# 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  $\mu$ m. 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  $\mu$ m would be a more appropriate upper limit as the unique behaviour of colloidal particles can still be observed with particle dimensions greater than 1  $\mu$ m.

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  $0.1-0.5 \,\mu\text{m}$  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

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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:

$$s_v = 6\pi \eta a \tag{1.1}$$

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:

$$v = \bar{x}/t \tag{1.2}$$

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  $k_BT$ , where  $k_B$  is the Boltzmann constant and T is the absolute temperature. Hence we can write

$$k_{\rm B}T = \bar{x} f_v \tag{1.3}$$

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

$$D = \frac{\bar{x}^2}{t} = \frac{k_{\rm B}T}{6\pi\eta a} \tag{1.4}$$

Equation 1.4 is the Stokes–Einstein equation for the diffusion coefficient, D, and has units of m<sup>2</sup> s<sup>-1</sup>. 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:

$$t = \frac{6\pi \eta a^3}{k_{\rm B}T} \tag{1.5}$$

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Table 1.1Types 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)

This is known as the Einstein–Smoluchowski equation. For an isolated particle in water at 20 °C with a diameter of 1  $\mu$ m, 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

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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.

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

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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;

- (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

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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-inoil 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.

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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

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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 *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 we 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 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 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'. 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,  $v_p$ :

$$\varphi = N_{\rm p} v_{\rm p} \tag{1.6}$$

The simulations show that a liquid–solid transition occurs at  $\varphi_t \approx 0.5$ . 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** Schematic of a particle with an adsorbed polymer layer which increases the effective volume fraction of the system

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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

$$\varphi_{\rm HS} = N_{\rm p} \frac{\pi \left(d + 2\delta\right)^3}{6} \tag{1.7}$$

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

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

so

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

and then

$$\varphi_{\rm t} \approx \frac{0.5}{\left(1 + \frac{2\delta}{d}\right)^3} \tag{1.8}$$

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 kinetic energy  $k_{\rm B}T/2$  along each of the x, y and z coordinates. Thus, an average value of the energy of a Brownian collision would now be  $k_{\rm B}T$ . 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.



Figure 1.2 Order-disorder regions calculated for a 100 nm particle

## 1.4 INTERFACES

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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

$$SSA = \frac{6}{d\rho_{\rm H_2O}} \tag{1.9}$$

Thus, for 11 of water (i.e. about 1 kg) before atomization, SSA  $\approx$  0.05 m<sup>2</sup>. After spraying to give droplets of 1 µm, SSA  $\approx$  6 × 103 m<sup>2</sup> kg<sup>-1</sup> 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

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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  $4 \,^{\circ}$ C when the density is  $1000 \,\text{kg}\,\text{m}^{-3}$  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 kJ mol<sup>-1</sup>, 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** 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,  $\gamma_l$ . 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

$$\partial W = \gamma_1 \partial A \tag{1.10}$$

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<sup>-1</sup>, 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  $1 \text{ m}^2$ , 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

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is that the process is endothermic and that the dispersed state is not the lowest energy condition. In other words, there is a natural tendency for droplets to coalesce and for particles to aggregate. To maintain the material in the colloidal state, we must set up the correct conditions.

We have just begun to explore the molecular implications of an interface or surface. The structure of the liquid surface in equilibrium with its vapour cannot be as well defined as that of a crystalline solid and the concept of a well-defined plane is a convenience rather than a reality as there is really an interfacial region. When a surface is expanded or contracted, diffusional motion to or from the bulk accompanies the changes and the intensive properties of the interface remain unchanged. With a solid surface, the situation can be more complex and crystal structure, for example, can result in anisotropy. The surface free energy described above appears to be straightforward. However, equating the surface free energy just with the surface tension can only hold for a pure liquid. Whenever another species is present, the distribution becomes important as this controls the details of the intermolecular forces in the interfacial region. If the concentration of solute species is lower in the surface region than in the bulk phase, the species is termed lyophilic as it 'prefers' the bulk phase to the surface phase. The solute species is *negatively adsorbed* at the surface or interface. Indeed, the stronger interaction between the lyophilic solute species and the solvent can even lead to a small increase in the surface tension. If the molecules tend to accumulate at the interface, they are termed *lyophobic*. This tendency for the solute species to accumulate at the interface implies that the intermolecular interactions are most favourable if there is a separation of the solvent and solute into the region of the surface. This is particularly marked with *amphiphilic* (also termed *amphipathic*) molecules. These are a class of molecules known as surfactants or surface-active agents. In this case, there are two distinct moieties making up the molecule: part of the molecule is lyophilic and the another part is lyophobic. In water, a polar group such as the salt of a carboxylic acid group would be a lyophilic moiety. In water, this is also described as being hydrophilic. A linear paraffin chain or an aromatic hydrocarbon would be a typical lyophobic or *hydrophobic* moiety. The increase in concentration at the interface is known as the surface excess.

The surface tension of water is lowered as solute molecules accumulate in the surface region. Water is an associated liquid and the solute molecules do not display the relatively strong hydrogen bonding forces that occur between adjacent water molecules. Hence, even if the London dispersion forces are stronger, the surface tension is lowered. A



Figure 1.4 Representations of a simple model for the liquid–vapour interface. Gds indicates the Gibbs dividing surface (see text for details)

diagrammatic picture of the surface of a solution is shown in Figure 1.4. Of course, this picture is not restricted to the surface of an aqueous solution.

There are some important ideas illustrated in this figure. The interface between the liquid phase and the vapour phase is not a plane when we work at the molecular level. Rather, it is a region a few molecules in thickness – say five or six – where the molecular density or concentration profile changes from that of the liquid to that of the vapour. Hence we can think of there being a *surface phase*. When there are two molecular species present, we can expect the concentrations to vary with the nature of the solute species, as indicated in the previous paragraph. In the figure, we have large solute molecules which are lyophobic and so there is a surface excess concentration. This illustrated with the peak in the concentration profile (Figure 1.4a) and, as shown, the large molecules have a much lower vapour pressure than the solvent molecules, but this,

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of course, is not a prerequisite. When we know the local concentration, in principle we can estimate the surface tension. Direct measurement of the concentration profiles is not something that has been achieved with precision so far, but it is possible to estimate the surface excess from measurement of surface tension. To do this we need to use just a little thermodynamics, as clearly laid out in the book by Everett [1].

First, we are going to choose a volume for our system at equilibrium which contains saturated vapour, v, the solution phase,  $\ell$ , and the surface phase, s. Our problem is to define the volume of this surface phase. What we are going to do is to model it as though it were just a planar surface with all the material in the surface phase located in that plane. This plane is known as the *Gibbs Dividing Surface* – the Gds line in Figure 1.4(a) – and for simplicity we will consider a volume with unit area Gds as in Figure 1.4(b). As this is a model, we may choose the location of the Gds to be the most convenient, i.e. to make the calculations as simple as possible. The appropriate concentration terms are defined as follows:

 $\Gamma_{1s}$  is the number of moles of solvent species per unit area at the Gds;

 $\Gamma_{2s}$  is the number of moles of solute species per unit area at the Gds;

- $c_{1\ell}$  is the concentration of solvent in the liquid phase;
- $c_{1v}$  is the concentration of solute in the vapour phase;
- $c_{2\ell}$  is the concentration of solute in the liquid phase;

 $c_{2v}$  is the concentration of solute in the vapour phase;

 $c_1$  and  $c_2$  are the total concentrations of solvent and solute in the system, respectively.

