

1 Introduction

1.1

From the Colloidal State to Nanotechnology

A colloidal dispersion comprises a collection of small particles, droplets or bubbles of one phase, having at least one dimension between about 1 and 1000 nm, and dispersed in a second phase. Either or both phases may be in gas, liquid, solid or supercritical phase states. Matter of colloidal size, just above atomic dimensions and overlapping with the emerging regime of nanotechnology, exhibits physico-chemical properties that differ from those of the constituent atoms or molecules yet are also different from macroscopic material. Colloidal materials have also been referred to as *ultra-divided matter* [1].

The atoms and molecules of classical chemistry are extremely small, usually having molar masses less than 1000 g mol^{-1} and measurable by freezing point depression. Macroscopic particles fall into the realm of classical physics and can be understood in terms of physical mechanics. Residing between these extremes is the colloidal size range of particles whose small sizes and high surface area to volume ratios make the properties of their surfaces very important and lead to some unique physical properties. Their solutions may have undetectable freezing point depressions, and their dispersions, even if very dilute, may sediment out very slowly, in apparent violation of Stokes' law (see Section 2.4.1). Although the particles of classical chemistry may have one or a few electrical charges, colloidal particles may carry thousands of charges. With such strong electrical forces, complete dissociation is the rule for colloidal species, rather than the exception. In addition, the electric fields can strongly influence the actions of neighbouring species.

The earlier definition of colloidal species encompasses not only particles, droplets and bubbles but also thin films on large surfaces (e.g. antiglare coatings on glasses) and thin liquid films such as foam films (separating two vapour phases), emulsion films (separating two droplets), suspension films (separating two solid surfaces) and wetting films (separating a solid or liquid from a vapour). For colloidal species the specific surface areas (surface area per unit mass) are relatively large, therefore the properties of the interfaces can have an important

influence on their properties. For this reason, colloid chemistry and interface chemistry are usually treated as a single scientific discipline.

Systems containing colloidal-sized particles, droplets or bubbles are important because they feature prominently in both desirable and undesirable contexts; in a wide variety of practical disciplines, products and industrial processes; and in everyday life. The problems associated with colloids and interfaces are usually interdisciplinary in nature and a broad scientific base is required to understand them completely. For this reason, the term *colloid and interface science* is often used in modern writing.

The field began to acquire its own identity when Graham coined the term *colloid* in 1861 [2–4]. Since that time, the language of colloid science has evolved considerably [5–8] and makes two principal distinctions: lyophobic (thermodynamically unstable) and lyophilic (thermodynamically stable) colloidal dispersions. If the dispersion medium is aqueous, then the terms *hydrophobic* and *hydrophilic*, respectively, are used. Lyophilic colloids are formed spontaneously when the two phases are brought together because the dispersion is thermodynamically more stable than the original separated state. The term *lyophilic* is less frequently used in modern practice because many of the dispersions that were once thought of as lyophilic are now recognized as single-phase systems in which large molecules are dissolved. Lyophobic colloids are not formed spontaneously on contact of the phases because they are thermodynamically unstable compared with that of the separated states. These dispersions can be formed with mechanical energy input via some form of agitation such as that provided by a propeller style mixer, a colloid mill or an ultrasound generator. The resulting suspension may have considerable stability as a metastable dispersion. Examples of lyophobic colloidal dispersions are emulsions, foams, suspensions and aerosols, and these form the main subjects of this book. Examples of lyophilic colloidal dispersions are surfactant micelles, protein solutions and viruses. These will be dealt with as well in this book, but in less detail.

In modern practise the terms lyophilic and lyophobic (especially hydrophilic and hydrophobic) are often used to characterize surfaces in addition to colloidal dispersions. This sometimes leads to confusing usage. For example, a clay dispersion in water could be classified as a lyophobic colloid with hydrophilic surfaces.

Simple colloidal dispersions are two-phase systems, comprising a dispersed phase of small particles, droplets or bubbles, and a dispersion medium (or dispersing phase) surrounding them. Although the classical definition of colloidal species (droplets, bubbles or particles) specifies sizes of between 1 nm and 1 μm in dealing with practical applications, the upper size limit is frequently extended to tens or even hundreds of micrometres. For example, the principles of colloid science can be usefully applied to emulsions whose droplets exceed the 1 μm size limit by several orders of magnitude. At the other extreme, the field of nanoscience is pushing the lower size limit below 1 nm for organized structures.

