Colloids and Interfaces with Surfactants and Polymers

Second Edition
Colloids and Interfaces with Surfactants and Polymers

Second Edition

Jim Goodwin

Life Technologies Corporation
Contents

Preface to the Second Edition ix
Preface to the First Edition xi

1 The Nature of Colloids 1
1.1 Introduction 1
1.2 Colloids in Action 4
1.3 Concentrated Colloidal Dispersions 9
1.4 Interfaces 14
1.5 Surfactants 22
1.6 Solution Polymers 27
1.7 The World of Nanoparticles 28
1.8 Preparation of Nanoparticles 29
1.9 Nanocomposites 39
1.10 Janus Particles 42
1.11 Summary 43

2 Macromolecules and Surfactants 47
2.1 Introduction 47
2.2 Macromolecular Definitions 47
2.3 Conformation in Dilute Solutions 49
2.4 The Flory–Huggins Theory of Polymer Solutions 52
2.5 Polymer Solution Phase Behaviour 57
2.6 Polymers at Surfaces 59
2.7 Polymer Characterization 63
2.8 Biopolymers 67
2.9 Surfactants in Solution 76

3 Interactions Between Colloidal Particles 93
3.1 Introduction 93
<table>
<thead>
<tr>
<th>Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 Intermolecular Attraction</td>
<td>95</td>
</tr>
<tr>
<td>3.3 Notes on Complex Number Manipulation</td>
<td>100</td>
</tr>
<tr>
<td>3.4 Dispersion Forces Between Particles</td>
<td>104</td>
</tr>
<tr>
<td>3.5 Retarded Dispersion Forces</td>
<td>111</td>
</tr>
<tr>
<td>3.6 The General or Lifshitz Theory of Dispersion Forces Between Particles</td>
<td>112</td>
</tr>
<tr>
<td>3.7 Summary and Calculation Guide</td>
<td>114</td>
</tr>
<tr>
<td>3.8 Calculation Strategy</td>
<td>115</td>
</tr>
<tr>
<td>3.9 The Depletion Interaction</td>
<td>120</td>
</tr>
<tr>
<td>4 Forces of Repulsion</td>
<td>129</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>129</td>
</tr>
<tr>
<td>4.2 Electrostatic Interactions</td>
<td>129</td>
</tr>
<tr>
<td>4.3 The Origins of Surface Charge</td>
<td>130</td>
</tr>
<tr>
<td>4.4 The Interaction Between Diffuse Double Layers</td>
<td>144</td>
</tr>
<tr>
<td>4.5 The Interaction Between Two Spheres</td>
<td>148</td>
</tr>
<tr>
<td>4.6 The Effect of Particle Concentration</td>
<td>149</td>
</tr>
<tr>
<td>4.7 Steric Interactions</td>
<td>152</td>
</tr>
<tr>
<td>4.8 Calculation Strategy</td>
<td>160</td>
</tr>
<tr>
<td>5 The Stability of Dispersions</td>
<td>163</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>163</td>
</tr>
<tr>
<td>5.2 The Stability of Charge-Stabilized Colloids – The DLVO Theory</td>
<td>163</td>
</tr>
<tr>
<td>5.3 Mechanisms of Aggregation</td>
<td>166</td>
</tr>
<tr>
<td>5.4 Hetero-Coagulation and Hetero-Flocculation</td>
<td>169</td>
</tr>
<tr>
<td>5.5 The Rate of Coagulation</td>
<td>177</td>
</tr>
<tr>
<td>5.6 Aggregation in Flowing Dispersions</td>
<td>181</td>
</tr>
<tr>
<td>6 The Wetting of Surfaces by Liquids</td>
<td>191</td>
</tr>
<tr>
<td>6.1 Introduction</td>
<td>191</td>
</tr>
<tr>
<td>6.2 The Contact Angle</td>
<td>192</td>
</tr>
<tr>
<td>6.3 Methods for the Measurement of Contact Angle</td>
<td>194</td>
</tr>
<tr>
<td>6.4 Contact Angle Hysteresis</td>
<td>198</td>
</tr>
<tr>
<td>6.5 Spreading</td>
<td>199</td>
</tr>
<tr>
<td>6.6 Curved Surfaces</td>
<td>204</td>
</tr>
<tr>
<td>6.7 Capillarity</td>
<td>205</td>
</tr>
<tr>
<td>6.8 Temperature Effects</td>
<td>212</td>
</tr>
<tr>
<td>6.9 Dynamic Contact Angles</td>
<td>214</td>
</tr>
<tr>
<td>7 Emulsions and Microemulsions</td>
<td>219</td>
</tr>
<tr>
<td>7.1 Introduction</td>
<td>219</td>
</tr>
<tr>
<td>7.2 Emulsification</td>
<td>220</td>
</tr>
</tbody>
</table>
CONTENTS