Thus, we have  $c_1 = c_{1\ell} + c_{1v} + \Gamma_{1s}$  and  $c_2 = c_{2\ell} + c_{2v} + \Gamma_{2s}$ , that is,

$$\Gamma_{1s} - c_1 = -(c_{1\ell} + c_{1v}) \text{ and } \Gamma_{2s} - c_2 = -(c_{2\ell} + c_{2v})$$

$$\frac{\Gamma_{1s} - c_1}{c_{1\ell} + c_{1v}} = \frac{\Gamma_{2s} - c_2}{c_{2\ell} + c_{2v}}$$

$$\Gamma_{2s} = c_2 + (\Gamma_{1s} - c_1) \left(\frac{c_{2\ell} + c_{2v}}{c_{1\ell} + c_{1v}}\right)$$

which gives

$$\Gamma_{2s} - \Gamma_{1s} \left( \frac{c_{2\ell} + c_{2v}}{c_{1\ell} + c_{1v}} \right) = c_2 - c_1 \left( \frac{c_{2\ell} + c_{2v}}{c_{1\ell} + c_{1v}} \right)$$
(1.11)

In principle, the latter term is experimentally accessible, but we can simplify Equation 1.11 if we choose the location of our Gibbs dividing surface carefully. We will define our dividing surface so that the excess number of solvent molecules on the vapour side is exactly matched by the deficit on the liquid side. This gives the value of  $\Gamma_{1s}$  as 0 and then we call the surface excess of the solute,  $\Gamma_{2s}$ , *the relative adsorption of solute* at the surface.

The Helmholtz free energy of the system is just the sum of the free energy of each phase:

$$F = F_{\rm v} + F_\ell + F_{\rm s} \tag{1.12}$$

The surface term is of importance for our colloidal systems where the surface area is large. For the bulk phases, we have the usual equation for the change in free energy with the amount n of species i:

$$dF_{v} = -S_{v}dT_{v} - p_{v}dV_{v} + \sum_{i} \mu_{vi}dn_{vi}$$
(1.13)

and an analogous equation for the surface:

$$dF_{s} = -S_{s}dT_{s} + \gamma_{s}dA_{s} + \sum_{i} \mu_{si}dn_{si}$$
(1.14)

Here, the pressure term has become the surface tension term and the sign has to change as it is a tension instead of a pressure. The phase volume is replaced by the area of the surface. The temperature is constant so when we integrate Equation 1.14 we have the Gibbs–Duhem equation for the surface:

$$F_{\rm s} = \gamma_{\rm s} A_{\rm s} + \sum_i \mu_{\rm si} n_{\rm si} \tag{1.15}$$

Differentiating Equation 1.15 generally gives

$$dF_{s} = \gamma_{s} dA_{s} + A_{s} d\gamma_{s} + \sum_{i} \mu_{si} dn_{si} + \sum_{i} n_{si} d\mu_{si} \qquad (1.16)$$

We can now equate Equations 1.16 and 1.14, recalling that the 'SdT' term is zero as we are working at constant temperature, to give the

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## following:

$$A_{\rm s} \mathrm{d}\gamma_{\rm s} + \sum_{i} n_{\rm si} \mathrm{d}\mu_{\rm si} = 0 \tag{1.17}$$

Dividing through by  $A_s$  gives us the relative adsorption of the components as follows:

$$d\gamma_{\rm s} = -\sum_i \Gamma_{\rm si} d\mu_{\rm si} \tag{1.18}$$

With a system with just two components, we can choose the Gds to give  $\Gamma_{s1} = 0$  and so remove the solvent from the equations. In addition, it is convenient to use the chemical potential of the solute in the liquid phase (at equilibrium the chemical potential of each species,  $\mu_i$ , is the same in each phase) and we have the *Gibbs adsorption isotherm*:

$$d\gamma_s = -\Gamma_{s2} d\mu_{\ell 2} \tag{1.19}$$

The chemical potential is related to how much of the solute we have in the liquid phase, that is, the activity of the solute:

$$\mathrm{d}\mu_{\ell 2} = RT\mathrm{d}\ln a_{\ell 2} \tag{1.20}$$

This now gives us a convenient means of estimating the relative adsorption of the solute at the surface by measuring the slope of the curve of the surface tension as a function of the natural logarithm of the activity:

$$\Gamma_{s2} = -\frac{1}{RT} \left( \frac{d\gamma_s}{d \ln a_{\ell 2}} \right)$$
(1.21)

This equation is frequently used to estimate the amount of strongly adsorbed material such as surfactants at the liquid surface. It will only be approximate if the molar concentration is used as even though the solution concentrations are usually low there are problems such as they are far from being ideal solutions with an activity coefficient of unity. When there are several components present the algebra is only slightly more complicated, and general expressions are clearly given in the book by Everett [1].

# **1.5 SURFACTANTS**

Surfactants are molecules which have a chemical structure that makes it particularly favourable for them to reside at interfaces, hence they are termed *surface-active agents* or simply *surfactants*. These molecules are a frequent component of colloidal systems whether synthesized or naturally occurring, so it is of great importance to know how much resides at the interfaces in our systems. It was shown above that the rate of change of surface tension with the logarithm of the activity gives an estimate of the amount of the solute adsorbed at the interface. Now, we should use Equation 1.21 to make all the algebraic manipulation worthwhile and to get a feel for what the equation can tell us. The example that we will take is the experimental data plotted in Figure 1.5 for a simple cationic surfactant in water.

The surfactant is hexadecyltrimethylammonium bromide ( $C_{16}TAB$ ). It consists of a straight 16-carbon aliphatic chain with the quaternary ammonium group as the terminal group at one end. The ionic terminal group carries a positive charge and is strongly solvated so that the long



Figure 1.5 Surface tension as a function of concentration for hexadecyltrimethylammonium bromide

#### **SURFACTANTS**

aliphatic chain is carried into solution in water. The solution behaviour of such surfactant molecules will be discussed in more detail in Chapter 2, but it is a good example for our current use. An aliphatic chain of 16 carbon atoms is not very soluble in water and the result is that there is strong adsorption at the water-vapour interface. The experimental curve of surface tension versus concentration is shown in Figure 1.5. The surface tension shows a monotonic decrease up to a concentration of  $9 \times 10^{-4}$  mol l<sup>-1</sup>. Beyond this, the curve is almost parallel to the x-axis. This point at which this abrupt change in slope occurs is known as the critical micelle concentration (cmc). We will come to this shortly, but let us concentrate on the first section of the curve. First, we must recognize that we are using molar concentrations and *not* the activities. Although the concentrations are low, the activity coefficient will be slightly less than 1, so our results will only be approximate, but still of use. The limiting slope of the curve prior to the cmc is  $1.18 \times 10^{-2}$ , which yields a value from Equation 1.12 for  $\Gamma_{s2} = 4.6 \times 10^{-6} \text{ mol m}^{-2}$ . At 35 °C we have the area occupied by a  $C_{16}$ TAB molecule as 0.36 nm<sup>2</sup>; this is about twice that found for an undissociated fatty acid which gives a close packed layer at 0.19 nm<sup>2</sup>. The first thing to note is that the trimethylammonium head group is larger than a carboxylic acid group, but is it twice as big? well, perhaps not. Hence the second feature that we should consider is that the group is positively charged. Like charges repel, and this acts to reduce the packing density.

