provides a measure of the diffusion time of the individual floc units. This is illustrated in figure 6.3.

![Diagram](image)

Figure 6.3 Diffusion of flocs causing relaxation of the stress in a stress relaxation experiment.

Intuitively, this appears to be similar to the yield stress where bonds are broken and consequently longer relaxation times would be found for more strongly flocculated suspensions. However, the number of bonds which need to break in order for the floc structure to relax is governed by the "connectivity" of the floc units and consequently longer relaxation times would also be found for suspensions with relatively high elastic moduli. Hence this combines elements from both the yield stress and oscillation experiments. A convenient way of interpreting stress relaxation results is to integrate the relaxation modulus, \( G(t) \), with respect to time as described in section 1.3.2 to yield a measure of the zero shear viscosity, \( \eta_0 \).

### 6.3 Effect of HEC Level

#### 6.3.1 Appearance of Suspensions.

The photograph in figure 6.4, shows latex C with differing levels of HEC after standing for two months. Without any added HEC, the suspension is uniform with a small iridescent region at the base. This indicates the formation of an ordered, crystalline lattice of particles which is a consequence of the particles slowly sedimenting to form a dense layer at the base of the tube. Addition of HEC at low levels results in separation of the latex into a particle rich lower phase, which becomes highly iridescent, and a less turbid upper layer. Higher levels of HEC form a highly volume filling, opaque sediment and a clear upper layer.

Evidently, the HEC has a marked effect on the state of the dispersion of the particles. Small additions of HEC result in weak flocculation of some of the particles, which then slowly sediment and rearrange into a more stable, ordered, iridescent lattice. The unflocculated particles remain suspended due to their thermal energy. Further additions of HEC cause strong
flocculation of all the particles into a random, volume filling network. In this the particles are held sufficiently strongly to prevent their rearrangement into an ordered lattice.

Figure 6.4 Latex C (424 nm) containing HEC after two months standing. HEC concentrations as shown, $\phi$, 0.3.

Dilution of the HEC flocculated latices with water, or with latices of the same volume fraction but without HEC, resulted in redispersion of the latex particles when the resultant HEC concentration was below that required to induce flocculation. From these observations it is evident that the flocculation is caused by a depletion mechanism and not by bridging of the HEC chains between particles. Bridging flocculation was reported in chapter 5 and was irreversible on dilution, thus discounting this possibility here. However, depletion flocculation has been observed previously with similar systems\textsuperscript{137,163} in which it has also been found that the adsorption of poly(ethyleneoxide) based non-ionic surfactants displaces and prevents any adsorption of HEC.
Figure 6.5 Flow curves for the suspensions shown in figure 6.4. HEC concentrations (%w/v) as shown.
Figure 6.6 Oscillation frequency sweeps for 424 nm latex flocculated by HEC.
6.3.2.1 Measurements at Large Deformations.

The shear stress - shear rate flow curves for these suspensions are shown in figure 6.5 as a log-log (a) and linear-linear (b) plot. Without HEC the suspension is virtually Newtonian (i.e. stress ∝ shear rate). At 0.051% HEC the stress rises slightly but the flow remains Newtonian. This thickening can be attributed to an increase in the viscosity of the medium rather than flocculation of the particles on account that the thickening occurs equally at all shear rates. At 0.086% HEC there is slight thickening at high shear rates but considerable thickening at low shear rates. Here, the flow is pseudoplastic with Newtonian plateaus at low and high shear rates and a region of shear thinning at intermediate shear rates. This is due to flocculation of the particles. The Newtonian flow at low shear rates tells us that the flocs are rearranging or diffusing more rapidly than the applied shear can perturb them and suggests that the flocs are small and discrete to allow for their rapid diffusion. This can also be seen in figure 6.4 where a proportion of the particles have flocculated into small clusters which have then separated relatively rapidly under gravitational stress to form an iridescent sediment. The shear thinning region is a consequence of the shearing breaking the flocs into discreet particles. Newtonian flow is reattained at high shear rates when all of the flocculated structure has been broken down. Higher levels of HEC produce a greater degree of shear thinning which can be seen in (b) as an increase in the extrapolated Bingham yield stress. The Newtonian plateau at low shear rates also becomes less apparent and the flow becomes more plastic telling us that the flocculated particles are forming a continuous network rather than discrete clusters. This is again apparent from the photograph of the suspensions where, as the HEC concentration increases, the volume of the sediment increases due to the network becoming stronger and more extensive and hence more able to support itself against the gravitational stress.

6.3.2.2 Measurements at Small Deformations.

More information on the flocculation can be obtained from measurements at sufficiently small deformations where the flocculated network is not broken down. The corresponding oscillatory frequency sweeps to the shear stress - shear rate flow curves are shown in figure 6.6. Without any HEC the latex behaves as a viscous fluid with the loss modulus, G″, greater than the elastic modulus, G′. Increasing the HEC content to 0.086% does not change the rheological properties which confirms the previous hypothesis from the flow behaviour that here the flocculation only forms discrete clusters and not an extensive network which would have a substantial elastic modulus. However, increasing the HEC level to 0.14%
clearly results in the formation of such a network since the elastic modulus is now greater than the loss modulus and of a significant value. Evidently, the flocculated particles become sufficiently flocculated to form an extensive three dimensional network at a concentration between these two levels of HEC. Increasing the HEC content results in a smaller rise in the moduli indicating that the "connectivity" of the floc network is increasing slowly.

The persistence of the network can be determined by examining the frequency dependence of the moduli. Where the network is formed, at 0.14, 0.3 and 0.8% HEC, the elastic modulus slowly decreases as the frequency of the applied oscillation is reduced. However, even down to frequencies as low as 0.005 Hz the elastic modulus still has an appreciable value. This tells us that the floc network has a broad range of half lives for its persistence. Some connections are very short lived while many persist for much longer times. More information can be obtained from stress relaxation measurements which can probe longer timescales in shorter periods. Data for the three highest HEC concentrations, 0.14, 0.3 and 0.8%, are shown in figure 6.7. At short times, the relaxation modulus, G(t), corresponds closely to the elastic modulus at high frequency, as expected for the Maxwell model. The time taken for this to decay or relax to zero increases as the concentration of the HEC increases, which tells us that the stronger, more highly connected networks are also the more persistent, as expected.

Figure 6.7 Decay of the stress relaxation modulus, G(t), for the flocculated suspensions.
Finally, information on the tortuosity of the network can be obtained from the strain sweep measurements where the elastic modulus is measured at a fixed frequency (0.5 Hz) as a function of strain. Data for the flocculated suspensions is shown in figure 6.8. At low strains the elastic modulus is constant indicating the linear viscoelastic region. Once this region is exceeded the elastic modulus falls as the structure is broken down. For the three concentrations of HEC measured, the critical strain decreases slightly as the HEC concentration rises. From the model introduced in section 6.2, this corresponds to a slight decrease in the tortuosity of the network structure. This is in line with the increase in the connectivity indicated by the oscillation measurements since, in order for more chains to be formed from the same number of particles, then fewer particles are available per chain thus effectively straightening and reducing the tortuosity of these chains.

![Figure 6.8 Strain sweep data for the flocculated suspensions.](image)

6.4 Effect of Latex Volume Fraction.

6.4.1 Measurements at Small Deformations.

In figure 6.9 the elastic modulus at a frequency of 0.5 Hz is shown as a function of increasing HEC concentration at four latex volume fractions. The data from figure 6.6 is the second curve from the top. As the HEC concentration is increased it can clearly be seen how the elastic modulus rises sharply when an extensive network is formed, at ca. 0.1% HEC. Increasing the latex volume fraction to 0.4 has two effects. Firstly, the modulus values are higher which is to be expected with a greater number of particles forming a more dense
network and secondly, the concentration of HEC required to form a network is lower, ca. 0.06% HEC. The same trends can be seen for the lower latex volume fractions although the point at which a network is formed is less obvious. Also shown is the pure, latex free HEC. Here the modulus values are very low and any contribution to the latex modulus values are insignificant and can be neglected. These results indicate that as more particles are added, more "chains" are formed throughout the network.

Further information on the structure can be obtained from the critical strain values obtained from the strain sweep measurements which are shown in figure 6.10. The data from

Figure 6.9 Elastic modulus values (0.5 Hz) as a function of HEC concentration. Latex volume fractions as given.

Figure 6.10 Strain sweep critical strain values as a function of HEC concentration.
Figure 6.8 is shown in the bottom line where there is a slight decrease in the critical strain with increasing HEC content which indicates that the network is becoming slightly less tortuous or twisted. Similar values are obtained for the latex volume fractions at 0.4 and 0.159. This is most interesting and means that these samples all have very similar degrees of tortuosity. Consequently, the network in each of these samples has formed in an identical fashion. However, the 0.1 latex volume fraction has a much higher critical strain value. This indicates that the chains in the network at this volume fraction are much more tortuous or twisted and suggests that the network has been formed in a different way, which is presumably a consequence of the lower volume fraction of particles giving rise to larger collision times between particles and thus enhancing the likelihood of particle rearrangement.

Examination of the scaling properties of the elasticity with latex volume fraction, i.e. $G' \propto \phi^f$, has been used to elucidate structural information with aggregated systems through the exponent, $f$, as discussed in section 1.4.4. Theoretically, for reaction limited aggregation, $G' \propto \phi^{4.5}$ while for diffusion limited aggregation $G' \propto \phi^{3.6}$.

The systems studied here are shown in figure 6.11 and table 6.1. The lowest HEC concentration, 0.14%, corresponds to the exponent for reaction limited aggregation. This is what would be expected where the strength of the flocculation is sufficiently weak such that
the aggregates rearrange their structure to give more compact structures in keeping with reaction limited aggregation. However, the higher levels of HEC give much lower values for the exponent, ca. 3. This is more in agreement with the diffusion limited case and suggests that at these higher HEC levels the strength of flocculation is sufficiently strong to prevent rearrangement of the flocs once they have formed. This is born out in figure 6.4 where the highest levels of HEC, 0.8 and 0.3%, have produced a strong, volume filling flocculated network which has resisted rearrangement under the gravitational stresses while the lower level of HEC, 0.14%, shows more sedimentation and also faint iridescence which indicates that the flocculated particles have rearranged their random structure to give an ordered crystalline lattice.

<table>
<thead>
<tr>
<th>HEC G concentration (%w/v)</th>
<th>exponent f  (±0.2)</th>
<th>pre-shearing</th>
<th>sheared</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>4.3</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>3.3</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1 Scaling exponents for \( G' \propto \phi^f \).

Kim and Luckham have also found a low value for the exponent, 2.4. In this case the flocculation was induced inside the rheometer cell by heating the suspension above the critical flocculation temperature, where the stabilising polyvinyl alcohol (PVA) layer passes through its theta temperature and then, instead of repelling, attracts other adsorbed PVA layers causing the particles to flocculate. Such conditions are ideal for diffusion limited aggregation where there is no repulsive barrier to flocculation and the particles stick on their first contact.

Sonntag and Russel found a low value, 2.5, too for aggregated systems which, as for Kim and Luckham’s experiments, were measured without perturbing the flocculated network. However, upon ageing for over a week, \( f \) increased to 4.4 indicating that the flocs had rearranged into more compact units, consistent with reaction limited aggregation. From these results it seems reasonable that the pre-treatment of the samples in the rheometer cell, namely an oscillatory strain sweep beyond the samples elastic limit, is sufficient to fully break up the flocculated structure such that it is able to reform in situ. It also appears that the strength of the flocculation can have considerable effects on the elastic properties of aggregated suspensions.
If we examine the critical strain values from the strain sweep experiments we can obtain further information on the flocculation process. In figure 6.12 the scaling of the critical strain with volume fraction is shown and the data presented in table 6.2.