To give some idea of the sizes involved here, the diameter of a human blood cell is about 7500 nm (7.5 μm), that of an individual haemoglobin molecule is about 2.8 nm and that of an oxygen molecule is about 0.16 nm (see Table 1.1).

A variety of types of colloidal dispersions occur, as illustrated in Table 1.2. In practice, many colloidal dispersions are more complex, as discussed in the following sections, so these dispersions are characterized by the nature of the continuous phase and a primary dispersed phase, according to the designations in Table 1.2. As already mentioned, one reason for the importance of colloidal systems is that they appear in such a wide variety of practical disciplines, products and processes. Examples include control of filtration, breaking emulsions, fire extinguishing foams, froth flotation and fractionation, dealing with environmental aerosols, managing multiphase fluid flow, preparing foods and formulating personal care products (see Table 1.3). Additional examples can be found in Tables 9.1, 10.1, 11.1, 12.1, 13.1, 13.3, 14.1 and 15.1. The colloidal involvement in a process may be desirable, as in the stabilizing of emulsions in mayonnaise preparation, of a foam for fire extinguishing, of a fluidized bed (suspension) for heavy oil upgrading or of the seeding of a cloud (aerosol) to induce rain. It may also be undesirable, as in the tendency of very finely divided and highly charged particles to resist settling and filtration in water treatment plants.

Example 1.1: It may happen that an emulsion that is desirable in one part of the oil production process may be undesirable at the next stage. For example, in the oilfields, an *in situ* emulsion (oil dispersed in water) that is purposely created in a reservoir as part of an oil recovery process may change to a different, undesirable type of emulsion (water dispersed in oil) when produced at the wellhead. This

Table 1.1 Illustrations of the picoscale, nanoscale and microscale size ranges.

| Species | Approximate size(s) | | |
|-------------------------------|---------------------|----------------|------------------------------|
| | Picoscale (pm) | Nanoscale (nm) | Microscale (μm) |
| Hydrogen atom | 100 | — | — |
| Oxygen molecule | 160 | — | — |
| Rubidium atom | 500 | — | — |
| Buckminsterfullerene | 700 | — | — |
| Single-walled carbon nanotube | 400–1800 | — | — |
| Six carbon atoms aligned | — | 1 | — |
| DNA molecule | — | 2 | — |
| Haemoglobin molecule | — | 2.8 | — |
| Proteins | — | 5–50 | — |
| Virus | — | 10–70 | — |
| Bacteria | — | — | 1–10 |
| Human blood cell | — | — | 8 |
| Airborne pollens | — | — | 5–100 |
| Airborne moulds | — | — | 2–200 |

Adapted from References [9–11].

Table 1.2 Types of colloidal dispersion.

| Dispersed phase | Dispersion medium | Name |
|-----------------|-------------------|----------------------------|
| Liquid | Gas | Aerosol of liquid droplets |
| Solid | Gas | Aerosol of solid particles |
| Gas | Liquid | Foam |
| Liquid | Liquid | Emulsion |
| Solid | Liquid | Sol, suspension |
| Gas | Solid | Solid foam |
| Liquid | Solid | Solid emulsion |
| Solid | Solid | Solid suspension |

emulsion may have to be broken and reformulated as a new emulsion is suitable for transportation by pipeline to a refinery. Here, the new emulsion will have to be broken and water removed from the emulsion, which otherwise would cause problems in the refining processes.

This book is focused on emulsions, foams, suspensions and aerosols, and their fundamentals and applications. The variety of systems represented or suggested by Tables 1.2 and 1.3 underscores the fact that the problems associated with colloids are usually interdisciplinary in nature, and that a broad scientific base is required to understand them completely. A wealth of literature exists on the topic of colloidal dispersions, including a range of basic colloid reference texts [12–29], dictionaries [5–8, 30, 31] and treatises on the myriad of applied aspects, of which only a few are cited here [32–43]. The widespread importance of emulsions, foams and suspensions, in particular, and scientific interest in their formation, stability and properties have precipitated a wealth of specialized publications dedicated to each of emulsions [44–49], foams [50–54], suspensions [32, 55–58] and aerosols [10, 59–63], of which only a few representative examples are given here.

1.1.1

Microscience, Colloids, Nanoscience and Nanotechnology

By definition, the ‘nano’ regime of 0.1–100 nm overlaps heavily with the colloidal size range of 1–1000 nm. As a result, some authors increasingly distinguish between nanoscience/nanotechnology and microscience/microtechnology, the latter referring to science, species and phenomena in the ‘micro’ regime of 0.1–100 μm . So the fields of nanoscience, colloid science and microscience overlap heavily.