7.3 Stability of Emulsions 225
7.4 Microemulsions 230

8 Characterization of Colloidal Particles 239
  8.1 Introduction 239
  8.2 Particle Size 240
  8.3 Microscopy 242
  8.4 Zonal Methods 260
  8.5 Scattering Methods 262
  8.6 Analysis of Scattered Radiation 265
  8.7 Neutron Reflection 275
  8.8 Dynamic Light Scattering 276
  8.9 Characterization of the Electrical Properties of Particles 278
  8.10 Viscosities of Dilute Dispersions 295
  8.11 Sedimentation of Dispersions 301

9 Concentrated Dispersions 309
  9.1 Introduction 309
  9.2 The Structure of Concentrated Dispersions 310
  9.3 Rheology 316
  9.4 Linear Viscoelasticity of Colloidal Dispersions 327
  9.5 Phenomenology 328
  9.6 Sedimentation in Concentrated Dispersions 355

Index 367
Preface to the Second Edition

The ubiquitous nature of colloidal systems means that we tend to accept their behaviour without recognizing the unique nature of the colloid state in that it is the fourth state of matter. The heterophase character coupled with size of the dispersed phase or phases results in an extraordinary range of systems that we rely on every day, whether naturally occurring or manufactured, with the size of the component phases lying between the atomic and the macroscopic. Few academic courses include more than a cursory study of the subject, with the result that many scientists working with colloids are unaware that there are many others working on similar problems on apparently quite unrelated materials or applications. So Food Scientists may have many interests in common with Material Scientists, Physicists working with soft matter or complex fluids, Paint Technologists or synthetic Inorganic Chemists.

Colloid Science as a subject reached a significant level of maturity during the second half of the twentieth century, with a good understanding of the forces acting between the components in many systems made up of, not only dilute phases, but also of condensed phases. The activity in recent years has redoubled as applications for nanoparticles, self-assembled systems, complex fluids, and soft solids have permeated the conventional disciplines. The need for a general basic text is greater than ever and this volume is intended to fulfil that need. This second edition is an expansion of the first edition and includes material on biopolymers, nanoparticles, fluorescence and confocal microscopy, in addition to the analysis of sedimentation behaviour. The mathematics used is of a straightforward nature so that many of the quantitative descriptions of the properties can be derived. Where more complex mathematical treatments are required, references to the original texts are included.
The volume should be accessible to undergraduates and postgraduates working in both the physical and life sciences.

Jim Goodwin
Oregon, 2009
Preface to the First Edition

We take for granted the behaviour of colloidal systems from a very early age and as we are formally taught the various scientific disciplines, the nature of colloids is rarely mentioned. This is surprising as it impacts on so many products that we use everyday. The processing and delivery of the correct properties are often dependent on the material being in the colloidal state and yet few courses cover the subject in depth, if at all. As a result, many scientific workers have to acquire their knowledge piecemeal while working on other problems. An introductory text is what is most used in this situation. Specialist texts are often left on the shelf as we search for attempts to solve a particular problem. This present text covers a little more ground than some of the older introductory volumes that are still available but I have attempted to help the reader in the more complicated regions by providing a strategy for any calculations. Some derivations are outside the scope of an introduction, but, where they are straightforward, they are included in order to help readers gain as much insight as possible. None of the mathematics is at a high level.

The references are mainly to specialist volumes in the area. This is not to discourage the reading of the original work but it is because the general volumes are more readily available in many libraries and often help to put the work in context. There will inevitably be some areas that are neglected, as with any introductory volume. This is in part due to what areas are perceived to be currently most generally needed and the composition of this volume has been governed by the questions which are currently asked when discussing problems in industry.

I would like to acknowledge with gratitude the help and encouragement of all of my previous colleagues in the Department of Physical Chemistry at the University of Bristol, UK, especially Professors Ron
PREFACE TO THE FIRST EDITION

Ottewill and Brian Vincent, the past and current holders of the Leverhulme Chair in that Department and also to Dr Paul Reynolds, the manager of the Bristol Colloid Centre.

Jim Goodwin
Portland, Oregon, 2003
1 The Nature of Colloids

1.1 INTRODUCTION

Colloids are all about size. They consist of at least two phases and the dimensions of the dispersed phase have traditionally been considered to be in the sub-microscopic region but greater than the atomic size range, that is, within the range 1 nm to 1 µm. The term ‘colloid’ was coined for ‘glue-like’ materials which appeared to consist of only one phase when viewed under the microscopes of the day. Of course, now we are able to see much smaller particles as microscopy has advanced. However, the size range is still taken to be the same, although 10 µm would be a more appropriate upper limit as the unique behaviour of colloidal particles can still be observed with particle dimensions greater than 1 µm.