![Figure 6.12 Scaling of critical strain with volume fraction. HEC concentrations (%w/v) as shown.](image)

<table>
<thead>
<tr>
<th>HEC G concentration (%w/v)</th>
<th>exponent f (±0.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>-2.0</td>
</tr>
<tr>
<td>0.3</td>
<td>-3.1</td>
</tr>
<tr>
<td>0.8</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

**Table 6.2 Scaling exponents for γ_c ∝ ϕ_f.**

At first the results appear to be uninformative but, on closer inspection, clear trends appear. To help with this, the exponent for each section of the curves is shown in table 8.2. At low volume fractions the exponent is high and negative, *ca.* -2 to -3, while at high volume fractions the exponent is positive, *ca.* 0.3 to 3. This trend is as predicted by Shih *et al.* in their scaling analysis of aggregated networks (section 1.4.4). Low volume fractions favour the formation of flocs in the strong link regime with an exponent of -2 to -2.3 while high volume fractions favour the formation of flocs in the weak link regime where the exponent is 0.8.
Clearly there is good agreement between their analysis and the experimental results presented here and appear to be the first results to show this trend. Similar trends with the critical strain have also been obtained in the laboratory from a wide range of pesticide suspensions and emulsions, further supporting this theory.

However, their predictions for the scaling for the elasticity with volume fraction do not hold with their scaling for the elastic limit. The results only support the existence of a strong link flocculated network.

The stress relaxation data are shown in figure 6.13 as the integral of the relaxation modulus, G(t), with respect to time. This is equivalent to the zero shear viscosity, \( \eta_0 \). Although these data show some scatter, the integrated relaxation modulus increases with increasing latex volume fraction and, at higher HEC levels, increasing polymer concentration. This is what we would expect as the extent of the flocculation increases and agrees with the other measurements.

![Figure 6.13](image)

**Figure 6.13** Integral of stress relaxation modulus (= \( \eta_0 \)) as a function of HEC concentration. Latex volume fractions as given.

### 6.4.2 Measurements at Large Deformations and Flocculation Strength.

The yield stress values for the four latex volume fractions are shown in figure 6.14. Similar trends to the oscillation results are seen here, namely an increase in the yield stress with both latex volume fraction and HEC concentration. With the data in this form, it is not possible to tell whether the increase in the yield stress is due to the strength of the flocculation increasing or the greater number of particles. In order to answer this it is necessary to
calculate the energy required to separate two flocculated particles, $E_{sep}$, which was introduced in chapter 1, section 1.4.3 and gives:

$$E_{sep} = \sigma_y \frac{8\pi a^3}{3\phi n}$$  \hspace{1cm} (6.1)

A value of four has been chosen here for $n$ which will be a lower limit for the number of contacts per particle.

Figure 6.14 Yield stress values as a function of HEC concentration. Latex volume fractions as given.

The resulting $E_{sep}$ values calculated from the yield stress results in figure 6.14 are shown in figure 6.15. Comparison between the two sets of results reveals that there is much less dependence on latex volume fraction when the $E_{sep}$ values are considered. This tells us that the magnitude of the depletion forces are similar for all volume fractions as would be expected from the depletion theories discussed in chapter 2, section 2.5.2. However, there is a slight increase in the strength of the depletion force with increasing volume fraction. This is more than would be expected due to the increased bulk HEC concentration which results from the volume excluded by the adsorbed polymer layer (at a $\phi$ of 0.4 this increases the HEC concentration from 0.8 to 0.85% w/v). This suggests that $n$ is increasing at high latex volume fractions.

It is also interesting to note that $kT$ values of ca. 5 or greater are required to form a fully flocculated network. Furthermore, an iridescent, ordered crystalline lattice is only
Figure 6.15 Calculated $E_{\text{sep}}$ values for the yield stress data in figure 6.14.

obtained for $kT$ values of the order of 0.2 to 1. This is as would be expected, since for an ordered crystalline lattice to form, the particles must be able to rearrange within their floc, which is only possible if the depletion forces are comparable to the thermal energy of the particles, $kT$.

In table 6.3 the $E_{\text{sep}}$ values are summarised along with the depletion potential energy, $G_{\text{dep}}$, calculated according to the theories of Asakura and Oosawa (AO model) and Fleer, Scheutjens and Vincent (FSV model) introduced in chapter 2, section 2.5.2.

<table>
<thead>
<tr>
<th>HEC content</th>
<th>$E_{\text{sep}}$ (kT)</th>
<th>$G_{\text{dep}}$ (kT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>%w/v</td>
<td></td>
<td>AO</td>
</tr>
<tr>
<td>0.0513</td>
<td>0.00038</td>
<td>$\phi_l = 0.1$</td>
</tr>
<tr>
<td>0.0856</td>
<td>0.00063</td>
<td>$\phi_l = 0.159$</td>
</tr>
<tr>
<td>0.143</td>
<td>0.00105</td>
<td>$\phi_l = 0.3$</td>
</tr>
<tr>
<td>0.300</td>
<td>0.00220</td>
<td>$\phi_l = 0.4$</td>
</tr>
<tr>
<td>0.800</td>
<td>0.00586</td>
<td>78.6</td>
</tr>
<tr>
<td>1.60</td>
<td>0.0117</td>
<td>894.9</td>
</tr>
</tbody>
</table>

Table 6.3 Summary of $E_{\text{sep}}$, $G_{\text{dep}}$ and $\Delta$ values for 424nm latex in HEC G.

For calculation of $G_{\text{dep}}$, the data obtained by Sperry$^{15}$ for HEC was used; the viscosity average molecular weight (223,500) and the Einstein equivalent hard sphere diameter for the coil size (24.8nm) while the solvent interaction parameter, $\chi$, was taken as 0.47$^{42}$ and the
molecular weight for each cellulose ring taken as 272. The effect of the adsorbed copolymer layer was accounted for by using an effective radius of the latex which included 6nm for the adsorbed layer thickness, as determined from viscosity measurements of the latex with and without an adsorbed copolymer layer in chapter 5. For the FSV model, Vincent's theory \(^{117}\) (equation 2.28) was used to account for the reduction in the depletion layer thickness with increasing HEC concentration. An appropriate value of \(r\) was calculated using a value of 5.7nm for the length of a structural unit and the Einstein hard sphere diameter for the coil size.

Both theories predict the increase seen in \(E_{sep}\) with increasing HEC concentration. The AO model is in good agreement at low HEC levels but underestimates the strength of the flocculation at high HEC concentrations. The FSV model overestimates the strength of the flocculation at the lower HEC concentrations. At higher HEC concentrations, the value of \(G_{dep}\) decreases. This is a consequence of the decreasing \(\Delta\) values predicted by Vincent's model which are shown in table 6.3. This is not seen in the experimental \(E_{sep}\) values suggesting that, in this case, Vincent's model overestimates the concentration at which \(\Delta\) begins to decrease. However, when the polydispersity and non-ideality of HEC are considered, the agreement between the theories and experiment is perhaps fair.

Liang et al. \(^{35-47}\) and Tadros \(^{42}\) have also performed such calculations with these theories and similar experimental systems and found comparable discrepancies.

### 6.5 Phase Behaviour:

From the oscillation data (figure 6.9) and yield stress data (figure 6.14) it is possible to obtain the gel point where a continuous flocculated network is formed for each latex volume fraction. This has been plotted in figure 6.16 to give a rheological phase diagram. A strong dependence of the phase boundary on the latex volume fraction is clearly visible and tells us that considerably more polymer is required to produce a flocculated network at low volume fractions. This has important implications for commercial, low solids suspensions such as new, high potency agricultural formulations where there may be insufficient solids to form a continuous network at practical depleting polymer levels, which prevents sedimentation of the suspended particles into a solid, clay like sediment. This can be seen clearly in figure 6.17 which shows flocculated suspensions after two months standing. Firstly, increasing the latex volume fraction drastically reduces the amount of separation as does increasing the concentration of HEC. However, even at the highest HEC concentration of 0.8% there is still considerable separation at the lowest latex volume fraction.
Figure 6.16 Rheological phase diagram for 424 nm latex (C) in HEC G. Yield stress (□) and elastic modulus (○).

Figure 6.17 Flocculated latex suspensions after two months standing. Volume fraction increases left to right for three different HEC concentrations.
From these tubes it is also possible to construct a phase diagram according to the phases described in figure 6.4 at the beginning of this chapter. These are shown in figure 6.18 where the rheological phase boundaries in figure 6.16 have been superimposed. The agreement between the observed phases and rheological measurements is good although the rheological measurements underestimate the phase boundary at low volume fractions and overestimate the boundary at high volume fractions. Therefore, at low volume fractions there are insufficient particles to form a continuous network while at high volume fractions a continuous network forms before complete flocculation has been caused by the HEC.

Figure 6.18 Visual phase diagram for 424nm latex (C) in HEC G. Dashed lines are rheological phase boundaries from figure 6.16.

6.6 Microscopic Observations.

In figure 6.19, photomicrographs, as a function of latex volume fraction and HEC G concentration are shown as a matrix. The third row corresponds to the samples shown in figure 6.4 and illustrates how the microscopic appearance compares to the bulk appearance.
As noted earlier for the bulk samples, the micrographs reveal that as the HEC concentration increases (from left to right) the structure changes from a dispersed structure with a few aggregates (crystallites), to a strongly flocculated network. Furthermore, the concentration of HEC at which a flocculated network forms increases as the latex volume fraction decreases, as was also inferred from the rheological data. Good agreement is found with the results summarised in section 6.5. However, the transition from reaction limited aggregation at 0.14% HEC to diffusion limited aggregation at 0.3% HEC as detected from the oscillation measurements (section 6.4.1) is not apparent. No change in the floc structure is visible.

6.7 Comparison of Latices and Emulsions.

In chapter 4, results were presented which showed that emulsions contained some three times the amount of Synperonic copolymer at the interface as latices. This resulted in a strong stretching, brush like structure for the PEO stabilising layer in the emulsion droplets. This is expected to form a much harder layer than found for the latex particles. Consequently, emulsions may be expected to show different flocculation behaviour to latices bearing the same stabilising copolymer.

Plotted in figure 6.20 is the effect of adding poly(ethyleneoxide) (M 35,000) on the yield stress and elastic modulus of both a 424 nm polystyrene latex and a 553 nm hexadecane emulsion stabilised by the Synperonic PE/P105. For the polystyrene latex the yield value and modulus, is approximately independent of the amount of PEO added, whilst for the emulsion, increases of 2-3 orders of magnitude in these rheological parameters are noted. Therefore, for the polystyrene latex system, no aggregation is occurring, whilst flocculation is noted for the emulsion following addition of PEO.

Before commenting further on these data it is interesting to compare the behaviour of the polystyrene latex bearing the adsorbed Synperonic, to the work of Liang et al.\textsuperscript{44-47} in which polystyrene latex bearing grafted PEO (M 2,000) was studied. In their work, Liang et al. observed flocculation of the particles above a PEO concentration of 0.5%. Here we see no change in the yield values or elastic modulus as the PEO concentration increases. Thus, from these rheological measurements, when there is an adsorbed polymer layer, little or no depletion flocculation is noted, whilst when there is a grafted layer, flocculation is clearly evident from the observed rheological changes.

Figure 6.19 (overleaf) Brightfield photomicrographs of flocculated 424nm latex suspensions as a function of HEC G concentration (shown - %w/v) and latex volume fraction (shown).
\( \phi_c = 0.1 \)

100\( \mu m \)

0.14%

0.30%
Microscopic observations of the polystyrene latex bearing adsorbed P105 at a polymer concentration of 2.5% do show very small weak flocs present. Thus it would appear as though depletion flocculation is much weaker when we have an adsorbed polymer layer than when we have a grafted layer. In order to explain these data it is necessary to recall the work of Cawdrey et al.\textsuperscript{166} who showed that the extent of depletion flocculation initially decreased with the amount of polymer grafted to particle surfaces, passed through a region of maximum stability before flocculation became more pronounced again as yet more polymer is grafted to the particle surface. The rationale given was that with increasing coverage, as grafted chains move from the "mushroom" configuration to the "brush" regime, the steric layers first become

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.20}
\caption{Bingham yield stress and elastic modulus for 424 nm latex (□) and 553 nm emulsion (○) with added PEO, M=35,000.}
\end{figure}
"softer" and then "harder" again, with respect to interpenetration by free polymer chains in solution. Such interpenetration weakens the interparticle depletion attraction as discussed in the previous section. It is likely that the amount of PEO grafted to the surface (~5.0 mg/m²) is considerably higher than that adsorbed through the ABA block copolymer (0.6-0.7 mg/m²), so that the interaction between the adsorbed Synperonic PE layers is likely to be much softer and hence give rise to a weaker depletion attraction. If this is so, one would expect a much stronger depletion interaction to be present when the Synperonic stabilises an emulsion, since the amount of PEO present at the interface of an emulsion droplet is around 2-3 mg/m². This is indeed what is observed here.