Some nanodispersions are simply nanoscale colloidal dispersions under a new name, and are dealt with as such in this book. At the present time, it seems to the author to be most helpful to consider nanoscience and colloidal science together since they overlap so strongly. However, it is important to remain aware that just as the properties of colloidal systems can depart greatly from those in macrosystems, so too can the properties of nanosystems depart greatly from those in colloidal and

Table 1.3 Some occurrences of emulsions, foams, suspensions and aerosols.

| Field | Foam | Emulsion | Suspension | Aerosols |
|---|--|---|--|--|
| Environment and meteorology | Polluted river foams, bubbles of air in oceans and rivers | Water/sewage treatment emulsions, oil spill mousse emulsions | Suspended particles in rain, ocean, lake and river water, glacial run-off | Lightning-generated carbon particles, forest fire ashes, fog cloud, sandstorm, snowstorm |
| Foods | Champagne, soda and beer heads, whipped cream, meringue, ice cream | Milk, butter, creams, mayonnaise, cheese, sauces, cream liqueurs | Jellies, chocolate drinks, semi-frozen drinks, ice cream, vegetable shortening | Aerosol topping sprays |
| Geology, agriculture, and soil science | Foam fumigant, insecticide and herbicide blankets, bubbles of volatiles in magma | Insecticides and herbicides, sulfidic melt in magma | Mud, quicksand, clay soil suspensions | Volcanic ash, forest fire smoke, ash |
| Manufacturing and materials science | Foam fractionation, pulping brownstock foam, detergent foam, flotation de-inking froth | Polishes, asphalt (paving) emulsion, latex paint | Ink, gel, paints, pulp fibre suspensions | Ink jets, industrial exhaust smoke and soot, welding fume, cement dust, asbestos fibres |
| Biology and medicine | Vacuoles, insect excretions, contraceptive foam, gastrointestinal foam | Soluble vitamin and hormone products, biological cells, blood, vesicles | Liniment suspensions, proteins, viruses, polymer-encapsulated drugs | Spray inhalers, airborne pollen, spores, bacteria, viruses |
| Petroleum production and mineral processing | Refinery foams, oil and bitumen flotation froth, fire extinguishing foam, explosion suppressant foam, mineral flotation froths | Emulsion drilling and stimulation fluids, <i>in situ</i> reservoir emulsions, process emulsions, transportation emulsions | Drilling fluids, drill cuttings, mineral process slurries, industrial process tailings | Smoke and soot emissions from flares, upgraders, refineries |
| Home and personal care products | Shampoo suds, shaving cream, contraceptive foam, bubble bath foam, hair styling mousse | Hair and skin creams, lotions | Exfoliating scrubs, facial masks, lip balms | Spray paints, spray polishes, air freshening sprays, insecticide sprays |

microscale systems (that is, the properties may be transitive). Also, some mechanical aspects of nanotechnology deal with colloidal dispersions, such as the use of colloidal ink dispersions in robocasting to build near-nanometre scale three-dimensional structures. Along these lines, books are now emerging that deal with colloidal and interfacial aspects of nanoscience [64, 65] or of nanoscale aspects of colloid and interface science [66–68].

There is also a distinction to be drawn between nanoscience and nanotechnology. Nanoscience is the sub-discipline of science that involves the study of nanoscale materials, processes, phenomena and/or devices. Nanoscience includes materials and phenomena at the nanoscale (typically 0.1–100 nm); hence, it includes areas such as carbon nanoscience (e.g. fullerenes), molecular scale electronics, molecular self-assembly, quantum size effects and crystal engineering. Nanotechnology involves the design, characterization, manipulation, incorporation and/or production of materials and structures in the nanoscale range. These applications exploit the properties of the nanoscale components, distinct from bulk or macroscopic systems. Naturally, there is a substantial overlap of scale between nanotechnology and colloid technology.

There are other important aspects of nanotechnology that are very distinctive, such as carbon nanotubes, quantum dots and the ‘nano’ or ‘bottom-up’ approach, by which is meant the precisely controlled assembly of structures up from the molecular scale that are well organized and with reproducible properties. This latter area is sometimes referred to as *molecular nanotechnology*. Numerous examples of nanoscience and molecular nanotechnology are given in References [8, 30]. Other than giving occasional examples, this book does not deal significantly with the field of molecular nanotechnology.