Let us consider the charge in more detail. We have a surface for which we estimate from the surface tension measurements that there would be one positive charge (i.e.  $1.6 \times 10^{-19}$  C) for every 0.36 nm<sup>2</sup> of surface. This gives a measure of the surface charge density,  $\sigma_s$ , of  $\sim$ 45  $\mu$ C cm<sup>-2</sup>. Experiments with solids, such as silver iodide, or oxides, such as titanium dioxide, yield surface charge densities in the range  $1-15 \,\mu\text{C}\,\text{cm}^{-2}$ , so this clearly would be a very highly charged surface. Of course, the head groups are just one half of the ion pair, while the bulky bromide ion is the counter-ion to the surface charge and will be strongly attracted to the positively charged surface. The binding of the counter-ions reduces the repulsion between head groups. The charge on the surface attracts the counter-ions but, as the concentration of the latter is high, diffusion acts in the opposite direction, tending to dilute the concentration at the surface. The model for the surface now consists of the hexadecyltrimethylammonium ions located in the surface with the hydrocarbon tails extended into the vapour and the head groups in a densely organized layer which is highly charged. The charge is balanced by many counter-ions which are closely bound to the surface and the

remaining counter-ions in a more diffuse layer where the remaining electrostatic attraction is balanced by diffusion. This concept of a charged surface with a layer of counter-ions, some of which may be strongly bound and the remainder are in a diffuse array, is a key concept which helps us to understand the behaviour of charged particles in a dispersion. It is known as the *electrical double layer* and will be discussed more fully in subsequent chapters.

This is an appropriate point to discuss the measurement of the tension of the surface. The data in Figure 1.5 were obtained by measuring the force exerted when attempting to pull a platinum ring out of the surface. The equipment is a DuNoüy tensiometer and this is just one technique for determining the surface tension of a liquid. Chapter 6 give details for several other methods. The inset in Figure 1.5 illustrates the geometry of the measuring element. As a force is exerted on the ring supported perpendicular to the surface, the surface resists the displacement of the ring. In principle, the force at which the ring will detach is given by the surface tension in Newtons per metre multiplied by twice the circumference of the ring (in metres) (remember the surface makes contact with both sides of the platinum wire of the ring). A computer-controlled microbalance does the job of measuring the maximum force very well. However, the points that we need to keep in mind here arise from the usual condition in thermodynamic calculations that at some point we have required the system to be at equilibrium. Thermostatting is, of course, a prerequisite. The first problem that we must deal with is that the vapour phase should be saturated. Hence our system should be enclosed and sufficient time taken for the vapour phase to come to equilibrium. This is particularly important if the vapour pressure of the solute is significant compared with the solvent. This is not a problem with large molecules such as C<sub>16</sub>TAB, however. The second problem of equilibrium is important in this case as at low concentrations of surfactant a significant time passes before the molecules in solution diffuse to the surface and equilibrium becomes established. Each point on the curve shown in Figure 1.5 usually follows a dilution of the solution and mixing. At concentrations close to the cmc there are many surfactant molecules close to the surface and equilibrium is quickly attained. However, at the other end of the curve several minutes are needed for consistent measurements to be achieved, repeat readings are necessary to confirm the values and the time taken to produce the full curve can stretch into hours!

The slope of the surface tension–log(concentration) curve increases steadily as the surfactant concentration is increased. This tells us that the relative adsorption of the  $C_{16}$ TAB is increasing as more is added to

#### **SURFACTANTS**

the water. However, at the cmc there is an abrupt change in slope and what then occurs is that the surface tension changes very little with more concentrated solutions. What we find here is that above the cmc, where the surface is closely packed, there are small aggregates of surfactant molecules in solution. In other words, surfactant in excess of that required to give a concentration equal to the cmc has self-assembled into macro-ions. These aggregates are called micelles with a surface charge, the nature of the charge reflecting that of the hydrophilic head group of the surfactant molecule. Typically, the aggregation number of surfactant molecules in a micelle is around 50–100 when the solution concentration is close to the cmc and the diameter of each micelle is a few nanometres. The core of the micelle can be pictured as rather like a small oil droplet with the surfactant head groups located at the surface. The latter moleties are strongly hydrated and the first two or three carbon atoms of the tail close to the head group are close enough to be influenced by the head group hydration. In fact, on the nanometre scale the concept of a clear distinction between the outer edge of the hydrocarbon core and the aqueous phase breaks down. This ability of surface-active species to self-assemble into various structures is extremely important in a wide range of applications, from cell membranes to washing clothes.

It is also possible to use the variation in surface tension with surfactant concentration to monitor the adsorption of the surfactant on the surfaces of particles in suspension. At equilibrium concentrations up to the cmc, the procedure can be similar to a titration where a surfactant solution of known concentration is added and the surface tension monitored without separating the solids from the liquid. However, beyond the cmc, the phases must be separated, for example by centrifugation, and an aliquot of the supernatant removed and diluted carefully to below the cmc prior to the measurement. The data in Figure 1.6 show the adsorption isotherm of C<sub>16</sub>TAB on a sample of china clay. For comparison, data obtained from radiochemical assay are also given. The faces of the clay particles were negatively charged and the edges positively charged at the pH of the experiment, so the adsorption occurs on the particle faces. The isotherm shape is typical of that of a high-affinity isotherm. Initially, the attachment is by the head groups of the surfactant molecules leading to a monolayer, which results in a hydrophobic surface, and further adsorption occurs to give a bilayer. This coverage occurs at an equilibrium concentration of the surfactant in the solution which is approximately half the value of the cmc. At much higher concentrations, there is evidence of yet further adsorption. The clay surfaces are not simple, however, as they possess 'steps' and the adsorption



Figure 1.6 Adsorption isotherm of hexadecyltrimethylammonium bromide on sodium kaolinite at 35 °C. Data for adsorbed amounts below  $4 \times 10^{-5} \text{ mg g}^{-1}$  were obtained by independent radiochemical assay

close to the step edges may require higher equilibrium concentrations. However, prior to the adsorption of the surfactant, the clay particles are aggregated edge-to-face in a 'house of cards' structure. As soon as the adsorption plateau is reached, the particles are completely dispersed and the surfactant titration technique is well suited to provide this type of adsorption data rapidly. At the plateau, the area occupied by each molecule (calculating the face area from the specific surface area measured by gas adsorption and reducing this by the fraction corresponding to the edge area) is  $\sim 0.5 \text{ nm}^2$  in each layer (note that this is fairly close to that found at the air–water interface at the same equilibrium concentration).