The particle size is similar to the range of the forces that exist between the particles and the timescale of the diffusive motion of the particles is similar to that at which we are aware of changes. These two factors, as we shall see later in this volume, are the key to understanding why so many colloidal systems have interesting behaviour and textures. Typically, the range of the interparticle forces is 0.1–0.5 µm whether they are forces of attraction between the particles or forces of repulsion. When we look at a colloidal sol in the microscope, we observe the particles to move around with a random motion. This is known as Brownian motion as it was recorded by the botanist Brown while studying a suspension of pollen grains in the microscope. The cause of this motion is, in turn, the motion of the molecules making up the suspending fluid. All the
atoms or molecules are in random or thermal motion and at any given instant the local concentration of a small volume element of the fluid will be either higher or lower than the global average concentration. The thermal motion of the colloidal particles will tend to be in the direction of the lower molecular densities. As these fluctuate in a random manner, so does the directional motion of the colloidal particles and the velocity is governed by the hydrodynamic drag. We know that diffusion tends to be away from high concentrations to low concentrations, so that if we have a high concentration of particles then there will be a directional drift away from this region. Now, for a sphere, the Stokes drag factor, $s_v$, is a function of the radius of the sphere, $a$, and the viscosity of the fluid, $\eta$, as follows:

$$ s_v = 6\pi \eta a $$  

(1.1)

The motion is random as we have already noted and the net velocity, $v$, is the average distance moved, $\bar{x}$, in the time interval $t$, namely:

$$ v = \bar{x}/t $$  

(1.2)

The work that has been done in moving a particle is simply the hydrodynamic force, $f_v = vs_v$, multiplied by the average displacement $\bar{x}$. The thermal energy available for this motion is $k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. Hence we can write

$$ k_B T = \bar{x} f_v $$  

(1.3)

Substituting for $v$ and $f_v$ and rearranging:

$$ D = \frac{\bar{x}^2}{t} = \frac{k_B T}{6\pi \eta a} $$  

(1.4)

Equation 1.4 is the Stokes–Einstein equation for the diffusion coefficient, $D$, and has units of m$^2$/s. We can define a characteristic timescale for this diffusive motion if we calculate the time it takes for a particle to diffuse a distance equal to the particle radius. This is done by a straightforward substitution of $a$ for $\bar{x}$ in Equation 1.4 as follows:

$$ t = \frac{6\pi \eta a^3}{k_B T} $$  

(1.5)
INTRODUCTION

Table 1.1  Types of colloidal dispersions

<table>
<thead>
<tr>
<th>Phase</th>
<th>Gas (bubbles)</th>
<th>Liquid (droplets)</th>
<th>Solid (particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Molecular solution</td>
<td>Liquid aerosol (mist)</td>
<td>Solid aerosol (smoke)</td>
</tr>
<tr>
<td>Liquid</td>
<td>Foam (shampoo)</td>
<td>Emulsion (mayonnaise)</td>
<td>Sol (ink)</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid foam (packaging)</td>
<td>Solid emulsion (butter)</td>
<td>Solid sol (stained glass)</td>
</tr>
</tbody>
</table>

This is known as the Einstein–Smoluchowski equation. For an isolated particle in water at 20 °C with a diameter of 1 µm, it takes about 0.5 s to diffuse one radius. When the colloidal dispersion becomes concentrated, the interactions with the neighbouring particles (hydrodynamic, electrostatic if the particles are charged or simply van der Waals forces) will slow the movement down. The timescale of our perception is approximately 1 ms to 1 ks so we should expect to observe interesting temporal behaviour with colloidal systems. We will re-visit this point later in this volume.

When we consider the number of possible phase combinations of our heterophase systems, we find that there should be eight different possibilities. This is illustrated in Table 1.1, where either phase could be a gas, solid or a liquid. Two gas phases will mix on a molecular level and do not form a colloidal system. Each of the other combinations results in systems with which we are familiar.

Gas bubbles and liquid droplets are spherical due to the surface tension forces unless the phase volume is very high. Solid particles may be spherical but are often non-spherical. The shape is a function of the history of the formation. Opals are an example of a solid sol with spherical silica particles in an aqueous silicate matrix. The silica particles are amorphous silica, and the distribution of sizes of the particles is narrow and the particles form a face-centred cubic array. It is diffraction of light by this highly regular structure which gives the characteristic colours seen in the polished gemstones. Colloidal dispersions in which the standard deviation on the mean size is less than 10% of the mean are usually considered to be ‘monodisperse’. If the particle size distribution is broader than this, the dispersion is considered to be ‘polydisperse’. Although this cut-off appears arbitrary, monodisperse systems have the ability to form colloidal crystals whereas polydisperse systems do not. Bimodal systems can also form crystalline structures if the size ratio is suitable. When the particles are formed by a crystallization process, other shapes are found.