1.2

Classification of Emulsions, Foams, Suspensions and Aerosols

1.2.1

Emulsions

Emulsions are colloidal dispersions in which a liquid is dispersed in a continuous liquid phase of different composition. The dispersed phase is sometimes referred to as the *internal (disperse) phase* and the continuous phase as the *external phase*. Practical emulsions may well contain droplets that exceed the classical size range limits given earlier, sometimes ranging upwards to tens or hundreds of micrometres. In most emulsions, one of the liquids is aqueous while the other is hydrocarbon and referred to as *oil*. Two types of emulsions are readily distinguished in principle, depending on which kind of liquid forms the continuous phase (Figure 1.1):

- oil-in-water (O/W) for oil droplets dispersed in water,
- water-in-oil (W/O) for water droplets dispersed in oil.

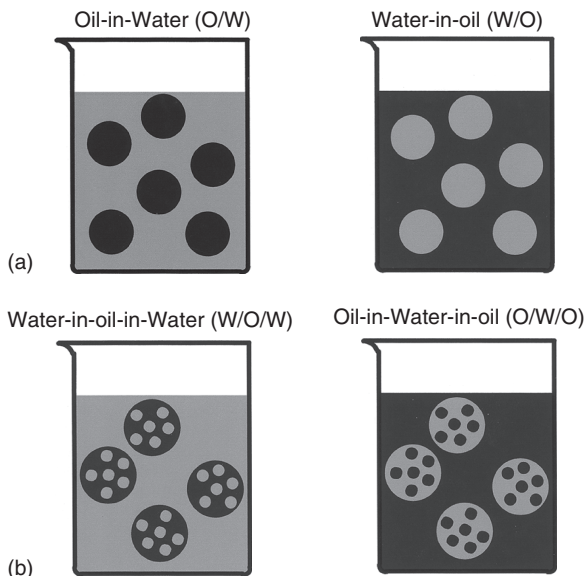


Figure 1.1 (a) The two simplest kinds of emulsions: oil-in-water (O/W) and water-in-oil (W/O). (b) The next level of complexity, water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O). The droplet sizes have been greatly exaggerated.

Subsequent chapters provide many examples of emulsions in industry and everyday life. Solid emulsions, dispersions of liquid in a solid, are not, in general, covered in this book.

Practical situations are not always so simple, and one may encounter multiple emulsions such as double emulsions, that is, emulsions that are oil-in-water-in-oil (O/W/O) or water-in-oil-in-water (W/O/W). For example, O/W/O denotes a double emulsion containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. The double emulsion droplets can be quite large (tens of micrometres) and can contain many tens of droplets of the ultimate internal phase. Developments in and applications of double emulsions have been reviewed by Garti and Bisperink [69]. There can even be more complex emulsion types [33]. Figure 1.2 shows an example of a crude oil W/O/W/O (water-in-oil-in-water-in-oil) emulsion. The type of emulsion that is formed depends on a number of factors.

If the ratio of phase volumes is very large or very small, then the phase having the smaller volume is frequently the dispersed phase. If the ratio is closer to 1, then other factors determine the outcome; see Chapter 11 (especially Table 11.1) for examples of petroleum emulsion types.

Most emulsions are not thermodynamically stable, but as a practical matter, quite stable emulsions can occur that resist demulsification treatments and may be stable for weeks/months/years. Most metastable emulsions that will be encountered in practice contain oil, water and an emulsifying agent (or stabilizer),

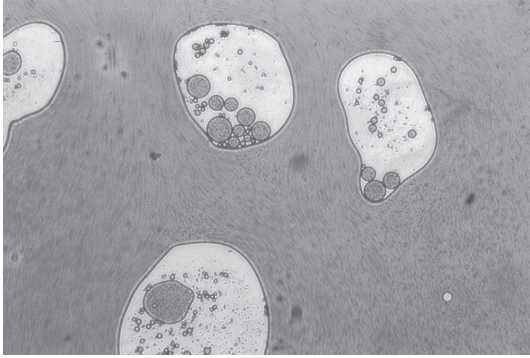


Figure 1.2 Example of a petroleum industry water-in-oil-in-water-in-oil (W/O/W/O) emulsion. (Adapted from Schramm and Kutay [70]. Copyright (2000), reprinted with permission of Cambridge University Press.)

which is usually a surfactant, a macromolecule (polymer), finely divided solids, or a combination of some or all of these. The emulsifier may be needed to make the emulsion easier to form, or it may form a protective film, that helps keep the emulsion from breaking. The one kind of emulsion that is thermodynamically stable, microemulsion, is discussed in Section 3.7.