6.8 Conclusion.

In this work it has been shown that addition of HEC to steric stabilised latices, bearing an adsorbed copolymer layer, results in flocculation once a critical concentration has been exceeded. This transition from a dispersed suspension to a flocculated system is gradual and passes through a two phase region in which both flocculated and dispersed particles coexist. Oscillation measurements can detect the point where a three dimensional volume filling network forms. As the latex volume rises, the yield stress rises slightly more than would be expected from a constant energy of separation between particles. This tells us that the number of contacts per particle is increasing. The elastic modulus scales with the volume fraction to give a fractal dimension in keeping with diffusion limited aggregation. Depletion theories give fair agreement with the experimentally determined $E_{sep}$ values. The AO model tends to underestimate $E_{sep}$ while the FSV model overestimates $E_{sep}$ at low free polymer concentrations. At high free polymer concentrations, the FSV model predicts a drop in $G_{dep}$ due to a reduction in $\Delta$. This is not observed in the experimental $E_{sep}$ values. A strong dependence of the amount of free polymer required for flocculation on latex volume fraction was found. Lower volume fractions require more free polymer to induce flocculation. This is essentially an entropic cause. Determination of the concentration of free polymer required to form a flocculated network from yield stress and elastic modulus measurements agrees favourably with values obtained from both direct visual and microscopic observation.

An emulsion, in which the stabilising layer is hard, was flocculated by free PEO while an identical latex, in which the stabilising layer is soft, was not flocculated. From these results it is expected that bulk properties such as rheology and sedimentation/consolidation of weakly depletion flocculated suspensions and emulsions can be strongly dependent on the nature of the interfacial stabilising layer.
Chapter 7. Nonadsorbing Polymers II: Effect of Molecular Weight of Depleting Polymer.

7.1 Introduction.

In this chapter, the latex volume fraction is now fixed at 0.3 and the molecular weight, $M$, of the depleting polymer is varied. Hydroxyethylcellulose (HEC) is used at four molecular weights from 85,000 to 1,000,000. This range is complemented by xanthan at ca. 2,000,000. These polymers were introduced in chapter 3 and are summarized below in Table 7.1.

<table>
<thead>
<tr>
<th>polymer</th>
<th>name</th>
<th>molecular weight g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>xanthan</td>
<td>Kelzan</td>
<td>2,000,000</td>
</tr>
<tr>
<td>HEC</td>
<td>Natrosol 250L (HEC L)</td>
<td>85,000</td>
</tr>
<tr>
<td></td>
<td>Natrosol 250G (HEC G)</td>
<td>300,000</td>
</tr>
<tr>
<td></td>
<td>Natrosol 250M (HEC M)</td>
<td>700,000</td>
</tr>
<tr>
<td></td>
<td>Natrosol 250HHX (HEC HHX)</td>
<td>1,000,000</td>
</tr>
</tbody>
</table>

Table 7.1 Properties of polysaccharide polymers.

Xanthan, a polysaccharide produced by the microorganism $Xanthomonas campestris$, is used as an anti-settling agent in concentrated suspensions in the agrochemical, ceramics, ink, paint, paper-making, food and textile industries on account of the highly elastic nature of its aqueous solutions on standing and their high degree of shear thinning under applied stresses or strains. It exists as individual molecules in low electrolyte which combine to form a relatively rigid double helix above 5mM electrolyte. Consequently, it is often regarded as rod-like as opposed to coil-like when in solution. Care is required when preparing xanthan solutions since the method of preparation can determine the state in which the molecules exist in solution.

7.2 Flocculation of Latices.

7.2.1 Phase Behaviour.

A photograph of the 424nm latex (C) flocculated by polymers of increasing molecular weight is shown in figure 7.1. If we examine the three tubes on the right where the depleting polymer concentration is 0.8%, phase separation or sedimentation of all the samples has
 occurred. Furthermore, the greatest separation is seen with the lowest molecular weight polymer, HEC L, and the least separation with the highest molecular weight polymer, HEC HHX. This trend is also seen with the lower concentrations of polymer, 0.3 and 0.14%. Here the xanthan samples show no separation whatsoever which is what we would expect from the above observations with its molecular weight being twice that of HEC HHX. Bearing in mind the results from chapter 6 whereby a stronger network was more able to resist sedimentation, it can be concluded that the xanthan causes the strongest flocculation resulting in the formation of a more rigid network. If the xanthan gives the strongest flocculation, then by this reasoning the HEC L must give the weakest flocculation. This appears to be so with the absence of a sharp interface and a cloudy upper layer, indicating that only partial flocculation has occurred. Evidently, there is a strong effect of the depleting polymer's molecular weight on the flocculation of this latex.

Figure 7.1 Photograph showing flocculation and phase separation after two months of a 424nm latex at a volume fraction of 0.3. Flocculating polymers and concentrations as shown.
7.2.2 Rheology.

A summary of the data obtained by changing the molecular weight of the flocculating HEC, whilst keeping the solids fraction of the latex constant at 0.3, are given in Figures 7.2-5, where the elastic modulus, critical strain, yield value and integrated relaxation modulus respectively are plotted as a function of polymer concentration. All these measurements show effects which appear to be related to the molecular weight of the depleting polymer. In keeping with previous work on depletion flocculation,$^{45,114,127,128}$ it is noted that flocculation, as monitored by changes in the rheology of the system occurs sooner for the highest molecular weight polymer. As an example, an order of magnitude more polymer is needed to bring about flocculation when the polymer has a molecular weight of 85,000 compared to a molecular weight of 1,000,000. Also shown on these figures is the effect of adding the polysaccharide gel, xanthan gum, which has a molecular weight of around 2,000,000. The same trend is observed, in that less of this material is required to flocculate the latex than for any of the HEC samples. Since xanthan gum is frequently added to industrial suspension formulations as a thickening agent this is a significant result. The nature of the flocculation by xanthan also appeared to be due to depletion which, as for the HEC, was reversible on dilution with water or latex when the resultant xanthan concentration was below that required for the onset of flocculation.

![Figure 7.2 Elastic modulus values for 424nm latex, volume fraction 0.3 in free polymer solutions shown.](image)
Figure 7.3 Critical strain values for samples in figure 7.2.

Figure 7.4 Yield stress data for samples in figure 7.2.
7.2.3 Microscopic Structure.

Photomicrographs, as a function of depleting polymer concentration, type and molecular weight are shown in figure 7.6. In agreement with the rheological results, increasing the polymer concentration (left to right) results in the flocculation of the particles and formation of a 3-dimensional network, with the onset of network formation occurring at higher polymer concentrations for lower polymer molecular weights. Furthermore, the rise observed with the elastic modulus corresponds to the polymer concentration where complete flocculation occurs and not where flocculation is first observed. For example complete flocculation occurs at 0.02-0.05% polymer for xanthan and HEC HHX, 0.05-0.14% for HEC G and 0.14-0.3% for HEC L. This is what would be expected when we consider that in order for a suspension to exhibit an elastic modulus a continuous network must be present.
With the HEC samples, dispersed (gas), dispersed and crystalline, and flocculated phases are all visible with increasing HEC concentration. However, with the xanthan gum a fluid like (liquid) flocculated phase within a dispersed (gas) phase is visible at low concentrations (0.05% and 0.02%). At higher concentrations this liquid phase freezes into a solid phase as seen with the HEC. The presence of three phases indicates the existence of a weaker, longer range interaction being present with the xanthan gum, presumably this is a depletion polymer size effect according to the theories of Gast et al., and Vincent et al. (see section 2.5.4). Furthermore, the flocculated structure for the HEC samples appears similar while the flocculated structure for the xanthan samples appears less granular suggesting that differences exist between the flocculation caused by xanthan and HEC.

### 7.2.4 Flocculated Structure.

An insight into what is happening can be obtained by interpreting the rheological results in terms of the model introduced in chapter 6 (section 6.2). Figures 7.2-5 show that these rheological parameters increase with increasing molecular weight of the depleting polymer. This relationship can be explored by plotting the rheological parameter as a function of the depleting polymer molecular weight. However, before this is done, the contribution due to the free polymer in solution needs consideration since it is the flocculated structure which is of interest.

![Flow curves for 0.3% polymer solutions](image)

Figure 7.7 Flow curves for 0.3% polymer solutions
The flow curves for all the polymers without latex, at a concentration of 0.3% are shown in figure 7.7. Xanthan, the top curve, has a substantial extrapolated yield stress showing that this polymer has very gel like properties in solution. By contrast, the highest molecular weight HEC, HHX, shows a much smaller yield stress and is much more Newtonian in its behaviour. The M grade of HEC shows only a slight yield while the G and L grades exhibit only Newtonian behaviour and do not contribute to the plasticity of the flocculated latex suspensions. Similarly, contributions to the elastic modulus of the latices were found for the higher molecular weight polymers, xanthan and HEC's HHX and M, at the higher polymer concentrations. Accordingly, these contributions were subtracted from the latex results in figures 7.2 and 7.4. There were no contributions to the critical strain while contributions to the relaxation time were insignificant and not considered.

![Graph](image)

Figure 7.8 Elastic modulus of 424-nm latex as a function of free polymer molecular weight. Polymer concentrations as shown.

The elastic modulus, corrected for the polymer contribution, at three polymer concentrations is shown in figure 7.8 and, surprisingly, scales smoothly with the molecular weight, M, of the depleting polymer with a power of 0.8±0.1, i.e. $G' \propto M^{0.8}$. There are no previous scalings of this type reported. However, increasing the molecular weight of the polymer increases both the range and strength of the depletion force, since both scale with the size of the polymer coils in solution. The corresponding critical strain results are shown in figure 7.9 and generally show a slight increase with increasing molecular weight of the
depleting polymer, indicating that the chains are becoming more tortuous.

Figure 7.9 Critical strain for 424nm latex as a function of free polymer molecular weight. Polymer concentrations as shown.

The contribution due to the increasing strength of flocculation on the oscillation data can be removed by utilising the yield stress values and assuming that the number of contacts per particle, n, is constant for all molecular weights of free polymer. For this, the polymer concentration for each polymer that gives a certain yield stress (a value of 2 Pa was used here) is obtained and the corresponding elastic modulus and critical strain values are chosen.

Figure 7.10 Elastic modulus and critical strain as a function of free polymer molecular weight at constant strength of flocculation and increasing range of attraction.
This gives the plot in figure 7.10. Here, the strength of the flocculation is constant for all the points so that the only variable is the range of the depletion force, which increases with increasing molecular weight. It can be seen that the elastic modulus is approximately constant while the critical strain increases as the molecular weight rises, telling us that the floc structure is becoming more tortuous.

We can understand the effect of the range of the depletion force by considering what happens when flocs are formed. In chapter 6, HEC G gave diffusion limited fractal structures. With a short range depletion force, particles will only see each other at relatively short separations and will stick at this first contact giving open structures in accordance with the observed diffusion limited aggregation. However, with a long range depletion force, a particle will see several other particles in the cluster well before any contact. These other particles will influence the particle's trajectory as it approaches the cluster and favour impact sites which contain as many contacts as possible, giving less open clusters. This is illustrated in figure 7.11. Aggregation of these clusters will then result in the formation of different floc structures.
termed here as "long range attraction floc structure" and "short range attraction floc structure" or LRAFS and SRAFS for short. The SRAFS is more likely to be a highly connected network which will fracture at relatively small strains, while the LRAFS will be much less connected and able to adsorb greater strains before fracture. In terms of fractal structures, increasing the molecular weight of the free polymer is equivalent to increasing the fractal exponent, \( f \), from 3.5 for diffusion limited aggregation towards 4.5 for reaction limited aggregation. To ascertain this, oscillation measurements would be required at several \( \phi \) for each molecular weight of free polymer. At present these are only available for HEC G which has a relatively low molecular weight (see section 6.4.1).

If we reconsider the model introduced in chapter 6, Liang et al.\(^{46}\) have postulated that the elastic modulus depends not only on the number of chains but also on the strength of the links between the particles in these chains. In the model, the elastic modulus only depended on the number of chains. Either of these cases could be correct here. We can try to answer this with information on the strength of the interparticle links from the yield stress results.

