Colloids and Interfaces with Surfactants and Polymers

AN INTRODUCTION

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Preface

We take for granted the behaviour of colloidal systems from a very early age and as we are formerly 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 is often dependent on the material being in the colloid 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 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.

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Chapter 1

The Nature of Colloids

1 INTRODUCTION

Colloids are all about size. They consist of at least two phases and the dimension of the dispersed phase has traditionally been considered to be in the submicroscopic 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 with the advance of microscopy. 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 to 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 of 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*, is a function of the radius of the sphere, a, and the viscosity of the fluid, η, as follows:

$$s_v = 6\pi\eta a \qquad (1.1)$$

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:

$$v = \bar{x}/t \qquad (1.2)$$

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 T is the absolute temperature and k_B is the Boltzmann constant. Hence we can write:

$$k_B T = \bar{x}vf_v \qquad (1.3)$$

Substituting for v and f_v and rearranging:

$$D = \frac{\bar{x}^2}{t} = \frac{k_B T}{6\pi\eta a} \qquad (1.4)$$

Equation (1.4) is the Stokes–Einstein equation for the diffusion coefficient, D, and has units of $m^2\,s^{-1}$. 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 achieved by a straightforward substitution of a for $\bar{x}$ in Equation (1.4), as follows:

$$t = \frac{6\pi\eta a^3}{k_B T} \qquad (1.5)$$

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 and

Table 1.1. Types of colloidal dispersions

Phase	Gas (bubbles)	Liquid (droplets)	Solid (particles)
Gas	Molecular solution	Liquid aerosol (mist)	Solid aerosol (smoke)
Liquid	Foam (shampoo)	Emulsion (mayonnaise)	Sol (ink)
Solid	Solid foam (packaging)	Solid emulsion (butter)	Solid sol (stained glass)

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, a 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. 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 while polydisperse systems do not. Bi-modal 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. Hematite 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 crysotile asbestos. These shaped particles show colloidal behaviour when the size is within the colloid range. For spheres or cubes, we have a three-dimensional colloidal size, with rods this is reduced to two dimensions, while 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 colloidal 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, lipids etc., can self-assemble to form multimolecular aggregates of colloidal size and show the effects of colloidal forces in addition to their individual phase behaviour.

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 are the important aspects and what characterization is desirable. Although each colloidal material appears to be very different from others, there are frequently generic aspects and so we can learn from solutions developed for quite disparate systems.

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. Secondly, 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 is also controlled by the surfactants. The advantages of using this colloidal synthetic route is 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 onto 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 and their subsequent redispersion. Thus, 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. Soluble polymers are added to adjust the viscosity and to control sedimentation. This is partly due to the increase in the medium viscosity 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.

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

(a) control of particle size (of both inorganic and organic polymeric 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.

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 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 in recycling. 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 onto the surface and give a filler aligned parallel to the paper surface. Kaolinite has both negatively and positively charged surfaces, which tend to stick very firmly together to give a strong open particle network. This aggregation is controlled either by inorganic ions, such as phosphates, or organic polyelectrolytes 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 a knowledge 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.

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 by 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 enable 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, as well as in the firing of ceramic materials, whether these are derived from clays or other oxides such as those employed in high-grade ceramics used, for example, as chip bases in the electronics industry. The generic colloidal problems that we can immediately identify in this case are as follows:

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

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 re-suspend particulate material. Hence, an understanding of detergent action is essential. Abrasive particles are required to break up the films that are responsible for staining 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 in size will be satisfactory. The creamy feel is also achieved by the formation of long branching 'worm-like' assemblies of the surfactant molecules and requires a sufficient understanding of surfactant phase behaviour to optimize this.

   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.

2.5 Butter

Milk is a colloidal dispersion of fat droplets which are stabilized by the protein casein. This 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 though 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.

3 CONCENTRATED COLLOIDAL DISPERSIONS

Traditionally, our ideas of colloidal interactions have stemmed from 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 weight or even the volume fraction. It is based on the mean separation of the particles compared to 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, i.e. randomly distributed and the spatial correlations are very weak. Now, this is only strictly true for dispersions of particles which approximate to hard spheres. If there are either forces of attraction or repulsion acting between particles there will be some deviation from random as the 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, i.e. any two particles will experience many changes of direction before colliding. This means that the concept of a 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, a little caution is required as the 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 the 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 as well as 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 quite rapid and is known as *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 *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 *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, 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, i.e. the structure has relaxed and the elastically stored energy has dissipated (as heat). This is known as the *stress relaxation time* and the material is behaving as a *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'. 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 quite 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, as follows:

$$\varphi = N_p v_p \tag{1.6}$$

The simulations show that a liquid/solid transition occurs at $\varphi_t \sim 0.5$. Below this 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 extensive polymer layers preventing 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.
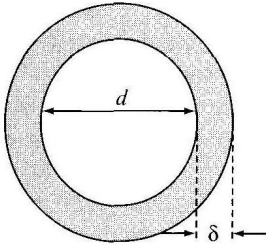

Figure 1.1. Schematic of a particle with an adsorbed polymer layer which increases the effective volume fraction of the system.

The thickness of the polymer layer is denoted by δ which gives the effective hard sphere diameter as $(d + 2\delta)$. The effective hard sphere volume fraction is now:

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

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

$$\varphi_{HS} \sim 0.5$$

so:

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

and then:

$$\varphi_t \sim \frac{0.5}{\left(1 + \dfrac{2\delta}{d}\right)^3} \tag{1.8}$$

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 $k_B T/2$