Silver chloride can be produced as a colloidal dispersion in water as monodisperse cubes. Haematite can form as ellipsoidal plates. Clays are
naturally occurring aluminosilicates that usually form plates. Kaolinite particles (‘china clay’) are hexagonal plates with an axial ratio of $\sim 10:1$. Montmorillonite particles can have much greater axial ratios and under the right conditions can be dispersed as crystals of one or two unit layers thick. Attapulgite has a lath shape and longer rod-like structures can be seen with chrysotile asbestos. These shaped particles show colloidal behaviour when the size is within the colloid range. For spheres or cubes we have three-dimensional colloidal size, with rods that is reduced to two dimensions whereas for plates only one dimension needs to be in the appropriate size range. This last case may seem strange but soap films are a good example of a system with two dimensions well within the macroscopic size range but with the third in the colloid range and being governed by colloidal forces.

This last example of a colloidal system brings into focus systems other than particles that have common ground with particulate colloids. Surface-active molecules or surfactants, such as soaps, detergents and lipids, can self-assemble to form multi-molecular aggregates of colloidal size and show the effects of colloidal forces in addition to their individual phase behaviour.

1.2 COLLOIDS IN ACTION

It will serve as a useful illustration to take some examples of colloidal systems and discuss why the colloidal state is used, what the important aspects are and what characterization is desirable. Although each colloidal material appears to be very different from others, there are frequently generic aspects which we can identify and so we can learn from solutions developed for quite disparate systems.

1.2.1 Decorative Paint

The function of this type of coating is twofold. First, it is intended to protect the surface from damage from environmental conditions. Second, it is intended to cover marks and produce an attractive colour. By choosing a colloidal system, we are able to manufacture and apply this very simply. A polymer film provides the surface protection. Synthesizing the polymer as colloidal particles dispersed in water can efficiently produce this. This material is known as a *latex* and is manufactured by the emulsion polymerization of vinyl monomers. The latter are dispersed as
an emulsion using surface-active materials (surfactants), which adsorb at the surface of the droplets and prevent them from coalescing. Once the polymerization reaction is initiated, the size and stability of the subsequent particles are also controlled by the surfactants. The advantages of using this colloidal synthetic route are excellent heat and mass transfer and simple handling of the product, which can easily be pumped out of the reactor and into storage tanks. Here we have to understand how the surfactants adsorb on different organic phases and operate at different temperatures.

The covering power of the film is provided by a white pigment and the colour by tinting with coloured pigments. Light scattered from the white pigment particles (usually titanium dioxide) hides the underlying surface. The particles must be fine enough to give a smooth film but not too fine or insufficient light will be scattered – 200 nm is about the optimum size. To manufacture this we must understand the control of crystal growth and the subsequent drying process to ensure easy redispersion of the dry powder down to the sub-micron level. The surface of the titanium dioxide is usually covered by a layer of alumina or silica to reduce catalytic breakdown of the polymer film when exposed to sunlight. The dispersion of dry powders in liquids requires surfactants and energy. Here, we have to understand how particles scatter light, the separation of colloidal particles and the ‘wetting out’ of dry powders followed by their subsequent redispersion. Hence this means how surfactants control the wetting of surfaces and how shear forces break up aggregates. The coloured pigments may be organic and therefore require different surfactant systems and so we may put together a system with three different surfactant materials and there will be ample opportunity for exchange at the various interfaces.

The final aspect of our paint is the application. At this point, the sedimentation of the pigment must be controlled and the viscosity has to be such that the wet film thickness is sufficient to give good hiding power. In addition, the brushmarks have to level out as much as possible and the polymer particles in the dry film must coalesce to give a coherent film. Soluble polymers are added to adjust the viscosity and to control sedimentation. This is partly due to the increase in the viscosity of the medium as a result of the entanglements of the long polymer molecules, but a major effect is for the polymers to induce a weak flocculation of the particles in a process known as depletion flocculation. Now, we must also understand how polymer molecules behave in solution, how they interact with particle surfaces and effect the particle–particle interaction forces.
6

THE NATURE OF COLLOIDS

The generic problems that we find when studying this coating areas are:

(a) control of particle size (of both inorganic and polymeric organic particles);
(b) surfactant behaviour in solution and adsorption;
(c) drying and the redispersion of powders;
(d) solution properties of polymers;
(e) particle interaction forces and the effect of surfactants and polymers on these;
(f) sedimentation in concentrated systems;
(g) flow properties of concentrated systems.