![Figure 7.12 Yield stress data corrected for polymer contribution as a function of free polymer molecular weight. Polymer concentrations as shown.](image)

The latex yield stress data corrected for the polymer contribution are shown in figure 7.12. As for the elastic modulus, there is good scaling with the molecular weight for the HEC with a power of 1.2±0.2, i.e. \( \sigma_y \propto M^{1.2} \). This increase and linearity is to be expected since the strength of the depletion force is governed in part by the size of the polymer coil which, in turn, scales with the square root of the molecular weight of the polymer. However, what is
most interesting is the drop in the yield stress for the xanthan flocculated suspensions. This was not apparent in figure 7.4 since the xanthan itself contributed considerably to the total yield stress. If the elastic modulus does depend on both the number of chains and the strength of the interparticle links, then the elastic modulus would be expected to drop for xanthan from these results. The fact that it does not (figure 7.8) suggests that the elastic modulus only depends on the number of chains, supporting the model postulated in chapter 6.

There was little correlation between the integrated stress relaxation modulus and polymer molecular weight although a general increase was observed with increasing polymer molecular weight and concentration.

7.2.5 $E_{sep}$ and Depletion Energy Calculations.

The energy of separation, $E_{sep}$, calculated from the polymer corrected yield stress values is listed in table 7.2. The assumptions made previously in chapter 6, section 6.4.2 have been used here also. In order to calculate the depletion force it necessary to know its range, which is of the order of the size of the polymer coils in solution, i.e. twice the radius of gyration, $R_g$. Sperry\textsuperscript{115,133} has determined this for Natrosol 250 LR, GR and MR grades by intrinsic viscosity measurements and is summarised in table 7.3. The R grades are identical to the grades used here with the exception of a coating to facilitate the dispersion of the HEC granules on addition to water. The diameter of coils was that required to yield the measured intrinsic viscosity according to Einstein's relationship (equation 1.19). Intrinsic viscosity measurements for HEC HHX indicated a molecular weight of ca. 1.0 x10$^6$ and an Einstein hard sphere diameter of 129nm.

<table>
<thead>
<tr>
<th>Polymer %w/v</th>
<th>HEC L</th>
<th>HEC G</th>
<th>HEC M</th>
<th>HEC HHX</th>
<th>Xanthan</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td>0.392</td>
<td>1.67</td>
</tr>
<tr>
<td>0.051</td>
<td>0.214</td>
<td>&lt;0.2</td>
<td>1.49</td>
<td>4.06</td>
<td></td>
</tr>
<tr>
<td>0.086</td>
<td>0.573</td>
<td>&lt;0.2</td>
<td></td>
<td>4.28</td>
<td></td>
</tr>
<tr>
<td>0.143</td>
<td>&lt;0.2</td>
<td>1.51</td>
<td>7.01</td>
<td>16.1</td>
<td>10.3</td>
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<td>0.30</td>
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<tr>
<td>0.80</td>
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<td>72.8</td>
<td>200</td>
<td>247</td>
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<tr>
<td>1.60</td>
<td>43.6</td>
<td></td>
<td>416</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.2 $E_{sep}$ values (kT) calculated from the Bingham yield stress with the polymer contribution subtracted. Latex 424nm, $\phi$=0.3.
Table 7.3 Properties of polysaccharide polymers. HEC L, G and M data from Sperry,\textsuperscript{115} xanthan data from Sato \textit{et al.}\textsuperscript{168}

For xanthan its radius of gyration was obtained from the data of Sato \textit{et al.}\textsuperscript{168} assuming a molecular weight of $2 \times 10^6$ and a value of 0.47 was taken for $\chi$. Xanthan is made up of monomers which are composed of five "saccharide" rings.\textsuperscript{169} In order to give realistic values for the osmotic pressure, one saccharide ring was taken as the monomer unit with a molecular weight of 132 g/mole, assuming half a pyruvic acid group per monomer of five saccharide rings.\textsuperscript{170} For the FSV model, the depletion layer thickness, $\Delta$, was calculated as before from the model derived by Vincent\textsuperscript{117} (equation 2.28).

Table 7.4 Calculated depletion flocculation strength for 424nm latex.

For the HEC the best agreement with the experimentally determined $E_{sep}$ values shown in table 7.2 is found with the AO model for HEC grades L and G at low HEC concentrations.
At both higher HEC concentrations and molecular weight, i.e. M and HHX grades, the AO model increasingly underestimates $E_{sep}$, while at low concentrations of HEC and xanthan, the FSV model considerably overestimates $E_{sep}$. With the high molecular weight polymers, the FSV model predicts a maximum in $G_{dep}$ with increasing free polymer concentration. This is due to a drop in $\Delta$ predicted by Vincent's model, which is not observed experimentally at these polymer concentrations.

With xanthan, the agreement with the AO model is surprisingly good. This is probably coincidental since xanthan tends to behave as a semi-rigid rod rather than a coil when in solution. Furthermore, the AO model does not predict the drop in the strength of the flocculation when xanthan is compared to the HHX grade of HEC, while the drop with the FSV model is a consequence of the decrease in $\Delta$. However, the reason for the lower $E_{sep}$ values with xanthan may well be due to its rod like behaviour, which can be understood if we consider the differences a coil and a rod have on the depletion zone between two particles:

The coil is depleted from the region between the particles once their separation is less than the size of the coil. With the rod conformation the polymer molecules can fit between the particles up to much closer separations, thus leading to a smaller depletion zone and consequently weaker flocculation of the particles. Therefore, it appears that the lower $E_{sep}$ values are due to the rod like shape of the xanthan and not to lower osmotic pressures in solution. Another possibility could be incompatibility between the HEC and PEO chains leading to enhanced depletion as found by Liang et al. However, this effect will have relatively little effect on the depletion layer thickness, since the adsorbed layer thickness is of the order of 6nm which is much smaller than the size difference between HEC HHX and xanthan (table 7.3).

So to what extent does xanthan exist as a rod rather than a coil? Southwick et al. have proposed that in very low electrolyte ($<1\text{mM}$) xanthan is a flexible chain composed of a cellulose backbone with trisaccharide side chains protruding outwards from alternative
glucose units on account of their negative charge:

\[
\text{disordered} \quad \longleftrightarrow \quad \text{ordered}
\]

\[
\text{monomer} \quad \longleftrightarrow \quad \text{dimer}
\]

\[
<1 \text{mM NaCl} \quad 10 \text{ mM NaCl} \quad >0.1 \text{ M NaCl}
\]

Adding electrolyte (10 mM) screens these charges and allows the side chains to align with the main backbone which results in considerable stiffening of the molecule. Kinetic studies\(^{173}\) have shown that these rigid molecules readily form dimers which then associate at higher levels of electrolyte (>0.1M) to form birefringent viscoelastic gels. Increasing the concentration of xanthan also favours the formation of dimers and their corresponding associated structures.

In the polystyrene latex systems studied here xanthan is most probably in the form of dimers, for which electron microscopy reveals sizes of ca. 4 nm by 1-10 µm.\(^{174}\) If xanthan was a truly rigid rod then, depletion effects would only be seen at a separation of ca. 4 nm. However, xanthan is known to behave as a semi-rigid rod with some coil-like behaviour\(^{171}\) and consequently, must have an effective diameter in solution between the extremes of 4 nm and 334 nm. This is confirmed by membrane partition chromatography which indicates a hydrodynamic diameter of 100-200 nm. Using a value of 150 nm for the size of the xanthan molecule gives better agreement for the \(G_{dep}\) models (see table 7.5).

<table>
<thead>
<tr>
<th>Polymer %w/v</th>
<th>AO model</th>
<th>FSV model</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.32</td>
</tr>
<tr>
<td>0.051</td>
<td>0.92</td>
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</tr>
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</tr>
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</tr>
<tr>
<td>0.30</td>
<td>5.36</td>
<td>8.96</td>
</tr>
</tbody>
</table>

Table 7.5 Calculated \(G_{dep}\) (kT) values for xanthan treated as a semi-rigid rod.
7.2.6 Phase Properties.

From the data given in Figures 7.2 and 7.4 it is possible to identify a critical polymer concentration above which flocculation occurs, this information is represented in figure 7.13. It is seen that an approximate exponential relationship between molecular weight and the critical polymer concentration is observed for these polysaccharide based systems, with even the xanthan gum being described by the same curve.

![Figure 7.13 Phase boundary from rheological measurements. Yield stress (☐) and elastic modulus (○).](image)

Taking the yield stress values gives a scaling to the power of -0.84 (i.e. \( \phi_p^* \propto M^{-0.84} \)). Sperry et al.\(^{133} \) in their studies of similar systems found a value of -0.7 for the exponent while the data of Liang et al.\(^{45} \) gave an exponent of ca. -0.55. The only difference here is that the particles contained a grafted steric layer of PEO rather than an adsorbed layer as in this work. An exponent of -0.5 has also been found by Vincent\(^{175} \) for aqueous, stericly stabilised suspensions.

Napper\(^{176} \) has estimated the dependence of the critical polymer concentration on the free polymer molecular weight from scaling arguments by assuming that a fixed minimum in \( G_{sep} \) was required for flocculation. This depends on the depletion layer overlap volume and the osmotic pressure of the free polymer and results in an exponent of -0.4 to -0.5, which is in agreement with some of the results. However, the picture appears to be more complex than this since de Hek and Vrij\(^{114,128} \) have found an exponent of -0.5 for non-aqueous silica.
suspensions stabilised with polyisobutylene, while changing the stabiliser to stearyl alcohol decreases the exponent to -0.25, suggesting that the nature of the stabilising layer is also important here.

7.3 Conclusion.

There is a strong effect of the free polymer molecular weight on the flocculation of aqueous latices stabilised with adsorbed PEO-PPO-PEO block copolymers. Increasing the molecular weight causes both the elastic modulus and the yield stress to rise. This is a consequence of the strength of flocculation increasing. Removing the contribution of the increasing strength of flocculation allows the effect of the range of the depletion force to be examined. Here, the critical strain increased with increasing molecular weight of the depleting polymer. This could be interpreted in the formation of a more compact flocculated network.

Xanthan showed a reduction in the strength of flocculation in relation to the HEC, which was considered due to its rod like shape reducing the volume of the depletion overlap region, rather than differences in the osmotic pressure between xanthan and HEC solutions. Agreement with the depletion flocculation theories for $G_{dep}$ was poor, the AO model tends to underestimate the strength of the flocculation while the FSV model with Vincent's relationship for the depletion layer thickness, overestimates this strength at low polymer concentrations. At higher polymer concentrations a maximum in $G_{dep}$ is predicted due to the decrease in the depletion layer thickness. This was not observed experimentally. The critical polymer concentration for flocculation scaled with the molecular weight of the free polymer with an exponent of -0.84, which is comparable to similar systems but larger than some other findings.

8.1 Introduction.

In this chapter, the influence of the adsorbed PEO-PPO-PEO stabilising polymer on latices is studied. If we recall the rheological properties of these stabilisers discussed previously in chapter 5, only the small latex exhibited any significant effects due to these polymers. Consequently, the small latex has been chosen to investigate the effect of the stabiliser. Experiments are presented for the small 67nm latex (D) with either Synperonic PE/P103, P105 or F108 adsorbed onto the latex surface at full coverage. Hydroxyethylcellulose (300,000 M.wt.), HEC G, has been added as the depleting polymer to flocculate the particles, which are at a core volume fraction of 0.159. This has been chosen to correspond to 60% of $\phi_{\text{max}}$, taken as the point where $G'$ rises sharply (=1 Pa), which is equivalent to the larger 424nm latex at a volume fraction of 0.3, studied in chapters 6 and 7. Rheology and microscopy have been used to characterise these suspensions. This chapter begins with the effect of increasing HEC concentrations on the phase properties of the 67nm latex.