One of the main uses of surfactants is to provide stability to dispersions of colloidal particles and the above titration technique provides a quick method to determine how much surfactant is required. However, the molecules are only physisorbed and *not* chemisorbed, so care has to be taken when additions to the system are made. If the system is diluted with solvent, then surfactant will desorb until a new equilibrium is attained. To prevent this, dilution should be carried out with a solvent phase containing the equilibrium concentration of surfactant required to maintain the value where the adsorption plateau occurs. In addition to the provision of colloidal stability, surfactants are also used to aid the wetting and hence the dispersion of powders in liquids, in addition to aiding the break-up of oil droplets in emulsification processes, as we shall see in later chapters.

#### SOLUTION POLYMERS

## **1.6 SOLUTION POLYMERS**

Macromolecules or polymers, like surfactants, are often a key component in colloidal systems and so it is important to introduce them here in this early part of the text. The robustness of the stability against aggregation of many colloids of biological origin is due to the presence of proteinaceous macromolecules on their surfaces. As an example, we have to look no further than the stabilization of the fatty acid droplets in milk which are stabilized by casein. We often add polymers which will adsorb on particles for this purpose. However, Nature has provided a very effective mechanism for keeping particles apart by three components. Only part of the macromolecule adsorbs, that is, is attached. This leaves the rest, which is solvated to expand away from the interface and prevent other particles from close approach. The proteins are also charged, and the charges repel other particles too, adding to the effectiveness of the stabilizing layer. That charges are located at the outer edge of the adsorbed layer brings an additional advantage in that the origin of the repulsion now occurs at a distance from the core particle surface, which is where we consider the origin of the attractive forces to be.

Synthetic polymers are also used as stabilizers. Homopolymers are not much use as stabilizers, because if they are readily soluble in the continuous phase, they will not form strong, effective attachments to the surface. Hence we emulate the smaller molecules like surfactants and synthesize the polymers with some lyophobic blocks along the chain. Frequently, these polymers are of relatively low molecular weight, typically in the range  $5 \times 10^3 - 50 \times 10^3$ .

Polymers of higher molecular weights are also in common use. These are employed to alter the flow or sedimentation behaviour of colloidal systems. For this reason, they are termed 'thickeners' or 'rheology modifiers'. A polymer in solution increases the viscosity of that solution and high molecular weight material is particularly effective at this so that only a small amount is required. When molecular weights  $>10^6$  are utilized, however, problems in rheological behaviour become apparent. For example droplets do not break away from the bulk cleanly: we see a 'stringy' behaviour, which is due to a marked resistance to stretching. That is, the extensional viscosity is high and applications such as spraying become difficult. One solution to this problem is to use a lower molecular weight polymer and make it behave like much higher molecular weight polymers under quiescent conditions but like lower molecular weight polymers on application. This is done by having a small molar percentage of lyophobic polymer on the backbone of the polymer, which

results in a weak assembly of these regions so all the polymers are associated with each other. This has similarities to the self-assembly of surfactant molecules and is becoming increasingly widely utilized.

It is interesting that when a soluble polymer is added as a rheology modifier to a colloidal dispersion, *a synergistic* effect is often observed. That is, the relative increase in viscosity of the dispersion is markedly greater than the relative increase found for the polymer solution on its own. What occurs here is that a solution polymer, which does not adsorb to the disperse phase, produces a weak, reversible aggregation of the disperse phase and this increased interaction is observed as a further change in the rheological behaviour.

Polymers with charged groups are known as *polyelectrolytes* and these can be added either as stabilizing agents for particulate dispersions or to cause aggregation. For example, poly(acrylic acid) produces good dispersion of china clay by adsorbing on the edges carrying a positive charge. Positively charged polyacrylamide can be used to remove negatively charged particulates by a bridging mechanism which holds particles together and makes them easy so separate. The polymer concentration required to do this is extremely low. Too high a level could give complete coverage of the surfaces by the cationic polymer and provide (unwanted) stability of the system.

## **1.7 THE WORLD OF NANOPARTICLES**

The smaller end of the colloidal size range has been important both in Nature and in manufactured products. However, it has only been recognized in the last decade or so that the small size can give rise to special properties that we may exploit. An important feature of nanoparticles is that they are small when compared with the range of the forces that govern the physical behaviour of colloidal dispersions. The term 'nanoparticle' is currently widely used to describe particles which have at least one dimension >100 nm. Figure 1.3 shows that the fraction of the water molecules making up a spherical drop that occupy a position at the surface of the drop increases rapidly as the drop diameter becomes >100 nm. This is a key factor in many of the applications as the molecules at the surface in a higher energy state and we can see the relationship between surface energy, surface tension and wetting, the macroscopic demonstration of which is discussed in Chapter 6. In water droplets, the intermolecular forces are much weaker than in a solid particle consisting of an inorganic crystal. The high surface energy in combination with the

#### PREPARATION OF NANOPARTICLES

high specific surface area accounts for the high catalytic activity of some metallic nanoparticles. A more exciting result of the marked difference in energy of an atom in the surface region compared with one in the bulk is that some metastable polymorphs, which will necessarily have a lower surface energy, can become the more stable form of the crystal if the size is reduced to the nanoscale so that a large fraction of the atoms have the lower energy. This phenomenon can be observed with alumina, titania, zirconia and the oxides of iron [2, 3]. For example, of the hydrated iron oxides, haematite is the most stable crystal structure until the particle size is reduced to a level where the specific surface area is  $>75 \text{ m}^2 \text{ g}^{-1}$ . Goethite then becomes the more stable structure until the diameter is  $>4.5 \text{ m}^2 \text{g}^{-1}$ , when akageneite is then more stable. The crystal structure controls the magnetic properties. The amount of information that can be stored on magnetic media, for example, is a function of particle size and so the interplay between structure and size is clearly important. The binding of atoms or molecules to the surface of crystals is a function of the surface energy and so the crystal structure will affect this. For example, a smaller extent of binding of lead to a surface would be disadvantageous if we were attempting to sequester contaminants, but an advantage if we were looking for a longer lived catalyst.

## **1.8 PREPARATION OF NANOPARTICLES**

A huge range of materials are now available commercially as nanoparticles, albeit many in small quantities at present. The discussion will therefore be limited to some general issues as the individual chemical issues can easily occupy a whole text and there is currently a huge research and development effort in this area.

## 1.8.1 From the Vapour Phase

Many metals, oxides and even carbon are prepared by condensation from the vapour phase to give nanoparticle dispersions in powder form. The use of the established plasma-gas process gives uniform nanosized particles. The problem here is that the dry powders that result have the nanoparticles in large agglomerates and we have to try to disperse these materials in a variety of media for the final application. The usual first step is to try to produce a liquid dispersion at as high a solids loading as possible. The object is to disperse the agglomerates and break them down

to the single particles, but retain the original surface character. Significant damage to the surface of the crystals can be the precursor to crystal structure change and a loss of activity. Nano-titania is a good example. It has a very high level of catalytic activity in the nanocrystal form, but if the deagglomeration process has been of high enough energy to damage the crystal surface, the material becomes amorphous, reagglomerates and loses its activity.