1.2.2 Paper

Paper is another material of colloidal origin, which we use without a second thought. It may be in the form of newsprint, a cardboard box, a glossy magazine or the high-quality material that our degree certificates are printed on. It is formed from cellulose, a naturally occurring sugar-based polymer most frequently obtained from trees. When wood is pulped for the manufacture of paper, the cellulose is separated into fibres with sizes stretching down into the colloidal domain. The fibres are filtered to give a mat and dried in a high-speed continuous process. The fibres are negatively charged and this plays a role in the tendency of fibres to aggregate, with the latter being an important feature in the formation of a dense filter mat in which the particles are aligned to give maximum strength in the direction of the moving sheet. The understanding of both particle aggregation and filtration is paramount for successful production in high-speed modern equipment.

Pigments such as titanium dioxide are added to give a white sheet. As the fibres are hollow, some of the pigment particles end up inside the fibres. Removal of this can become a problem when the paper is subsequently recycled. Ink from printing on the exterior of the paper is less of a problem but does require the removal by detergent action of surfactant materials. The attachment and detachment of particles from surfaces require an understanding of the interparticle forces and how we can manipulate them whether by chemical environment or surfactant type.

Glossy paper requires additional colloidal treatment. Well-dispersed kaolinite platelets are coated on to the surface and give a filler aligned parallel to the paper surface. Kaolinite consists of particles with negatively charged faces and positively charged edges, so they tend to stick
together very firmly to give a strong open particle network. This aggregation is controlled either by inorganic ions such as phosphates or organic polyelectrolytes [poly(acrylic acid), for example] and again the ability to manipulate interparticle forces is important. A binder is used with the clay surface to give a sealed, smooth and glossy final surface. A colloidal dispersion of polymer particles makes a suitable material. Emulsion polymerization is the normal route for this type of material. The application of the coating mix requires an understanding of the flow of concentrated dispersions.

Some of the generic problems that we may identify here are as follows:

(a) control of particle-particle forces;
(b) separation of colloidal systems;
(c) interaction of surfactants with surfaces and detergent action in the removal of particulates;
(d) hetero-aggregation and its control;
(e) particle size control.

1.2.3 Electronic Inks

Modern hybrid circuits are built up from sequential printing of fine circuits and layers of insulating material. The circuits are printed using inks with metallic colloidal particles dispersed in organic media. For example, gold or palladium has first to be produced as fine particles, separated and dried. Sufficient knowledge to allow the control of particle size and the subsequent separation of the colloidal particles is paramount here.

To make it into an ink suitable for printing, the system is dispersed in organic solvents with the aid of a surfactant to prevent the particles from sticking together. The mechanism of the stabilization must be understood. The viscosity of the concentrated dispersion has to be suitable for both flow during the screen-printing and the production of the correct film thickness. After drying, the circuits are completed by sintering the particles to give optimum conductivity. This process has parallel problems to film formation with polymer particles in other coatings, and also in the firing of ceramic materials, whether these are derived from clays or other oxides which are employed in high-grade ceramics used, for example, as chip bases in the electronics industry. The generic colloidal problems that we can immediately identify are as follows:

(a) particle size control;
(b) separation and drying of particles;
(c) wetting of dry powders;
8

THE NATURE OF COLLOIDS

(d) adsorption of surfactants;
(e) stabilization of particles in a dispersion;
(f) control of flow properties;
(g) wetting of surfaces;
(h) sintering of fine particles.

1.2.4 Household Cleaners

A large amount of surfactant is sold for domestic cleaning purposes, whether for clothes, skin or other surfaces. Each of these will have a different detailed formulation, of course, and as an example we will choose a cleaner for a surface such as a sink. The first requirement is that there is a high surfactant concentration. This is needed to solubilize grease and resuspend particulate material. Hence an understanding of detergent action is essential. Abrasive particles are required to break up the films that are responsible for staining the surface being cleaned, but these particles should not be of such a size that they produce deep scratches or produce a ‘gritty’ feel. Particles of a micron or two will be satisfactory. The creamy feel is also achieved by the formation of long branching ‘worm-like’ assemblies of the surfactant molecules, which requires a sufficient understanding of surfactant phase behaviour to optimize this requirement.

The size and density of the abrasive particles are such that sedimentation will occur in a short period, and to prevent this the system can be gelled by the addition of a soluble polymer. This has the side benefit of enhancing the texture or feel of the material. The solution behaviour of polymers and the control of the flow properties have to be understood in order to optimize the formulation. The generic problems here can be identified as follows:

(a) phase behaviour of surfactants in solution;
(b) detergent action;
(c) control of particle size;
(d) solution behaviour of polymers;
(e) control of flow properties.