8.2 Effect of HEC.

8.2.1 Phase Properties.

In figure 8.1, is a photograph of 4 tubes containing the polystyrene latex stabilised with F108 at increasing concentrations of HEC (from left to right). Without any HEC an off white, homogenous phase may be seen. At 0.15% HEC two phases may be clearly seen, a lower slightly brown phase is in equilibrium with a somewhat cloudy phase, which is clearly of a lower particle volume fraction. On increasing the polymer concentration further to 0.3%, three phases may be seen to be in coexistence with each other, at the bottom of the tube is a brownish sediment, above this is a light brown phase and in the top of the tube is a milky white phase. At higher polymer volume fractions, two phases, dominated by a brown sediment with a small amount of a milky white phase are seen. Clearly the lower phases in the tubes are the most dense and hence contain the most particles. Thus, for example, one would expect that in the third tube (0.3%) where three phases are in coexistence with each other, the lower phase will correspond to a colloidal "solid" phase, the middle phase would correspond to a colloidal "liquid" phase and the upper region to be a colloidal "gas" region. Further, by analogy with molecular systems, one would expect the solid-liquid interface to be more rigid.
Figure 8.1 Phase separation induced by HEC in a 67nm polystyrene latex suspension stabilised with F108. Concentrations (%w/v) of HEC as shown.

than the gas-liquid interface. This is confirmed when the tubes are tilted to an angle of around 30°. In the third tube (0.3%) the lower interface, the solid-liquid interface, remains parallel to the bottom of the tube, whilst the upper interface, the liquid-gas interface flows readily. In this way it is also possible to identify the interface in the second tube (0.15%) to correspond
to the gas-liquid interface. When these tubes were originally prepared it took a few days for the phases to separate, however after a week the equilibrium seemed to be reached as leaving the tubes for a further six months did not noticeably affect the extent of the phase regions. The true equilibrium nature of this separation is readily illustrated when the bottom solid phase from the tube containing all three phases is removed and placed in a second tube. The "solid" phase separates into three phases which are indistinguishable both in terms of appearance and proportions from the original sample.

Such suspensions exhibit analogous phase behaviour to molecular systems. According to Gibbs' phase rule, the sum of the variance, \( F \), and number of components, \( C \), of a molecular system is equal to the number of phases, \( P \), plus two. For a single component and one phase, the variance is two which means that there are two degrees of freedom for the system, i.e. the temperature (\( T \)) and pressure (\( p \)) can be varied independently without encountering a phase boundary. For two phases, \( F=1 \) and either the temperature or pressure is fixed which corresponds to a line representing the equilibrium between the two phases on a T-p phase diagram. When three phases are present there are no degrees of freedom (\( F=0 \)) and the equilibrium between these phases corresponds to a point on a T-p phase diagram which is the triple point. This is illustrated in figure 8.2. With colloidal suspensions in the presence of non-adsorbing polymer, the analogue of pressure is particle volume fraction while free polymer concentration is the analogue of the reciprocal of temperature.

In contrast to molecular systems, the three phase region was found to extend over a small range of free polymer concentrations rather than a specific concentration. However, when these phase boundaries are converted to the corresponding axes for colloidal suspensions, latex volume fraction and free polymer concentration, a three phase coexistence region rather than a triple point is predicted. These observations confirm the predictions of
Lekkerkerker's model and correspond to the vertical line \( x-x' \) drawn upwards from the x-axis in the theoretical phase diagram given in figure 8.3.

8.2.2 Microscopy.

To further validate the above findings the various phases eluded to above were subjected to a microscopic study ten minutes after formation, i.e. sufficient time was left for micro phases to form, but not for bulk phase separation to occur. Normaski Differential Interference Contrast microscopy was used for all observations since this technique is highly sensitive to refractive index changes in the plane of the slide, which exist with multiphase systems. Such changes are apparent as variation in the colour of objects and results in a three dimensional relief like image. The results are presented in figure 8.4 for the P103 stabilised latex. Without any HEC just a continuous phase is present, i.e. a gas phase. Adding HEC causes no change until at ca. 0.194%, condensing droplets of the liquid phase appear in entirely an analogous way to the condensation of water droplets from a saturated vapour. At higher polymer concentrations, the liquid phase grows (0.3%). Here the droplets are roughly the same size and spherical, indicating the presence of a genuine surface tension between the phases. As the polymer concentration is increased (0.544%) the two phases invert, i.e., the gaseous phase is now dispersed in the liquid phase, by analogy with molecular systems, the liquid is "boiling." Increasing the polymer concentration further (0.594%) causes solid lumps to appear in the liquid phase. Here the liquid phase is "freezing" into a solid. At 0.641% HEC, all three phases are now visible, a solid phase within a liquid phase, which was able to readily flow around these lumps of material, and a gas phase. This corresponds to the three phase coexistence region predicted by Lekkerkerker.

Figure 8.3 Colloidal phases predicted by Lekkerkerker.

Figure 8.4 (overleaf). Differential Interference Contrast photomicrographs of 67nm latex stabilised with P103. Concentrations of HEC G (%w/v) as shown.
At higher polymer concentrations (0.8%), the liquid phase reduces until just solid aggregates of particles in a dilute matrix of gaseous polystyrene latex are observed. Increasing the polymer concentration further (1.6%) results in little change in the structure of the suspension.

8.3 Effect of Stabilising Polymer.

8.3.1 Phase Properties.

Photographs of the suspensions are shown in figure 8.5. There are considerable differences between the three Synperonic copolymers. For example, with the P103 stabilised samples the white cloudy layer at low HEC levels gives way to a cloudy upper layer and a brown, semi-translucent lower layer which appears not to flow in the tilted tubes. At 1.6% HEC a white cloudy flocculated suspension is again observed. In contrast, at 0.3% HEC, the P105 stabilised latex has two cloudy phases which flow when tilted while the F108 stabilised latex has three layers, an upper almost clear layer, a middle cloudy layer and a lower brown, semi-translucent layer. Of these the upper two layers flow when tilted. These layers formed over a period of a week, after which no further changes were observed. Further information on these differences between the different stabilising copolymers can be obtained from microscopic analysis.

Figure 8.5 Photograph of 67nm latex suspensions stabilised with P103, P105 or F108 and with increasing levels of HEC G.
8.3.2 Microscopy.

In figure 8.6 photomicrographs are shown for the different stabilising copolymers. Firstly, the three stabilisers at the same HEC concentration of 0.3%w/v are compared. For the P103 (a), a colloidal liquid is visible dispersed within a colloidal gas. On changing to P105 (b), a gas phase is found dispersed within a liquid phase. By comparison with figure 8.4 we see that this is similar to P103 with 0.544% HEC. So changing the stabiliser here is equivalent to increasing the HEC content from 0.3 to 0.544%. If we change the P105 to F108 (c), we obtain a solid/liquid type phase dispersed within a gas. This corresponds to P103 with 0.594% HEC in figure 8.4. This is seen more clearly if we look at the three phase regions for each of the three stabilisers (d,e,f). Here, the existence of a solid phase within a liquid phase can be seen, which in turn is surrounded by the gas phase. This is shown most clearly with F108 (f) where the liquid phase can be seen flowing in the gas phase between the lumps of solid phase. For the P103, 0.641% HEC is required, while for the P105 and F108 only 0.448 and 0.304% HEC are required. Evidently the three copolymers have a large effect on the critical polymer concentration required for these phase changes, with the highest molecular weight, F108, causing flocculation at the lowest concentration of HEC and the lowest molecular weight, P103, requiring the highest concentration of HEC for flocculation.

From these observations it is possible to construct a phase diagram, which is shown in figure 8.7. At low concentrations of HEC only the gas phase is observed which forms the two phase gas+liquid region with higher levels of HEC. There is then a region of three phase coexistence containing gas+liquid+solid phases followed by the two phase gas+solid region at high HEC levels. This clearly shows the trend with the amount of HEC required for a phase change decreasing with increasing PEO molecular weight of the stabilising copolymers. The three vertical sets of points correspond to P103, P105 and F108 from left to right. Surprisingly, with the F108 stabilised particles the liquid phase appears at very low levels of HEC indeed and extrapolation suggests that a stabilising copolymer with a higher molecular weight PEO chain would be in the gas-liquid phase region without any HEC.

More information on the structure of the flocculated phases can be obtained from rheological measurements, which are presented in the next section.

Figure 8.6 (overleaf). Photomicrographs (DIC) of 67nm latex stabilised by P103, P105 and F108. Concentrations of HEC as shown.
(a) P103 + 0.3% HEC G

(b) P105 + 0.3% HEC G

(c) F108 + 0.3% HEC G

(d) P103 + 0.641% HEC G

(e) P105 + 0.448% HEC G

(f) F108 + 0.304% HEC G

100μm
8.4 Rheology.

From the results obtained with flocculated particulate networks in chapters 6 and 7, it should be possible to detect the formation of the solid phase from oscillatory shear measurements, provided that it forms a continuous network throughout the sample, while, yield stress measurements should be capable of probing the depleting forces between particles bearing layers of each of the Synperonic copolymers.

8.4.1 Measurements at Small Deformations.

In figure 8.8 the elastic modulus at 0.5 Hz is plotted for the three stabilising copolymers as a function of HEC concentration. The elastic modulus initially rises sharply and then plateaus as the particles flocculate to form a three dimensional network. This suggests that once the network is formed, its structure does not change with further HEC addition, as shown by the constant value of G' between of 0.8 and 1.6% HEC. Furthermore, identical plateau values are obtained for each of the stabilising polymers which tells us that the floc structure for each copolymer contains the same number of chains on account of the coinciding plateau values. There is an indication with these results that the flocculated network forms at a lower HEC concentration with the F108 in accord with the observed phase properties.
In addition to this structural information, we can also obtain knowledge of the tortuosity of these chains from the maximum strain the floc structure can withstand before it breaks down i.e. the limit of the viscoelastic region, the critical strain, $\gamma_c$. In chapter 6 a model was introduced whereby a high critical strain indicates a highly tortuous or meandering chain while a low critical strain indicates a relatively linear chain.

Figure 8.8 Elastic modulus as a function of HEC G concentration for latex D (67nm) stabilised with P103 (A), P105 (○) and F108 (□).

Figure 8.9 Critical strain as a function of HEC G concentration for latex D (67nm) stabilised with P103 (A), P105 (○) and F108 (□).
In figure 8.9 the critical strain for the flocculated latices is shown. As for the elastic modulus, no differences are apparent between the different copolymers implying that the stabilising layer has no effect on the tortuosity of the floc structure. However, the critical strain does increase slowly with increasing HEC content implying that the structure does become slightly more tortuous and may reflect the stronger flocculation. The high critical strain value at low HEC levels (0.3%) is due to only partial flocculation where a continuous network has not fully developed. Interestingly, this point corresponds to the three phase coexistence region and indicates that some network structure does exist in the sample. This is also apparent in the value of the elastic modulus (figure 8.8) which is just beginning to rise towards its plateau value. From these oscillation results it can be concluded that each of the three stabilising copolymers give identical flocculated structures.

8.4.2 Yield Stress Measurements.

In figure 8.10 the Bingham yield stress is plotted against increasing HEC concentration. Here, unlike the oscillation measurements, differences between the three stabilising copolymers are found. It can be clearly seen that the F108 gives the highest yield stress values while P103 gives the lowest. This correlates to the molecular weight of the PEO, the highest of which gives the greatest yield stress. Furthermore, the trend in the yield stress agrees with the observed phase dependence on the stabilising copolymer shown in figure 8.7.

![Figure 8.10](image.png)

**Figure 8.10** Bingham yield stress as a function of HEC G concentration for latex D (67nm) stabilised with P103 (△), P105 (○) and F108 (□).
since, in order for a solid phase to form there must be a certain minimum attractive force between particles, which is greatest for the F108. The yield stress values have been converted to their corresponding $E_{\text{sep}}$ values in table 8.1 (previously introduced in chapter 1, section 1.4.3) where it can clearly be seen that the strength of flocculation with the F108 is some 2-3 times stronger than for P103.

<table>
<thead>
<tr>
<th>HEC %w/v</th>
<th>P103</th>
<th>P105</th>
<th>F108</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.030</td>
<td>0.044</td>
<td>0.370</td>
</tr>
<tr>
<td>0.66</td>
<td></td>
<td></td>
<td>2.15</td>
</tr>
<tr>
<td>0.8</td>
<td>0.924</td>
<td>1.75</td>
<td>2.77</td>
</tr>
<tr>
<td>1.6</td>
<td>5.50</td>
<td>7.98</td>
<td>13.1</td>
</tr>
</tbody>
</table>

Table 8.1 $E_{\text{sep}}$ (kT) values for 67nm latex stabilised with P103, P105 or F108.

The $E_{\text{sep}}$ values found here are much smaller than for the 424nm latex in chapter 6, table 6.3, yet the yield stress values are larger. This is a geometrical consequence of the smaller particles having a much smaller depletion overlap zone when flocculated and thus a lower $E_{\text{sep}}$ value. However, for the same volume fraction, there is a much greater number of small particles with a greater total surface area, which results in a greater total depletion zone, resulting in higher yield stress values.