The process with the lowest energy inputs is the use of a high-speed mixer, which may be sufficient to produce a good dispersion. Higher energy inputs may be required and an ultrasonic probe may be required. In small volumes, heating effects may limit the time or energy input. With larger volumes, a flow-through cell of small internal volume may be used to process large volumes of material. This ensures that all volumes of the material have similar exposures to the energy input and both temperature and exposure time can be controlled by the flow rate. In many cases, however, a higher energy process is required and we may have to resort to bead milling.

Ball milling has been a used for many years to disperse pigments in paint media. In its simplest form, the mill consists of a rotating cylinder which contains the paint mix and 1 cm diameter ceramic balls. The tumbling action of the balls produces collisions with enough energy to fracture aggregates. The relative motion between the surfaces of adjacent balls creates a high-shear region which aids the dispersion. However, it is the impact energy of the collisions that does most of the work. In a conventional ball mill, the surfaces of the pigment particles can be badly damaged. This usually results in some reagglomeration so that well-dispersed nanosized particles are not produced. Smaller beads are more effective and can be run to produce a gentler and less damaging process.

The modern generation of bead mills for ultrafine grinding uses beads in the size range  $50-100 \mu m$ . A flow-through design is used in which the energy input is via a central rotor with multiple triangular vanes. The outlet pipe has a fine screen so that the grinding medium is retained. In order to prevent build-up of the medium on the screen and concomitant back-pressure build-up, the outlet is located in a slotted cylindrical cavity in the end of the rotor. This configuration acts as a centrifugal pump which returns the grinding medium to the agitated region. The critical principle here is that the microbeads are very large in number and so make multiple low-energy impacts with the aggregates that are being disrupted. In addition, at the bead loadings used, the grinding medium acts as a dynamic filter that holds the aggregates back in the grinding

#### PREPARATION OF NANOPARTICLES

zone and prevents them from reaching the outlet screen. These mild milling conditions enable the aggregates of nanoparticles to be dispersed successfully with no surface damage if the energy input is carefully controlled. Beads may be made from yttria-stabilized zirconia or quartz and are effective in the preparation of nanoparticle dispersions of materials such as diamond for polishing applications, titania for catalysts and nickel for capacitors.

## 1.8.2 Templated Growth

Carbon nanotubes have interesting electronic properties and have great potential in areas such as microelectronics and wearable electronics. Single-walled carbon nanotubes have a high current-carrying capacity along the tube, that is, metallic conductance, but they can also be produced as semiconductors. The challenge is to produce bundles of aligned nanotubes of similar dimensions. A quartz substrate can be used as a template for growing single-walled carbon nanotubes by chemical vapour deposition in a direction perpendicular to the crystal surface [4]. Kocabas *et al.* [5] used the step edge of mis-cut quartz crystals to permit orientated nanotube growth horizontally along the surface. When iron catalyst is printed in certain regions, the growth in these regions gives a random orientation, with the result that these regions are highly conducting zones within the semiconducting area of the aligned nanotubes, and offer potential contacts for a carbon nanotube-designed transistor.

## 1.8.3 Formation from Solution

The formation of nanoparticles from solution is a widely used technique and can be applied to both the formation of nanosized crystals and the precipitation of polymers. Although the chemistries will depend on the type of particle being produced, there are some common physical process characteristics that are required to produce nanoparticles with a narrow size distribution. It should be noted that in order to utilize the properties of the nanoparticles fully, monodispersity, that is, a narrow size distribution, is desirable. The first process requirement is to achieve a rapid nucleation process. This is then followed by a slower growth process. If further nucleation can be avoided during this phase of the formation process, the nuclei will grow simultaneously and a monodisperse system will be formed. Finally, stability of the particles against aggregation is

required and this can be achieved by the adsorption of surfactants or by the build-up of charged species at the growing interface. At this point. it will be instructive to describe briefly some nanoparticle syntheses.

#### 1.8.3.1 Gold nanoparticles

Colloidal gold is one of the earliest nanoparticle dispersions formed in a controlled way in the laboratory, originally by Michael Faraday. A sol of monodisperse 40 nm gold particles can be formed by heating a 0.1% solution of chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O) to 100 °C followed by the addition of 1% sodium citrate solution to give a final citrate concentration of 0.25%. The citrate reduces the gold chloride and a stable sol is produced which has negatively charged particles with a diameter of ~40 nm [6]. The gold sol has a strong ruby colour. Surface functionality can be added by reaction with a variety of thiols.

Gold nanoparticles are being used in the medical diagnostics industry for point-of-care devices based on lateral flow platforms. These assays use gold particles with physically adsorbed antibodies that are dried down on a membrane. When hydrated with body fluids (blood, urine or saliva), the particles move chromatographically through the membrane. If antigens from the condition of interest are present in the fluid, they attach to the antibodies on the particles and are carried forward with these to a read-out zone which has some antibodies attached to the membrane matrix. These capture the gold particles, which now have an antigen-covered surface and a red-brown band develops if the condition is present. If not, the gold particles pass through and can be captured in a narrow zone with antigens linked to the matrix. This second region provides a negative control, indicating that no antigens were present in the body fluid and that the capture antibodies were not saturated by a very high level of free antigen. Each manufacturer has their own variant on this general format, but in all cases lateral flow test units are cheap, give results in a few minutes and can be used in the field, clinics or hospitals.

#### 1.8.3.2 Silver halides

When  $\sim 20 \text{ mM}$  solutions of silver nitrate and sodium halide are rapidly mixed at room temperature, a silver halide sol is formed. The particle-solution interface functions like a reversible electrode so that the charge is a function of the ion type that is in excess in solution (silver or halide) and its concentration. For example, monodisperse 50 nm

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cubes of silver iodide can be formed with a high enough negative surface charge if the iodide concentration in solution has  $pI \approx 4$ . If the silver nitrate is in excess, stable, positively charged silver iodide particles are produced if pAg  $\approx 4$ . The particles are single crystals and have a cubic shape with the occasional tetrahedron formed from twinned crystals.

The largest use of silver bromide nanoparticles is in the photographic industry as the particles decompose when exposed to electromagnetic radiation to give silver. The particles are dispersed in a gelatin gel which is used to coat either polymer film or glass plates. Sodium thiosulfate is used to dissolve unreacted silver bromide leaving the well-known negative image.

#### 1.8.3.3 Iron oxide

Magnetite is often produced in nanocrystal form. The crystal contains iron in both of its oxidation states so that we may write the formula as FeO·Fe<sub>2</sub>O<sub>3</sub>. To produce this material, a mixture of ferric and ferrous chlorides is prepared in water in a 3:2 mole ratio and ammonium hydroxide is added to precipitate the magnetite [7]. At this stage, the nanocrystals are heavily agglomerated. For an application such as ferrofluids, the particles need to be dispersed on an organic medium such as tetradecane or hexadecane. A strategy to achieve this is to add oleic acid (hexadecenoic acid) to the mixture and slowly heat with stirring to evaporate the water and ammonia. The dry powder can then be dispersed in the organic phase by ultrasonication, giving hydrophobic, stable nanocrystals with a diameter of ~10 nm.