1.2.5 Butter

Milk is a colloidal dispersion of fat droplets which are stabilized by the protein casein. The protein prevents the coalescence of the fat drops
by a combination of electrostatic repulsion and a steric barrier as the protein layers make contact. On standing, the fat drops rise to the top in a process known as *creaming*, which is analogous to sedimentation. So far, colloid stability and creaming (*sedimentation*) can be identified as areas of importance.

In the churning process, a phase inversion is produced and a water-in-oil emulsion is formed from an oil-in-water system. The saturated animal fats have a molecular weight such that they crystallize at temperatures close to body temperature. This is the reason why butter is difficult to spread at low temperatures. Many spreads are produced by blending in lower molecular weight vegetable oils with a lower melting point. The generic colloidal aspects are as follows:

(a) interaction forces between particles;
(b) coalescence of emulsion droplets;
(c) phase inversion of emulsions;
(d) flow behaviour of concentrated dispersions.

There are many other materials that are colloidal at some stage of their use, but the colloidal problems can still be reduced to just a few generic problems. It is important to recognize this in spite of the complexity of a particular system. At first sight, it is often difficult to understand how the apparently abstract physics and chemistry presented in most courses and texts can apply to a ‘practical system’. The application of the general principles, however, are usually sufficient to enable the problems to be both defined and tackled in a systematic manner. All of these points will be addressed in the following chapters.

### 1.3 CONCENTRATED COLLOIDAL DISPERSIONS

Traditionally, our ideas of colloidal interactions have stemmed from the study of the behaviour of dilute systems of colloidal particles and the theoretical work based on two isolated particles interacting. This is nearly always in quite a different concentration region from the systems in which we employ colloids. However, in recent years this situation has changed and we now have a great body of work on concentrated dispersions. Of course, most of the academic work has been on model systems, but general principles apply to the more complicated systems that are in everyday use.
As a starting point, it is important to describe what we mean by a dilute dispersion. This is not based on just the value of the percentage by weight of the disperse phase or even the volume fraction. It is based on the mean separation of the particles compared with the range of the interaction forces between the particles. In the dilute state, the particles are well separated so that the particle interactions are negligible at the mean separation. The consequence of this is that the particles diffuse in a random fashion due to the Brownian motion, with a diffusion constant that can be described by Equation 1.4. The distribution of the particles in space can be considered as uniform, that is, randomly distributed, and the spatial correlations are very weak. Now, this is strictly true only for dispersions of particles which approximate to hard spheres. If there are forces of either attraction or repulsion acting between particles there will be some deviation from a random distribution as particles collide. This point can be important but we do not need to consider it in detail at this stage; we only need to be aware of the possibility. In a fluid continuous phase, the motion of particles can be described by the hydrodynamics appropriate to an isolated particle. This is true for diffusion, sedimentation or viscous flow. The behaviour of the dispersion can be thought of as analogous to that of a gas except that the motion is Brownian and not ballistic, that is, any two particles will experience many changes of direction before colliding. This means that the concept of mean free path is difficult to apply.

If we now steadily replace the continuous phase by more particles, as the concentration increases our colloid becomes a condensed phase and we have a more complicated behaviour. This is a familiar concept to the physical scientist, who will immediately recognize this behaviour as similar to that which occurs when a molecular gas is compressed until it forms a liquid and finally a solid. Many of the thermodynamic and statistical mechanical ideas translate well from molecular liquids to colloids in the condensed state. However, some caution is required as forces can be quite different. A liquid medium, for example, can result in hydrodynamic forces with a range of a few particle diameters. A very attractive feature though is that the colloidal forces can be readily manipulated by changes in the chemical environment of our colloidal particles. This, in turn, can dramatically alter the behaviour and thus it provides the means of manipulating our material to suit our needs more closely.

Now, in this condensed phase there will always be strong interactions between the particles. This is the case whether the interactions are repulsive or attractive. Such a situation gives rise to strong spatial correlations.
and we have a shell of nearest neighbours. The number of particles in this shell is the coordination number and this reflects both the magnitude and type of force in addition to the concentration or particle number density. For example, if the particles are of very similar size and the forces are repulsive, colloidal crystals can be formed with very long-range order. The spatial arrangement is face-centred cubic and, if the lattice spacing is of the order of the wavelength of light, strong diffraction will be seen. Opal is a naturally occurring colloid where this effect is utilized as a gemstone. When the particles are in a liquid medium, ‘exciting behaviour’ can be seen. Three modes of diffusive motion can be identified. The particles are all moving due to the thermal or Brownian motion but are generally constrained to be within their individual coordination shell. This motion is fairly rapid and is known as the \textit{short-time self-diffusive} motion. The motion is still random and, if we were to take a series of ‘snapshots’ of a particular volume, we would see that the number density of particles in that region would fluctuate about the global mean for the dispersion. The diffusion of these regions is the \textit{collective diffusion} and the constant is slower than for short-time self-diffusion. All liquids behave in this way and it is this local density fluctuations in the continuous phase that produces the Brownian motion of the particles. Occasionally, the fluctuations will allow sufficient separation in a coordination shell for a particle to move through and change its neighbours. This is known as \textit{long-time self-diffusion}.