If we once more examine the data in figure 8.8, the sample in the three phase coexistence region, F108 at 0.3% HEC, has an $E_{\text{sep}}$ value comparable to the energy of a particle, kT, which in section 6.4.2 corresponded to ordered crystalline structures in the 424nm latex. When all the samples are compared, a transition in the yield stress is apparent at HEC concentrations of 0.3 to 0.8% HEC. This corresponds to the formation of the three dimensional network which agrees with the appearance of the gas+solid phase observed microscopically. Unfortunately, in this case, this information cannot be obtained from the oscillation data since the transition is only apparent when the elastic modulus rises sharply and cannot be obtained by extrapolation from the plateau values which are identical, irrespective of the HEC concentration or stabilising copolymer.

8.5 Effect of Stabilising Layer on Phase Properties.

What is the reason for this trend in the phase behaviour with the adsorbed copolymer molecular weight? One possibility is the change in the effective volume fraction of the latex
due to the different adsorbed layer thicknesses from the three PEO-PPO-PEO copolymers. In chapter 6 it was shown how the onset of flocculation depended on the volume fraction of the dispersed phase. Using values previously determined from rheological measurements for this latex in chapter 5 and other data from chapter 6, where the effect of latex volume fraction on the fluid-gel phase transition was investigated, it can be seen in figure 8.11 that the effect of the adsorbed polymer layer on the phase boundaries is much greater than that expected due to volume fraction effects, thus discounting this possibility.

Consequently, if volume fraction changes are not responsible for these trends, then the structure of the stabilising polymer layer must be the cause, but the question is how? In chapter 5 the effect of these stabilising copolymers on the zero shear viscosity of latex D (without HEC) was presented in figure 5.5 which revealed that each of the copolymers causes a large deviation from hard sphere behaviour, with F108 giving the greatest and P103 the least. This suggests that these latices are relatively soft with F108 giving the softest latex and P103 giving the hardest. However, Milling et al.\textsuperscript{177} have shown that softer latices require more depleting polymer to induce flocculation which is in contrast to these observations. Evidently, more information is needed about the structure of the adsorbed polymer layer.

If we now consider the adsorbed amount and the adsorbed layer thickness, which were determined in chapters 4 and 5, the amount of PEO per unit volume in the adsorbed layer can be calculated. This gives volume fractions of 0.044, 0.056 and 0.087 for P103, P105 and F108 respectively, with P103 being the "softest" and F108 the "hardest." Therefore, the F108 has
the highest concentration of PEO in its steric layers which strongly repels the HEC coils from the surface of the particles to give relatively thick depletion layers. In contrast, the P103 has the lowest concentration of PEO in its steric layers which allows considerable penetration by the HEC coils and thus has relatively thin depletion layers. This is illustrated in figure 8.12.

![Figure 8.12 Illustration of effect of steric stabilising layer on depletion layer thickness.](image)

According to the theory of Vincent, Edwards, Emmett and Jones, the true depletion layer thickness is given by \( \Delta + \delta - p \), where \( \Delta \) is the hard sphere depletion layer thickness which is of the order of the size of the HEC coils, \( \delta \) is the steric stabilising layer thickness and \( p \) is the depth the free HEC polymer coils penetrate the steric layer. Therefore, it can be readily seen that more penetrable, less dense steric layers will have higher values of \( p \) and thinner depletion layers, resulting in weaker flocculation. However, in order to determine the minimum in the interaction energy, \( G_{T,\text{min}} \), it is necessary to also consider the repulsive elastic and mixing contributions (see section 2.2.3.1) such that the total interaction energy is given by:

\[
G_T = G_{\text{dep}} + G_{\text{el}} + G_{\text{mix}}
\]  

(8.1)

The van der Waals forces were considered to be relatively small at these separations and not included. Results for \( G_{T,\text{min}} \) obtained by evaluating \( G_T \) as a function of separation, \( h \), with \( p \) calculated from the uniform adsorbed layer profile (equation 2.36) and \( G_{\text{dep}} \) from equation 2.32, are listed below in table 8.2. Liang et al. have shown that PEO and HEC do not mix and so, in order to account for this restricted penetration of the steric layer, a \( \chi \) value of 0.4 was used for the \( p \) and \( G_{\text{dep}} \) calculations. For the repulsive, elastic steric interaction, \( G_{\text{el}} \), the published value of 0.47 was used. A \( \chi \) value of 0.5 corresponds to complete mixing. The
decrease in the depletion layer thickness with increasing HEC concentration was accounted for by Vincent's relationship, equation 2.28. The results of these calculations are listed below in Table 8.2.

<table>
<thead>
<tr>
<th>%w/v</th>
<th>Δ</th>
<th>nm</th>
<th>P103</th>
<th>P105</th>
<th>F108</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>18.9</td>
<td>5.73</td>
<td>(4.83)</td>
<td>6.15</td>
<td>(3.79)</td>
</tr>
<tr>
<td>0.66</td>
<td>15.6</td>
<td>9.87</td>
<td>(4.45)</td>
<td>10.61</td>
<td>(3.50)</td>
</tr>
<tr>
<td>0.8</td>
<td>14.6</td>
<td>11.03</td>
<td>(4.34)</td>
<td>11.83</td>
<td>(3.41)</td>
</tr>
<tr>
<td>1.6</td>
<td>9.45</td>
<td>12.29</td>
<td>(3.43)</td>
<td>12.78</td>
<td>(2.70)</td>
</tr>
</tbody>
</table>

Table 8.2 $G_{T,min}$ and $Δ$ values calculated according to the VEEJ theory. Figures in brackets correspond to calculated values of $p$.

Comparison of these results with the experimentally determined values in Table 8.1 gives good agreement with the numerical trends but poor correlation with the actual values. The VEEJ theory overestimates the values for $G_{T,min}$ but does predict the trend in increasing flocculation strength from P103 to F108. Vincent's theory for the depletion layer thickness, $Δ$, predicts a large drop at 1.6% HEC which corresponds to similar values for the 0.8% and 1.6% HEC samples. This again, as for the larger latex in chapter 7, is not observed with the experimental results suggesting that there is much less compression of the HEC coils at this concentration. The $p$ values show a substantial degree of penetration for the P103 which decreases for the P105 and F108 in accord with the increasing density of the steric stabilising layer.

8.7 Conclusion.

Addition of free HEC to small particles results in the formation of gas, liquid and solid phases which exhibit behaviour similar to molecular systems. Regions were found where two, or even all three phases coexisted in equilibrium, in accord with the theory of Lekkerkerker et al. These phases could be readily distinguished by visual or microscopic observations. The free polymer concentrations over which these phases existed depended on the nature of the stabilising layer. Harder steric layers were more readily flocculated than softer layers. The Synperonic PE/F108 produced the hardest steric stabilising layers and the
P103 the softest. Once a flocculated network had formed, a constant value for the elastic modulus was found which was independent of both the free polymer concentration and the nature of the stabilising layer. This means that the floc structure is also constant and does not depend on these components either. Yield stress measurements revealed stronger flocculation for the harder particles. The VEEJ theory gave qualitative agreement with the experimental results and predicted substantial penetration of the steric layer by the HEC for the P103, which decreased for the P105 and F108.

From these results it is expected that bulk properties such as rheology and sedimentation/consolidation of weakly depletion flocculated suspensions, such as agricultural and pharmaceutical preparations, can be strongly dependent on the nature of the interfacial stabilising layer.

9.1 Introduction.

Suspension concentrates are an important formulation type in the design of crop protection products and is one of the vehicles through which an active ingredient is applied to its target crop by the farmer in a stable, safe and biologically active form. Typically, a suspension concentrate is composed of an insoluble, micron sized, crystalline dispersion of one or more pesticides, suspended in an aqueous medium. Surfactants are also incorporated to wet and disperse the particles, which can combine both steric and electrostatic stabilisation. However, in order to maintain its potency, a suspension concentrate must be stable to any change over its lifetime, which may extend for up to three years. For example, there must be no significant chemical degradation of the active ingredient(s) and no irreversible sedimentation of the dispersed phase. The latter, if not controlled by an anti-settling agent, can lead to dilatant layers which are difficult to redisperse. This can be particularly acute in agricultural suspension concentrates where a balance of properties are required since a suspension needs to be sufficiently viscous to prevent sedimentation and yet also be sufficiently fluid to allow it to be readily emptied and rinsed from its pack. This is often achieved by forming a weak, volume filling, three dimensional network of particles which is sufficiently strong to overcome gravitational stresses and prevent sedimentation. However, upon application of a slightly greater stress, such as encountered when inverting the pack or pouring out the contents, the three dimensional network must be sufficiently weak such that it is able to breakdown and allow the suspension to flow. Rheologically this corresponds to a "solid" on standing which breaks down to a fluid on application of a stress or shearing, i.e. a plastic material.

In order to study such suspensions it is necessary to make measurements both in its "solid" state i.e. within the linear viscoelastic region before the sample flows and also in the "fluid" state where the sample is flowing. However, care must be taken in defining the "solid" state since over a very long timescale an apparent solid may actually flow, behaving as a highly viscous fluid. Sedimentation has long been recognised as an inherent problem in such systems.

Xanthan, a polysaccharide produced by the microorganism *Xanthomonas campestris*, is commonly used as an anti-settling agent in concentrated suspensions in the agrochemical,
ceramics, ink, paint, paper-making and textile industries on account of the highly elastic nature
of its aqueous solutions on standing and their high degree of shear thinning under applied
stresses or strains.

The effect of xanthan on the sedimentation behaviour and rheology of an aqueous
suspension of the acaricide, clofentezine has been studied with the aim of determining the
mechanism by which xanthan inhibits sedimentation and ultimately predicting how such
suspensions will sediment. Although a large amount of work has been carried out on the
properties of aqueous xanthan solutions there appears to be very little literature describing
work on xanthan gum thickened suspensions. Some workers believe that it is the high
viscosity of the gel like xanthan solutions which retards the sedimentation of any particles
suspended in it. In contrast, Howe and Robins have reported that the addition of xanthan
to non-ionic stabilised oil in water emulsions results in their flocculation by a depletion
mechanism and a reduction in the rate of creaming. This suggests that the xanthan may also
flocculate suspensions in a similar manner and that it may be the flocculated network of
particles which prevents sedimentation rather than the high viscosity of the xanthan gel.
Wedlock et al. posed this very question when they studied the sedimentation profiles of
xanthan thickened suspensions. However, they were unable to answer this unequivocally.

Three distinct types of sedimentation in suspensions have been identified, namely
those of dispersed, aggregated and reversibly flocculated dispersions. The sedimentation of
monodisperse, dispersed systems has been much studied and is well understood. Here the
particles sediment individually according to Stokes' law with a correction for dispersed phase
volume due to Kynch. Richardson and Zaki empirically correlated the sedimentation rate
for hard spheres and found that they were described by the following relationship:

\[
\text{Relative sedimentation rate} = \frac{U_s}{U_i} = (1-\phi)^\beta
\]

(9.1)

where \(U_s\) is the sedimentation rate of the suspension, \(U_i\) is the sedimentation rate of a single
particle at infinite dilution and \(\beta = 5\) at the limit of slow sedimentation where the particle's
drag is given by Stokes' law, which is the case with colloidal suspensions. This correlation has
been confirmed both for a wide range of volume fractions and for colloidal sized
polystyrene latices and silica particles with \(\beta\) values of ca. 5.4. Rheologically these systems
normally exhibit Newtonian flow at very low volume fractions and pseudoplastic flow at
higher concentrations, with this behaviour originating from the interparticle and Brownian
forces at low shear rates and the hydrodynamic flow of the medium around the particles at high shear rates.