Small single crystals of magnetite are super paramagnetic, that is, they respond strongly to a magnetic field but show zero residual magnetism when that field is removed. Organic dispersions of magnetite nanoparticles have the potential to be used as ferrofluids. These are dispersions with a moderately high solids loading so that they flow with a viscosity which is only slightly higher than that of the continuous phase but, when subjected to a strong magnetic field, each particle becomes a small magnet and all the magnetic dipoles align with the field so that the particles stick together in a linear structure perpendicular to the flow direction, forming a solid or, at least, a strongly pseudoplastic material. As soon as the field is removed, the sol changes from a solid to a fluid again and flow can resume. The response time is very short, but the greatest problem to their use in units such as high-speed actuators is the mass of the electromagnets required for the high fields.

Magnetite nanoparticles have a strong potential for use in biological applications; however, a limitation is their sensitivity to the chemical environment. Core-shell particles consisting of an iron core with a gold shell can be used successfully as they are inert, biocompatible and can be surface functionalized. Example applications are magnetic resonance imaging (MRI) enhancement, cell sorting and targeted drug delivery [8–10]. Iron-platinum core-shell nanoparticles have a strong potential use in microelectronics as very high-density storage materials when self-assembled into arrays. This is due to the high degree of magnetocrystalline anisotropy of the particles.

#### 1.8.3.4 Semiconductor nanocrystals

Nanocrystals made of semiconductors are known generically as quantum dots and show fluorescence with a high quantum yield. The fluorescence emission maximum is a function of the crystal size. The most common nanocrystals have a cadmium-selenide core with an outer shell of zinc sulfide. High temperatures are used to produce rapid nucleation of the crystals followed by a lower temperature growth stage. Originally pyrophoric organometallic materials were used for the core synthesis [11], but cadmium salts are now used in conjunction with an organic solvent that is stable at high temperature [12]. The colloid stability of the crystals is provided by the adsorption of trioctylphosphine oxide on the surface. After the crystals have been grown to the desired size, as determined from the fluorescence spectrum, the zinc sulfide shell is synthesized by the decomposition of a zinc organometallic material and a sulfur compound. Both spherical and anisometric nanocrystals can be produced, with the former being the easiest to produce with uniform shells. The photostability and quantum yields are a function of the shell quality and the narrow emission spectrum is governed by the degree of monodispersity.

Even in a crystal as small as  $\sim 5$  nm in diameter, there is of the order of  $10^6$  atoms and hence a large number of electrons in the valence orbitals so that there is a band with a continuum of energy levels. Electrons in crystalline solids behave as waves as they move through the solid. As with all semiconductors, the excited electrons 'jump' into a conductance band, which also consists of a continuum of energy levels. The width of these bands is, of course, a function of the number of electrons as there can only be a maximum occupancy of two at any energy level. The minimum energy difference between the highest level of the valence band and the lowest level of the conduction band, the 'band gap', is a function

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of the particular types of atoms making up the semiconductor but also the size of the particle. We can model the electrons in the quantum dot as a 'particle in a box' problem so that the kinetic energy, *E*, is [13, 14]

$$E \propto \frac{\hbar \pi^2}{m^* L^2} \tag{1.22}$$

in which  $\hbar$  is Planck's constant/ $2\pi$ , L is the length of the box, which in this case is the diameter of the quantum dot or the minor axis if the dot is asymmetric, and  $m^*$  is the effective mass of the electron in the crystalline solid ( $\sim 8\%$  of the free electron mass). With our box dimension in the size range 5-8 nm, our band gap energy is in the visible part of the electromagnetic spectrum. Note that it is higher for a 5 nm than a 10 nm crystal, so that when an electron drops from the bottom of the conduction band to the top of valence band we see emission in the blue and into the red with an 8 nm nanocrystal. The surface states of the crystal can act as surface traps so that we can lose electrons from the 'box'. To prevent this, a shell of a larger band gap semiconductor material is grown on the cadmium-selenide core crystal. Any electrons escaping from the core are funnelled down through the zinc sulfide conduction band and then move from the lowest energy in that band back into the cadmium-selenide conduction band. The cadmium-selenide band gap is the minimum downward jump. Figure 1.7 illustrates the band structure of a core-shell quantum dot. The higher the quality of the nanoengineering of the nanocrystal core-shell, the brighter and more photostable are the quantum dots.

Currently, the most widespread use of quantum dots is in the life sciences area, where they are being used in cellular imaging and as molecular tags for research and diagnostic purposes. This use demands that the dots are dispersible as single particles in aqueous buffers. To achieve this, the dots are coated with an amphiphilic polymer which provides colloidal stability to the particle in an aqueous environment and provides chemical functionality for covalently linking biomolecules such as antibodies and nucleic acid oligomers. The brightness of imaged cells is equal to or greater than that which can be achieved by organic dyes; however, the dots open up different and new possibilities because they can all be excited by a single wavelength source at the blue/UV end of the spectrum. (Organic dyes have excitation and emission wavelengths fairly close to each other.) This immediately introduces the possibility of multiplexing and producing images of different labelled parts of a cell without using composite images obtained with different filter sets. 36

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**Figure 1.7** A representation of the electronic band gaps of zinc sulfide-coated cadmium-selenide nanocrystals showing how the band gap reduces with the size of the nanocrystal, which indicates that the emission moves towards the red. The larger band gap of the zinc sulfide shell serves to direct excitons back into the core

In well-engineered dots, such as Q-Dots<sup>®</sup>, the photostability is remarkably good and archiving of fluorescently stained samples without loss of definition is now easily attained.

In the non-life sciences areas, the dots have promise in electro-optical devices and displays. The possibility now exists of photovoltaic cells being manufactured by painting nanocrystals on to a metallized polyester film to make large solar panels. In the future, conducting polymers could replace the metallized film so that solar cells could be spray painted directly on to the roofs and walls of buildings. The greatest barrier to these applications is currently the ability to make large quantities of material with the core–shell quality that is available in the life sciences areas where the volume demand is much smaller.