The flow properties reflect this interesting behaviour. To illustrate the point, let us consider a simple system of uniform particles with strong repulsive forces at a high concentration. The particles are highly spatially correlated in a face-centred cubic structure. If we deform the structure into a new shape, the arrangement of particles is distorted. We have had to do work on the structure and the energy is stored by the movement of the particles to a higher energy configuration. An elastic response is observed. Over time, the particles can attain a new low energy configuration in the new shape by the long-time self-diffusion mechanism. The system now will remain in the new shape without applying the external force, that is, the structure has relaxed and the elastically stored energy has dissipated (as heat). The time for this process is known as the \textit{stress relaxation time} and the material is behaving as a \textit{viscoelastic} material. In other words, we are saying that the material is now exhibiting a ‘memory’ and it takes several relaxation times before the original shape is ‘forgotten’. The information that is ‘remembered’ or ‘forgotten’ is in the detailed interaction between individual particles or molecules. When this timescale falls within that of our normal perception we are aware of
the textural changes and many concentrated colloids are manipulated to take advantage of this.

The transition from a dilute to a condensed phase can be very sharp and is a function of the range of the forces, as noted above. We may now move back to consider a system of hard spheres — a system, incidentally, which can only really be attained in a computer simulation but which we can get fairly close to under very limited conditions. In a computer simulation, it is possible to take a fixed volume and increase the fraction of that volume which is occupied by particles, all in random Brownian motion of course. The volume fraction of the ‘dispersion’ is simply the product of the number of particles per unit volume, $N_p$, and the particle volume, $v_p$:

$$\phi = N_p v_p \quad (1.6)$$

The simulations show that a liquid–solid transition occurs at $\phi_t \approx 0.5$. Below the transition, we have a viscoelastic liquid and above it a viscoelastic solid. How does this relate to systems with colloidal particles stabilized by long-range electrostatic repulsion or with extensive polymer layers that prevent the particles from coming together? We can introduce the concept of an effective volume fraction, which is calculated from the particle volume which has been increased by a volume from which neighbouring particles are excluded due to repulsion. For example, we can easily visualize the case for a dispersion of spherical particles, each of which has an attached polymer layer which physically prevents approach of another particle. Figure 1.1 illustrates this schematically.

![Figure 1.1](image)

Figure 1.1 Schematic of a particle with an adsorbed polymer layer which increases the effective volume fraction of the system
The thickness of the polymer layer is denoted by $\delta$, which gives the effective hard sphere diameter as $(d + 2\delta)$. The effective hard sphere volume fraction is now

$$\varphi_{HS} = \frac{N_p \pi (d + 2\delta)^3}{6}$$  \hspace{1cm} (1.7)

and the liquid–solid transition would fall to a lower value of the volume fraction calculated from the core particles. Thus

$$\varphi_{HS} \approx 0.5$$

so

$$\varphi_t \approx 0.5 / (\varphi_{HS}/\varphi)$$

and then

$$\varphi_t \approx \frac{0.5}{(1 + \frac{2\delta}{d})^3}$$  \hspace{1cm} (1.8)

When the stability is due to long-range electrostatic repulsion between particles, we may also define an effective hard sphere diameter. The simplest approach in this case is to recognize that the principle of the equipartition of energy applies to colloidal particles so that a particle moves with kinetic energy $k_B T/2$ along each of the $x$, $y$ and $z$ coordinates. Thus, an average value of the energy of a Brownian collision would now be $k_B T$. We may then take the distance $\delta$ as the distance at which the repulsive energy reaches this value and again define an effective hard sphere diameter as $(d + 2\delta)$. This now enables us to try to estimate the concentration of the liquid–solid transition. Figure 1.2 illustrates the result for a particle with a radius of 100 nm. We will return to this in more detail in a later chapter, but we should note at this point that because the electrostatic interactions are relatively ‘soft’ the material will form a soft solid. That is, the application of an external force can cause large deformations which can be permanent. This is a natural consequence of the range of the interparticle interactions compared with the particle size. The further we move to the right in Figure 1.2, the harder the solid becomes.
1.4 INTERFACES