Aggregated systems are very different and form a continuous network of permanently flocculated particles. Since the particles are locked into the network they cannot sediment in the true sense of the word. Here, the whole structure "consolidates" at its base if the weight of the whole flocculated structure above is sufficient to overcome the strength of the individual bonds between the particles, i.e. the network yields. Michaels and Bolger\(^{37}\) described this in terms of a compressive yield stress, \(P_y\), which must exceed the static stress at the base of the network, \(P_s\), for consolidation to occur. The static stress at the base of the network is given by:

\[
P_s = \Delta \rho g H_0 \phi_0
\]

(9.2)

where \(\Delta \rho\) is the density difference between the dispersed and continuous phases, \(g\) is the acceleration due to gravity, \(H_0\) is the initial height of the network and \(\phi_0\) is the initial volume fraction of the dispersed phase. It can be clearly seen that the rate of consolidation depends not only on the effective weight of the network but also on the height of the sample and that consolidation continues only until the weight of the structure is balanced by the strength of the interparticle bonds. However, in order for consolidation to occur, the network must also shear at the walls and as for the compression case, the wall shear stress, \(\sigma_s\), must exceed the static stress at the wall, \(\sigma_w\), which is given by:

\[
\sigma_s = \frac{\Delta \rho g \phi_0 d}{4}
\]

(9.3)

where \(d\) is the diameter of a cylindrical container. Therefore, consolidation also depends on the diameter of the container and for sufficiently narrow tubes the contribution from the walls may be so great that consolidation will not occur. Michaels and Bolger studied the effect of container height and diameter with kaolin slurries and found that the consolidation rate depended strongly on height while diameter had little effect. This was confirmed by Buscall\(^{180}\) with polystyrene latices where \(P_y\) was some 40 to 1000 times greater than \(\sigma_s\). Rheologically these systems are gel like and exhibit plastic flow with a yield stress, below which the sample does not flow. Examples of such systems include clay dispersions and aqueous latices coagulated by electrolyte.\(^{37,69}\)

Reversibly flocculated dispersions are those where the particles are weakly flocculated and rearrange their structure on the same timescale as sedimentation. These systems lie in
between dispersed and aggregated systems and are more complex to study, showing both true sedimentation and consolidation, and pseudoplastic or plastic behaviour rheologically. Accordingly such systems have received limited attention amongst researchers. Buscall and McGown\textsuperscript{184} studied the behaviour of a 1µm polystyrene latex weakly flocculated, probably through bridging, by sodium carboxymethylcellulose (NaCMC). Despite being flocculated, pseudoplastic flow was observed and there appeared to be no minimum gravitational stress below which sedimentation did not occur. Also, when suitably scaled, the sedimentation rate measured as a function of centrifugal acceleration correlated with the shear flow rate measured as a function of applied shear stress. This suggested that shear stress and gravity were having a similar effect on the structure. In a study of a weakly flocculated latex, Partridge\textsuperscript{185} showed that at high concentrations sedimentation occurred after a delay time. This indicated that the structure was changing with time. Weakly flocculated suspensions may also be achieved through depletion flocculation by the addition of a non-adsorbing polymer. Above a certain concentration of polymer, depletion flocculation can create a structure capable of resisting sedimentation. Tadros and Zsednai\textsuperscript{186} used HEC to prevent the formation of dilatant sediments in an aqueous suspension of the fungicide ethirimol. Addition of the HEC resulted in depletion flocculation of the particles into a rigid three dimensional network which was able to resist sedimentation under gravitational stress. Interestingly, this mechanism for preventing sedimentation was considered to be different from the effect caused by xanthan. Buscall and coworkers\textsuperscript{187} studied the sedimentation of polystyrene latices in HEC solutions. They found that the sedimentation was governed by the zero shear viscosity. However, the authors were interested in the sedimentation of stable dispersions and obtained there findings at low latex volume fractions (ca. 0.05) where any depletion flocculation is unlikely. At the other extreme at high volume fractions, Wedlock and coworkers\textsuperscript{188} measured the consolidation rates of a herbicide suspension in xanthan and succinoglycan solutions. The latter, which showed the least separation, also exhibited no yield stress rheologically but a low shear Newtonian plateau at low shear stresses. The authors inferred from this that the resistance to sedimentation arises from the very high resting viscosities and not from a yield stress which inhibits particle movement.

The following work examines the mode of action by which xanthan, which is used extensively in the agrochemical area, inhibits the sedimentation of crop protection suspensions.
9.2 Sedimentation and Rheology of Clofentezine Suspensions.

9.2.1 Compositions.

Three series of clofentezine suspensions were prepared from the suspension described in section 3.1.3 comprising: B to D at 0.3% xanthan, F to H at 0.15% xanthan and I to K without xanthan. Each series contains increasing levels of clofentezine and samples A and D are the corresponding xanthan solutions without clofentezine. The compositions are summarised in table 9.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clofentezine %w/v</th>
<th>Xanthan %w/v *</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>21.5</td>
<td>0.3</td>
<td>0.141</td>
</tr>
<tr>
<td>C</td>
<td>36.6</td>
<td>0.3</td>
<td>0.241</td>
</tr>
<tr>
<td>D</td>
<td>53.0</td>
<td>0.3</td>
<td>0.350</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>20.0</td>
<td>0.15</td>
<td>0.131</td>
</tr>
<tr>
<td>G</td>
<td>36.6</td>
<td>0.15</td>
<td>0.241</td>
</tr>
<tr>
<td>H</td>
<td>53.0</td>
<td>0.15</td>
<td>0.350</td>
</tr>
<tr>
<td>I</td>
<td>21.5</td>
<td>0</td>
<td>0.141</td>
</tr>
<tr>
<td>J</td>
<td>36.6</td>
<td>0</td>
<td>0.241</td>
</tr>
<tr>
<td>K</td>
<td>53.0</td>
<td>0</td>
<td>0.350</td>
</tr>
</tbody>
</table>

* refers to concentration in continuous phase only.

Table 9.1 Compositions for suspension concentrate samples.

9.2.2 Rheology.

Flow curves for samples A to I are presented in figure 9.1. The clofentezine suspensions without any xanthan, I to K, exhibit low, Newtonian viscosities which increase as the clofentezine volume fraction is increased. This is in accordance with the latex results presented in chapter 5. In contrast, the 0.15% xanthan solution, E, is much more viscous, highly shear thinning and exhibits a low shear Newtonian plateau. Adding clofentezine (samples F to H) results in an increase in the viscosity and loss of the low shear Newtonian plateau to give power law behaviour. Similar results but with higher viscosities were found for the samples containing 0.3% xanthan (A to D). The increase in the viscosity of the xanthan solutions and loss of the low shear Newtonian plateau on addition of the clofentezine indicates flocculation of the particles, as found with the latex samples in chapter 8.
Figure 9.1 Viscosity - shear rate data for suspensions A to K.
This flocculation is confirmed with the elastic modulus results presented in figure 9.2. Without any xanthan the elastic modulus values are very low indicating a dispersed system. Addition of xanthan causes a large increase in the modulus. This is partly due to the gel like nature of the xanthan as can be seen from the values at zero clofentezine volume fraction. However, addition of clofentezine increases the modulus values further telling us that a flocculated network of clofentezine particles has formed. This was confirmed by microscopic observations.

Both the viscosity and oscillation measurements agree with those found for the polystyrene latices presented in chapters 6 to 8. Consequently, it may be assumed that the analysis and explanations offered previously are also valid here, namely, that the higher xanthan concentrations would have a more strongly flocculated structure and furthermore, the higher clofentezine volume fractions would, on account of their greater number of particles, form more rigid networks. Both of these effects would be expected to reduce the rate of sedimentation in these suspensions.

9.2.3 Sedimentation.

The sedimentation of samples B to D and F to H, in 50 ml glass measuring cylinders stored at room temperature, was monitored for 2 years and is shown in figure 9.3. With each
sample there was a sharp interface between the sedimenting clofentezine bulk and the supernatant, which was clear of any clofentezine. Wedlock et al.\textsuperscript{163} have measured the volume fraction profiles of sedimenting dispersed and flocculated herbicide suspensions by an ultrasonic velocity scanning technique. Dispersed systems tended to develop a diffuse interface while flocculated systems exhibited a sharp interface. This is in agreement with findings from the rheological measurements in the previous section. Also, two further effects can clearly be seen, there is less separation with both the higher level of xanthan and higher concentration of clofentezine. In fact, the samples containing 0.3\% xanthan had only shown limited sedimentation after two years. However, the lower level of xanthan, 0.15\%, had shown virtually complete sedimentation of the samples in less than a year while sample F with the lowest clofentezine content had completely sedimented in some 30 days. Interestingly, there is a slight increase in the rate of separation of the suspensions after an initial period of time. This is most noticeable with the samples containing 0.3\% xanthan. This indicates that some restructuring of the suspensions occurs with time and is similar to the induction period observed by Partridge\textsuperscript{185} and also by A. Parker et al.\textsuperscript{189} with xanthan flocculated emulsions.

![Graph](image)

**Figure 9.3** Sedimentation of clofentezine suspensions. Samples top to bottom: D, C, B, H, G, F.

Sedimentation of sample D in a range of container sizes showed no dependence on either diameter (12 to 84 mm) or sample height (60 to 144 mm). This means that there is no contribution from the wall shear stress, which other workers have also found to be of minor
importance, and sedimentation is not by consolidation, implying that the structure in the suspensions is of a relatively short range. Here the suspension is behaving as a dispersed system rather than a strongly flocculated network.

After two years, the samples were examined by probing their consistency for the formation of any hard sediment. Sample F and to a small degree G, had formed a dilatant, non-resuspendable clay like sediment while H, B, C and D had soft, redispersable sediments. Such dilatant sediments must be avoided in agricultural formulations since their presence results in an unsprayable product. From these results F and G are unsuitable as agricultural suspensions while H, B, C and D would be rehomogenisable and sprayable. Interestingly, Tadros and Zsednai found similar results for a HEC flocculated fungicidal suspension. Once a flocculated network had been formed, the sedimentation rate was sufficiently reduced and any sediment which had formed was readily resuspendable. This suggests that xanthan is working here in a similar way to the HEC and that it is the floc structure which is important in controlling the sedimentation and preventing the formation of dilatant sediments.

In order to obtain more information on the state of flocculation, the particle size distributions from both the top and bottom of each of these samples were measured and found to be the same and unchanged from the original value. This is also consistent with a flocculated network where fractionation of particles due to their size differences cannot occur.

These findings suggest that the suspensions containing xanthan are flocculated sufficiently weakly that the floc structure can rearrange itself on the timescale of the sedimentation such that behaviour typical of both dispersed and permanently flocculated suspensions is observed. More information can be obtained from further analysis of the data.

Using the Richardson-Zaki correlation (equation 9.1) the relative sedimentation rate is plotted as a function of clofentezine volume fraction in figure 9.4. Due to the polydispersity of these samples it was not possible to measure the terminal velocity of a single sedimenting particle at the limit of zero volume fraction and consequently, this value was obtained by extrapolation of the sedimentation rate to zero clofentezine content. Good agreement was found at 0.3%. However, at 0.15% xanthan the agreement was poor and for the purpose of this comparison the extrapolation was taken through point H with the same slope as the 0.3% samples. It should be noted that this gives apparently high relative sedimentation rates in some cases. The data at 0.3% fits the Richardson-Zaki correlation with $\beta=6.5$ and tells us that the scaling is similar to dispersed suspensions and also that there are no changes in the floc structure as the clofentezine volume fraction increases. However, the data at 0.15% xanthan only fits at the highest clofentezine volume fraction (where it has been scaled to fit) and
deviates significantly at the two lowest volume fractions. This suggests that a change in the floc structure occurs as the clofentezine volume fraction increases from 0.24 to 0.35.

![Relative sedimentation rate graph](image)

Figure 9.4 Relative sedimentation rate for clofentezine in xanthan at 0.3 % (□) and 0.15 %w/v (○). Richardson-Zaki correlation with β=6.5 (line).

In order to detect this change rheologically, data from the "solid" state, below the strain at which the sample starts to flow, must be used since this is a measure of the structure that exists in the sedimenting samples. In chapters 1 and 5 it was shown that the relative viscosity can be used to describe the flow of suspensions according to the Krieger-Dougherty equation (equation 1.24). This can be applied here by replacing the shear viscosity with the complex viscosity from the oscillation measurements. In figure 9.5 this is shown for the suspensions A to K. Both the 0.3% xanthan and xanthan free samples fit the Krieger-Dougherty equation, which again implies that the 0.3% xanthan samples (A to D) are behaving like dispersed systems and have no change in their structure as the clofentezine content is increased. However, at 0.15% xanthan, deviation is seen at the highest clofentezine volume fraction (H). This confirms the sedimentation data findings of a change occurring in the floc structure between the volume fractions of 0.24 and 0.35 and tells us that the strength of the floc network increases. Evidently, the sedimentation behaviour appears to be more complex than particles settling through a highly viscous gel like medium.
9.3 Effect of Xanthan Concentration.