#### 1.8.3.5 Polymer nanoparticles

Polymer nanoparticles are synthesized from vinyl monomers using the technique of 'emulsion polymerization'. An extensive recent review is available in the book edited by van Herk [15]. Common vinyl monomers used to produce polymer nanoparticles are styrene and acrylate esters. Although many other vinyl monomers are polymerized using emulsion polymerization, the final particle size is larger than the nanosize range

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of  $<10^2$  nm. The technique is straightforward and consists of using an emulsion of a monomer with a low water solubility and a source of free radicals which initiates polymerization in the aqueous phase. Persulfate ions thermally decompose to two sulfate free radicals at a convenient rate at temperatures between 50 and 100 °C. The ionic free radical attacks the  $\pi$ -bond of the vinyl group attaching the initiator fragment to one of the carbon atoms, leaving the other carbon atom as the radical. The chain rapidly propagates as other dissolved monomer molecules come into contact with the radical. Nucleation occurs as the rapidly growing chains become insoluble and precipitate – this occurs after the addition of about five monomer units for styrene but is a function of the solubility of the monomer. The precipitation of a very large number of live polymer chains occurs at a very short time into the reaction. The nuclei adsorb monomer and will aggregate with each other as there is insufficient charge to make them colloidally stable. However, there is also a surfactant present at a concentration in excess of the cmc; sodium dodecyl sulfate is a common example, and this adsorbs on the growing nuclei and suppresses further aggregation so that most of the reaction is dominated by particle growth both by the adsorption of monomer into colloidally stable particles and by adsorption of newly precipitated nuclei. Again, the principle of a short nucleation phase followed by a long growth phase leads to the highest degree of monodispersity. About 20 nm is the smallest particle size attainable by this technique and, with the high nucleation rates required for this, some monodispersity has to be sacrificed and distribution becomes narrower as the size is increased towards the upper end of the nanosize region.

An alternative method to polymer nanoparticles is similar to the comminution process used for some solid systems described earlier in this section. The monomer phase containing an oil-soluble initiator is mixed with an aqueous phase containing a high level of surfactant. The surfactant decreases the interfacial tension markedly, but normal homogenizers will give a droplet size of around 1  $\mu$ m; however, ultrasonics can deliver an emulsion with a narrow size distribution with a mean droplet diameter <100 nm. The curvature of the smaller droplets is more marked than that of the larger droplets, so the Laplace pressure (see Chapter 6) is higher, which drives the monomer phase through the aqueous phase and into the larger droplet fraction. This is 'Ostwald ripening' and will drive a broadening of the size distribution which, in most cases, is undesirable. The solution to this problem is to add a water-insoluble component to the monomer phase. It might seem that a good candidate would be some preformed polymer, but this is not the case. The reason is that as a droplet

shrinks, the osmotic pressure increases at a rate which is dependent on the mole fraction of solute for simple solutions but with the volume fraction in the case of polymer solutions (see Chapter 2). A mole fraction of >1% is required to provide a sufficiently high osmotic pressure and if a high molecular weight polymer were to be added at a volume fraction >1%, the result would be a marked increase in the viscosity of the oil phases and concomitant changes in the emulsification dynamics. An extensive review of the preparation of polymer nanoparticles by the use of miniemulsion processes has been provided by Landfester [16].

Microemulsions are a thermodynamically stable nanoparticle heterophase system and can be used in polymerizing systems [17]. Microemulsion droplets are not static entities and as polymerization occurs drop sizes move to the upper end of the nanoparticle size range. A major advantage of the technique is that the molecular weights obtained are higher than by other heterophase techniques rather than in the size range produced.

#### 1.8.3.6 Swelling clay particles

These types of clay minerals are formed from a 2:1 layer lattice structure and montmorillonite is typical of this class. The clay structure consists of an alumina layer located between to silica layers. The silicon and aluminium atoms are linked via oxygen atoms. Isomorphous substitution within the layers results in a net negative charge which is balanced by cations located between the trilayer sheets. When the cations are monovalent, the trilayer structure can expand as water is drawn in between the sheets by the osmotic pressure difference between the outer medium and that inside the clay particles. The individual sheets are 1.1 nm in thickness; however, the length and breadth are of the order of microns, hence such particles are not usually described as nanoparticles but should included here as some of their properties, for example specific surface area, are characteristic of nanoscale materials.

Clearly in the class of nanoparticles is the synthetic hectorite clay laponite. This clay can be crystallized from a solution of salts containing the correct ion concentrations. At moderate temperatures, crystals are produced which disperse in stacks of three or four sheets. Small-angle X-ray measurements show that the stack dimensions are of thickness  $\sim$ 3.5 nm and diameter  $\sim$ 40 nm [18]. Both lithium and fluoride atoms are present in the clay sheets and the stack structure is thick enough that the edge shows a positive charge (controlled by the fluoride level)

#### NANOCOMPOSITES

and the face has a negative charge (controlled by the lithium level). Laponite is used commercially as a transparent rheology modifier and in specialist paper coatings and is showing some promise as a medium for the synthesis of silver nanoparticles by photoreduction [19].

## **1.9 NANOCOMPOSITES**

A huge range of objects that are in use today are manufactured from or are coated with polymers. It is also common practice to modify the polymer properties by the addition of a filler material. For example, carbon black is added to car tyres to make the elastomer more abrasion resistant, clays to solid polymers to increase the hardness and titanium dioxide to paints to enhance the optical properties. In many cases the particulates are in, or are bordering on, the nanosize range. The drive now is to push the size of the disperse phase down in order to enhance the properties further.

The key feature of the fillers is not simply the loading but what is occurring at the filler-bulk interface. Good adhesion is required otherwise weak points are added, from which stress cracks can propagate. If there is good adhesion, the inclusions can be effective in stopping cracks propagating and, clearly, as the particle size is reduced for a given disperse phase loading, the number density increases and each particle shares in shutting off crack propagation. It is even possible to toughen polymers by inducing small-sized inclusions from phase separation of an incompatible polymer. At high loadings of nanoparticles, the polymer is dominated by the properties of the polymer in the interfacial region as this is now where most of the polymer resides. Hence the way in which the polymer is arranged at the interface can, for example, align chains and increase the net van der Waals forces and enhance mechanical properties such as tensile strength. We will now consider a few examples of nanocomposites which make use of the special properties that are the result of at least one component being in the nanoscale size range.

## 1.9.1 Polymer–Clay Nanocomposites

Sodium montmorillonite is the most common clay to be used in this role. In order for these composites to be successful, the clay needs to be very well dispersed so that most of the high specific surface area is in contact with polymer. The isomorphous replacement of some of the

trivalent aluminium ions by divalent magnesium ions in the octahedral layer results in a net negative charge balanced by cations sandwiched between the tetrahedral silicate layers of adjacent sheets. When these cations are exchanged for cationic surfactant molecules, an oleophilic clay is formed that can be finely dispersed in a polymer matrix with the oleophilic chains acting as steric stabilizing moieties. Single-, di- or tri-chain cationics can be used with the head consisting of a quaternary ammonium group. If high-temperature applications are contemplated, such as in some automobile components, an imidazole head group will be more stable as it is not subject to catalytic degradation at the clay surface at temperatures in excess of 200 °C [20]. The book edited by Pinnavaia and Beal provides a wide range of examples of applications for a variety of polymer matrices [21].