As soon as we consider a fine dispersion of one phase in another, the issue of the interface between the two phases becomes of major importance. As an illustration of the points that arise, consider the atomization of water into fine droplets in air. The area per unit mass is known as the specific surface area (SSA). The disperse phase is in the form of spherical particles because there are surface tension forces that we will discuss in a moment. The calculation of the SSA is based on the area of a sphere of diameter \( d \) \((\pi d^2)\) divided by its mass \( [(\pi d^3/6)\rho_{H_2O}] \), where \( \rho_{H_2O} \) is the density of water. This gives

\[
SSA = \frac{6}{d\rho_{H_2O}}
\]

Thus, for 1 l of water (i.e. about 1 kg) before atomization, SSA \( \approx 0.05 \) m\(^2\). After spraying to give droplets of 1 \( \mu \)m, SSA \( \approx 6 \times 10^3 \) m\(^2\) kg\(^{-1}\) and we are now dealing with an interfacial area larger than the area of a football field! It is easy to see why the effectiveness of a catalyst is maximized when in a finely divided form and also why the oxidation of finely
divided materials such as metals or flour can be a dangerous problem due to the exothermic reaction becoming uncontrollable. If the droplet size were reduced to the order of 10 nm, the SSA would be $\sim 10^6 \text{ m}^2 \text{ kg}^{-1}$. It is interesting now to consider the fraction of the molecules that would be at the interface as the size of the drop is made smaller. The approximate number is shown in Figure 1.3 and it is a significant fraction for drops in the colloidal size range – particularly when the droplets would be in the nanoparticle size range, that is, up to a few tens of nanometres in diameter. This looks just like a simple exercise in geometry so far, but the implications are important. To illustrate this, let us think about the amount of work we would have to do to take our 1 kg of water down to droplets of 300 nm in diameter where $\sim 0.1\%$ of the water molecules are at the surface. Remember that the intermolecular forces in water are dominated by hydrogen bonding – giving the tetrahedral structure – and at $4^\circ \text{C}$ when the density is 1000 kg m$^{-3}$ this would be nearly complete.

Thus, if we make the crude assumption that each surface molecule is one hydrogen bond short and that the energy of a hydrogen bond is $\sim 40 \text{ kJ mol}^{-1}$, then we may estimate how much work we would have to do to disperse the water into a fog. (Note that there is a factor of 2 as each hydrogen bond broken would result in two fresh surface areas.) The result is also illustrated in Figure 1.3. Of course, if we had broken

![Figure 1.3](image-url)  
**Figure 1.3**  The fraction of water molecules in a drop that are located at its surface. Solid line, fraction of water molecules at the surface; dashed line, work to disperse 1 kg of water.
all the hydrogen bonds, we would have boiled the water (this would take \( \sim 2.5 \times 10^3 \text{kJ} \)), but a lot of work is required to reduce bulk water to drops in the sub-micron level.

The above illustrates that we have to do work to create a new surface and that the origin is the work done against the intermolecular forces. This is a key concept when we consider surfaces or interfaces. Here, the term ‘surface’ is taken to refer to a surface of a liquid or solid in contact with a gas or vapour, and the term ‘interface’ is used to describe the region between two condensed phases, whether two liquids, two solids or a liquid and a solid. In the bulk of a condensed phase, the intermolecular forces act between the atoms or molecules in essentially a symmetrical fashion. At the surface or interface, there is an imbalance as the local chemical environment changes. If we think of the intermolecular forces as molecular springs, the imbalance in attractive force results in a surface tension, \( \gamma \). This acts to minimize the surface area. Now, when the surface area of the liquid is increased by an amount \( \partial A \) against this surface ‘spring’ tension, the amount of work is given by

\[
\partial W = \gamma \partial A 
\]

This is the case only for a pure material. If there are dissolved species present, we must consider the presence of those species at the surface or interface, as we shall see when we explore surfactants. The units of the surface tension are J m\(^{-2}\) (i.e. energy per unit area) and, as energy is force multiplied by the distance moved, the dimensions are also written as N m\(^{-1}\), which is the spring constant. Water, for example, has a value of \( \gamma_1 = 72 \text{mN m}^{-1} \). If we integrate Equation 1.10 up to an area of 1 m\(^2\), we have the energy required to create a fresh surface of unit area, and we see that if the area is the SSA of droplets 300 nm in diameter, we require 1.4 kJ. This value compares favourably with the simplified estimate illustrated in Figure 1.3.

In water, the hydrogen bonding interaction is the strongest intermolecular force but it is not the only contribution. The usual van der Waals forces also play a role and contribute about 25% of the surface energy of water. These are the forces that cause an interaction between all atoms and molecules, even the inert gases. They are the London dispersion forces, which are due to the coupling of the fluctuations of the charge density of the electron clouds of one atom with its neighbours. This will be discussed in some detail in Chapter 3, with aspects of surface energy being discussed in Chapter 6. An important feature of the recognition that an appreciable amount of work is required to generate new surfaces