To further understand the sedimentation, aqueous suspensions of clofentezine were prepared at a volume fraction (φ) of 0.241 and a range of xanthan concentrations from 0 to 0.26 %w/v (in the continuous phase). The sedimentation of these samples in 15ml vials is shown in figures 9.6 and 9.7. The vial on the left is without any xanthan and settles slowly with a diffuse interface indicating the particles to be well dispersed. Addition of small amounts of xanthan (0.018 to 0.059%) results in rapid separation of the clofentezine and a sharper interface between the sedimenting clofentezine particles and aqueous supernatant. However, there is also a small amount of clofentezine present in the supernatant. This is likely to be composed of particles at the fine end of the particle size range based on the findings from the latices in chapter 8, where the small latex required more depleting polymer for flocculation. This suggests that the xanthan causes weak flocculation of the larger particles. It is not until ca. 0.1% xanthan is present that a clear supernatant free of any clofentezine particles is found. Here, all the clofentezine is flocculated into a continuous network. This also corresponds to a reduction in the sedimentation rate of the clofentezine.
Figure 9.6 Clofentezine suspensions after standing for 11 days. Xanthan concentrations (L-R): 0.00, 0.018, 0.030, 0.059, 0.103, 0.150, 0.262 %w/v.

Figure 9.7 Elastic modulus for suspensions and xanthan solutions and sedimentation rate for suspensions shown in figure 9.6.
Higher levels of xanthan (0.150 and 0.262%) reduce the rate of separation further. Wedlock et al.\textsuperscript{162} have observed a similar peak in the sedimentation rate with a herbicide suspension, sterically stabilised by a PEO block copolymer, which has been depletion flocculated by free HEC. Again this implies that the xanthan behaves in a similar manner to the HEC.

Comparing the elastic modulus with the sedimentation rate for each of these samples (figure 9.7) reveals a transition at ca. 0.8% xanthan with the modulus which appears to correspond to a reduction in the sedimentation rate of the suspensions. Also shown is the elastic modulus of xanthan solutions without clofentezine particles. Below this transition point, the modulus for the xanthan and suspensions are virtually identical which means that there is no contribution to the modulus from the clofentezine particles and that the particles do not form a continuous network. Above the transition point the suspensions have a greater modulus than the xanthan which means that a continuous flocculated network of clofentezine particles has formed. Interestingly, there is also a transition in the elastic modulus of the clofentezine free xanthan in solution at about the same concentration, suggesting that either the gel structure of the xanthan or the floc structure of the particles network, or both could be responsible for retarding the sedimentation of the dispersed phase. However, if we recall samples F, G and H from the previous section, differences were seen in the separation rate even though the concentration of the xanthan remained constant. Sample F had a very weakly flocculated network which sedimented rapidly while samples G and H had much stronger networks which were more able to resist the gravitational stresses. From this it appears evident that it is the flocculated network rather than the gel structure of the xanthan which is responsible for controlling the sedimentation here.

The sedimentation results suggest that flocculation of clofentezine particles occurs at the lowest level of xanthan added here. This is confirmed in figure 9.8 where photomicrographs of these suspensions are shown. All of the samples have a grainy appearance due to flocculation with the exception of the xanthan free sample (0.000%) which is uniform and is a stable dispersion. However, oscillatory shear measurements reveal that a continuous network of particles only forms once a xanthan concentration of ca. 0.8% is exceeded.

These photomicrographs also show that the flocculation is caused by a depletion mechanism. Addition of water to the slides causes complete dispersion of the particles and can be seen on the right hand side of the 0.150% sample where the flocs are breaking down into their primary particles when the water dilutes the xanthan to a concentration below that required for flocculation.
9.4 Conclusions.

The behaviour reported here can be interpreted accordingly. The addition of xanthan to a suspension of clofentezine particles produces three distinct regions which are illustrated in figure 9.9:

I dispersed, which contains (virtually) no xanthan.

II composed of dispersed particles and small flocculated clusters which may or may not be weakly interconnecting.

III a continuous flocculated network with no dispersed particles.

Figure 9.9 Illustration of flocculated regions.

The transitions between regions I and II can be readily detected from sedimentation or microscopic observations while the transition between regions II and III can be determined by sedimentation and oscillatory shear measurements.
For clofentezine at a volume fraction of 0.241, the transition from region II to III occurred at ca. 0.085 %w/v of xanthan in the continuous phase. This is slightly higher than concentration of 0.02 to 0.05% required to flocculate the 429nm latex but is in fair agreement if we consider the differences in nature and size of the particles.

The series of samples A to K can also be interpreted in terms of these regions. Samples B, C, D and H are in region III while F and G are in region II. Only region III is deemed suitable for commercial formulations.

In region III
- The Richardson - Zaki correlation can be used for predicting sedimentation.
- Pack height and diameter are non-contributory factors in stabilisation.
- Any sediment formed is resuspendable.
- Sedimentation is not by consolidation but by a slow settling of the flocculated network.

In region II
- Rapid separation occurs resulting in a hard, permanent, clay like sediment.

In region I
- A hard, permanent sediment is also formed.

Depletion flocculation is the major contributory factor to stabilisation within these systems and only when a sufficiently rigid network of particles is present can sedimentation be controlled. The existence of a highly viscous xanthan gel in the continuous phase is insufficient to prevent sedimentation. It is expected that the results obtained here with clofentezine would also be applicable to suspensions of other crop protection agents. No direct correlation was found between rheology and sedimentation. However, rheological measurements can provide information on the floc structure of networks, the strength of flocculation between particles and the diffusion rate of floc units. From this it should be possible to ascertain the likely rate of sedimentation of suspensions.

10.1 Conclusions.

10.1.1 Adsorbing Polymers.

In this work, the adsorption of ABA block copolymers on latices and emulsions, and the rheology of the resulting dispersions has been studied by investigating:

(a) the molecular weight of the PEO A blocks of the adsorbing copolymers.
(b) the adsorbed amount of the block copolymers.
(c) the volume fraction of the latices and emulsions.

The polymers adsorption was Langmuirian and all adsorbed strongly onto the latices. The adsorbed amount was sufficiently low for the PEO chains to exist as coils which were extended from the surface. However, the copolymers were some three times more densely packed at the oil-water emulsion interface with the PPO extending into the oil core of the droplet. Here, the polymers were much more like a brush with only a slight dependence on area with length of the PEO chain.

Rheologically, the large latex (429nm) behaved as a hard sphere system in oscillatory shear, showing no differences between the three polymers. However, differences were seen under steady shear at the high shear rate limit. Much larger differences were seen with the small 67nm latex. In each case, the deviation from a hard sphere increased with molecular weight of the stabilising polymer. These differences lead to thicknesses for each of the adsorbed layers, which increased with molecular weight and were in the region of 2-3 times \(2R_g\), but considerably less than the extended chain length, consistent with the picture of extended coils.

Under oscillatory shear, the smaller, soft latex appeared to exhibit compression of the adsorbed polymer layer at high volume fractions. No compression was observed with the larger, hard particles.

10.1.2 Nonadsorbing Polymers.

The interaction of the systems characterised in section 10.1, with nonadsorbing polymers has been studied by investigating:

(d) the concentration of the nonadsorbing polymer (HEC and xanthan).
(e) the molecular weight of the adsorbing polymer.
(f) the molecular weight of the PEO A blocks of the adsorbing copolymers.
Addition of HEC to large (424nm) steric stabilised latices, bearing an adsorbed copolymer layer, results in flocculation once a critical concentration has been exceeded. This transition from a dispersed suspension to a flocculated system is gradual and passes through a two phase region in which both flocculated and dispersed particles coexist. Oscillation measurements can detect the point where a three dimensional volume filling network forms. The elastic modulus scales with the volume fraction to give a fractal dimension in keeping with diffusion limited aggregation. There is a strong dependence of the amount of free polymer required for flocculation on latex volume fraction. Lower volume fractions require more free polymer to induce flocculation. Determination of the concentration of free polymer required to form a flocculated network from yield stress and elastic modulus measurements agrees favourably with values obtained from both direct visual and microscopic observation. Rheological parameters were interpreted in terms of the floc structure.

There is a strong effect of the free polymer molecular weight on the flocculation of aqueous latices stabilised with adsorbed PEO-PPO-PEO block copolymers. Increasing the molecular weight causes both the elastic modulus and the yield stress to rise. This is a consequence of the strength of flocculation increasing. Removing the contribution of the increasing strength of flocculation allows the effect of the range of the depletion force to be examined. Here, the critical strain increased with increasing molecular weight of the depleting polymer. This could be interpreted in the formation of a more compact flocculated network.

Xanthan showed a reduction in the strength of flocculation in relation to the HEC, which was considered due to its rod like shape reducing the volume of the depletion overlap region, rather than differences in the osmotic pressure between xanthan and HEC solutions. Agreement with the depletion flocculation theories for $G_{\text{sep}}$ was poor, the AO model tends to underestimate the strength of the flocculation while the FSV model with Vincent's relationship for the depletion layer thickness, overestimates this strength at low polymer concentrations. At higher polymer concentrations a maximum in $G_{\text{sep}}$ is predicted due to the decrease in the depletion layer thickness. This was not observed experimentally. The critical polymer concentration for flocculation scaled with the molecular weight of the free polymer with an exponent of -0.84, which is comparable to similar systems but larger than some other findings.

Addition of free HEC to small particles results in the formation of gas, liquid and solid phases which exhibit behaviour similar to molecular systems. Regions were found where two, or even all three phases coexisted in equilibrium, in accord with the theory of Lekkerkerker et al.\textsuperscript{139} The free polymer concentrations over which these phases existed depended on the nature of the stabilising layer. Harder steric layers were more readily
flocculated than softer layers. The highest molecular weight copolymer produced the hardest steric stabilising layers and the lowest the softest. Once a flocculated network had formed, a constant value for the elastic modulus was found which was independent of both the free polymer concentration and the nature of the stabilising layer. This means that the floc structure is also constant and does not depend on either the free or stabilising polymer. Yield stress measurements revealed stronger flocculation for the harder particles. An emulsion, in which the stabilising layer is very hard, was flocculated by free PEO while an identical latex, in which the stabilising layer was soft, was not flocculated.

From these results it is expected that bulk properties such as rheology and sedimentation/consolidation of weakly depletion flocculated suspensions and emulsions, such as agricultural and pharmaceutical preparations, can be strongly dependent on the nature of the interfacial stabilising layer.

10.1.3 Agricultural Suspensions.

Finally, this work has also included a "real" system in which the rheology and sedimentation of a microcrystalline suspension of the acaricide clofentezine, suspended in xanthan has been studied.

Depletion flocculation is the major contributory factor to stabilisation within these systems and only when a sufficiently rigid network of particles is present can sedimentation be controlled. The existence of a highly viscous xanthan gel in the continuous phase is insufficient to prevent sedimentation. Three regions were distinguished which exhibited different rheological and sedimentation behaviour. Only one of these was suitable for agricultural suspensions. No direct correlation was found between rheology and sedimentation. However, rheological measurements can provide information on the floc structure of networks, the strength of flocculation between particles and the diffusion rate of floc units. From this it should be possible to ascertain the likely rate of sedimentation of suspensions. It is expected that the results obtained here with clofentezine would also be applicable to suspensions of other crop protection agents.

10.2 Further Work.

This work could be usefully extended by further investigating the effects of the hardness of particles on flocculation, by varying the surface concentration and thickness of the adsorbed layer. The importance of the surface properties of particles has been illustrated vividly in this work, and has often been overlooked by other workers. More detailed
comparisons between the experimental data and the soft sphere depletion theories are required to determine where they are right and where they have shortcomings. Such work will require greater characterisation of systems for example, steric layer volume fraction profiles and penetration depths of steric layers by free polymer by methods such as neutron scattering.

The liquid phase and three phase coexistence are relatively recent discoveries which require more work to fully investigate their structure and fascinating properties.

The sedimentation of agricultural suspensions has been investigated. Further work building on the rheological advances and the greater understanding of the role of the flocculated network in preventing sedimentation could lead to the development of models capable of predicting sedimentation behaviour in such systems.

The work presented in this thesis has advanced understanding in the rheology of flocculated suspensions, its interpretation in the structure of flocculated networks and the process of depletion flocculation, particularly in the area of the softness of particles and the presence of two and three phase regions.
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