## 1.9.2 Quantum Dot–Polymer Nanocomposites

We discussed in Section 1.8.3.5 how polymer nanoparticles can be prepared, but putting a secondary disperse phase inside such particles at a high loading and with a high degree of dispersion can be challenging. Semiconductor nanocrystals or quantum dots as initially synthesized are hydrophobic and sterically stabilized with strongly bound surfactants on their surfaces. At this stage, they are easily dispersed in a wide range of organic solvents. One strategy for producing a composite is to use cross-linked polymer nanoparticles in a swelling solvent and mix with the organic quantum dot dispersion. Bradley et al. showed that when the very heavily swollen particles had become highly expanded microgels, it was possible to obtain a large number of quantum dots dispersed throughout the gels [22]. Deswelling such gels and transferring the particles back into an aqueous phase, although possible, is not very easy, especially if the polymer particles are small. An alternative is to disperse the particles in a monomer first and then to use the miniemulsion route [16] to prepare nanoparticles containing quantum dots by using ultrasonics, an oil-soluble initiator and the correct surfactant. It is worth noting that other nanoparticle materials such as carbon and titania can be prepared as polymer nanocomposites by this route.

Quantum dots inside a polymer matrix are extremely well protected from oxidants that can cause quenching, so their optical behaviour is extremely robust. An interesting application of these materials was described by Fleischhaker and Zentel [23], where nanocomposites of quantum dots in the cores of core-shell polystyrene-poly(methyl

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methacrylate) nanospheres were then taken to a high total solids content. Monodisperse charged stabilized nanospheres maximize their interparticle separation due to the long-range repulsion and, when concentrated, can form cubic colloidal crystals. Although body-centred cubic structures can be formed, face-centred cubic is the most common form. After this stage was reached, further drying produced a regular lattice structure with quantum dot-rich regions precisely spaced on a three-dimensional lattice. The self-assembled structure produced photonic crystals with photonic stop bands which modified the photoluminescence of the quantum dots, so leading the way to novel optoelectronic devices.

## 1.9.3 Polymer–Cement Nanocomposites

In the initial state, Portland cement is ground into the microparticle size range with a specific surface area of  $\sim 0.5 \text{ m}^2 \text{ g}^{-1}$ . When setting occurs, calcium and aluminosilicates start to crystallize. Water-soluble polymers such as poly(ethylene glycol) can be mixed in at moderate to high concentrations and, if the system is subjected to ultrasonics, very fine structures can be formed such that the resulting set composite has hardness and strength greater than those of steel, although it is brittle. It is possible to form thin, light structures such as gutter or springs from these materials. It is surprising that these fine structure composites have been ignored industrially whereas much coarser composites using polymer particles have wide use.

## 1.9.4 Polymer–Iron Nanocomposites

Polymer microspheres with embedded magnetic iron oxide are now a well-established system for the separation of biological materials such as cells and proteins and are available commercially in a format that lends itself to automation. Ugelstad *et al.* [24] pioneered the methodology of building the nanocomposite *in situ* by using porous polystyrene particles with nitro functionality in the pores, which converted iron salts to a magnetic oxide in nanocrystalline form. The resulting paramagnetic particles are readily functionalized with antibodies and can then be used to attach specifically to particular cells that can subsequently be separated from a matrix [25]. The iron content of these particles can be as high as 35% and the small domain size of the iron oxide ensures excellent paramagnetic behaviour. A high iron loading and large particles

(i.e. diameter >500 nm) make separation very effective even in flowing systems. Ramírez and Landfester used a miniemulsion process to encapsulate magnetite in polymer particles with diameters in the nanosize range [26]. Particles as small as 40 nm containing 30% magnetite were obtained.

## 1.9.5 Polymerized Pickering Emulsions

A 'Pickering emulsion' is an emulsion in which the droplets are stabilized by particles residing at the liquid–liquid interface. When the drops consist of a vinyl monomer, they may be polymerized by the inclusion of a thermally activated oil-soluble initiator. Silica nanoparticles have been used as the stabilizer for polystyrene particles [27]. To aid the stabilizing behaviour, 4-vinylpyridine was added as a minor comonomer. The nitrogen group can protonate to form a pyridinium cation, which adsorbs strongly to the negatively charged silica surface resulting in stable 'armoured' polymer nanocomposite particles with diameters of  $\sim 150$  nm. Titania nanoparticles have been used to stabilize polystyrene particles [28]. In this case, the polymer controls the crystal form and the subsequent catalytic properties of the titania nanoparticles.

# **1.10 JANUS PARTICLES**

The term 'Janus particle' is used to describe particles which have opposing faces with different physico-chemical properties such as hydrophobicity/hydrophilicity or positive/negative charge. The silica nanoparticles producing the Pickering emulsion described in Section 1.9.5 is a good example as the half of a particle in the oil is rendered hydrophobic by the interaction with vinylpyridine whereas the other half of the particle in the water is hydrophilic. Naturally occurring particles, such as kaolinite, which has negatively charge basal surfaces and positively charged edges so that an open aggregate structure resembling a 'house of cards' is formed, begin to indicate some of the types of colloidal behaviour that can be anticipated. However, these examples of split surface behaviour only serve to encourage us to look more closely into how we might engineer biphasic particles of different forms. We already know that amphiphilic molecules show important behaviour at interfaces and so we are immediately led to ask 'how do biphasic nanoparticles behave at interfaces?'. Large particles can be surface modified so that only part

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of the surface has been affected, but we shall not discuss these here as the nanoscale particles appear to have more promise in applications.

Currently, the most studied form of Janus nanospheres is synthesized from terpolymers with a well-defined triblock structure. The centre block is a cross-linkable moiety such as polybutadiene or polyisoprene and the end blocks are made up of linear polymers with different degrees of hydrophilicity. These polymers can self-assemble into micellar units; the cores are then cross-linked to give insoluble cores and the nanoparticles are dispersed with ultrasonics [29]. The nanoparticles have a 'corona' of polymer with different character in each hemisphere. Casting the terpolymer as a film on to a flat substrate allows the polymers to selfassemble into layers. After cross-linking of the butadiene layers, they were swollen with solvent and then sonicated to give discs with the two basal surfaces having different degrees of hydrophilicity [30]. Cylinders have also been prepared from the same terpolymer so that the Janus character is of two hemi-cylinders connected by a cross-linked core [31].

The amphiphilic nature of Janus particle makes them good candidates for study at oil-water interfaces [32] and air-water interfaces [33]. The adsorption energy of a particle at an interface is made up of the sum of the contributions from all the moieties in each phase and so the displacement from the interface is much more difficult than it would be for a single amphiphilic molecule. As a result, we can expect good stabilization of the interface as shown by high emulsion or foam stability, and the particles would not be good emulsifiers as their mobility to an interface is slower than that of small amphiphilic molecules.

## 1.11 SUMMARY

This introductory chapter has defined what we mean by colloidal systems and has illustrated how widely different systems can fit into this form of matter. The related systems of surface-active molecules and macromolecules have also been introduced and it has been shown how they are intimate adjuncts to colloidal dispersions. A few common systems have been described, which, although they appear to be widely disparate, have some basic or generic aspects. These will be a focus of this book and will show why the subject has a marked interdisciplinary flavour.

Nanoparticles have been strongly featured in this introductory chapter. This is a relatively new and fast-moving area of colloid science and the fascination in this area lies in the combination of the range of the colloid forces being the same as or larger than the particle size and the

fact that a very large fraction of the atoms making up these small particles are located at an interface. The latter changes the interatomic forces compared with atoms in bulk material and we can see new physical properties for the materials in this very finely divided form.

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