Emulsions may contain not just oil, water and emulsifier (usually a surfactant) but also solid particles and even gas. Figure 1.3 shows a practical O/W emulsion that contains suspended particles in addition to the oil drops. In the large Canadian oil sands mining and processing operations, bitumen is separated from the sand matrix as an emulsion of oil dispersed in water, and then further separated from the tumbler slurry by a flotation process. The product of the flotation process is bituminous froth, an emulsion that may be water (and air) dispersed in the oil

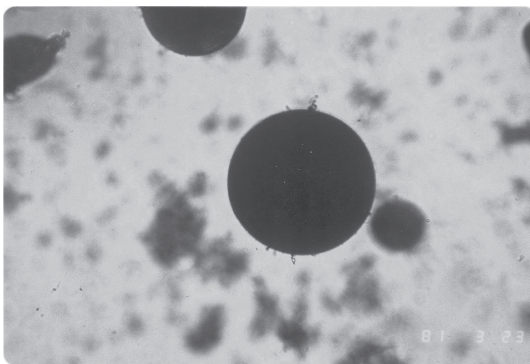


Figure 1.3 Photomicrograph of an emulsified droplet of a crude oil, dispersed in the aqueous solution that was used to release it from the mineral matrix in which it was

originally held. Note the obvious presence of an interfacial film at the surface of the drop. Photomicrograph by the author.

(primary flotation) or the reverse, oil (and air) dispersed in water (secondary flotation) [71]. In either case, the emulsions must be broken and the water removed before the bitumen can be upgraded to synthetic crude oil, but the presence of solid particles and film-forming components from the bitumen can make this very difficult (see Section 11.3.2).

1.2.2

Foams

A foam is a colloidal dispersion in which a gas is dispersed in a continuous liquid phase. The dispersed phase is sometimes referred to as the *internal (disperse) phase* and the continuous phase as the external phase. Despite the fact that the bubbles in persistent foams are polyhedral and not spherical, it is nevertheless conventional to refer to the 'diameters' of gas bubbles in foams as if they were spherical. In practical occurrences of foams, the bubble sizes usually exceed the classical size limit given earlier, as may the thickness of the thin liquid films. In fact, foam bubbles usually have diameters greater than $10\ \mu\text{m}$ and may be larger than $1000\ \mu\text{m}$. Foam stability is not necessarily a function of drop size, although there may be an optimum size for an individual foam type. It is common but almost always inappropriate to characterize a foam in terms of a given bubble size since there is inevitably a size distribution. This is usually represented by a histogram of sizes or, if there are sufficient data, a distribution function.

Subsequent chapters provide many examples of foams in industry and everyday life. Solid foams, dispersions of gas in a solid, are not covered in much detail in this book, although some examples are briefly mentioned in Sections 12.5 and 12.11.

A two-dimensional slice of a general foam system is depicted in Figure 1.4. The general foam structure consists of the bulk liquid at the bottom and a second bulk phase, in this case gas, on the upper side. In a persistent foam, the bubbles are not spherical but have become transformed into foam cells, polyhedra separated by almost flat liquid films. Such foams are referred to as *dry foams* or *polyederschaum*. The polyhedra are almost, but not quite, regular dodecahedra. Within the magnified region of Figure 1.4, the various parts of the foam structure are clarified. The gas phase is separated from the thin liquid film by a two-dimensional interface. In reality, there does not exist a sharp dividing surface between gas and liquid properties. Dictated by mathematical convenience, the physical behaviour of this interfacial region is approximated by a two-dimensional surface phase (the Gibbs surface). For the purposes of this book, a lamella is defined as the region that encompasses the thin film, the two interfaces on either side of the thin film and the part of the junction to other lamellae.

The arrangement of films coming together at equal angles of 120° (called the *Steiner angle*) results from the equalization of the surface tension vectors, or contracting forces, along the liquid films. The bubbles in a foam arrange themselves into polyhedra such that, along the border of a lamella, three lamellae always come together at angles of 120° ; the border where they meet is termed a *Plateau border*. In three dimensions, four lamellae meet at a point at the tetrahedral angle,

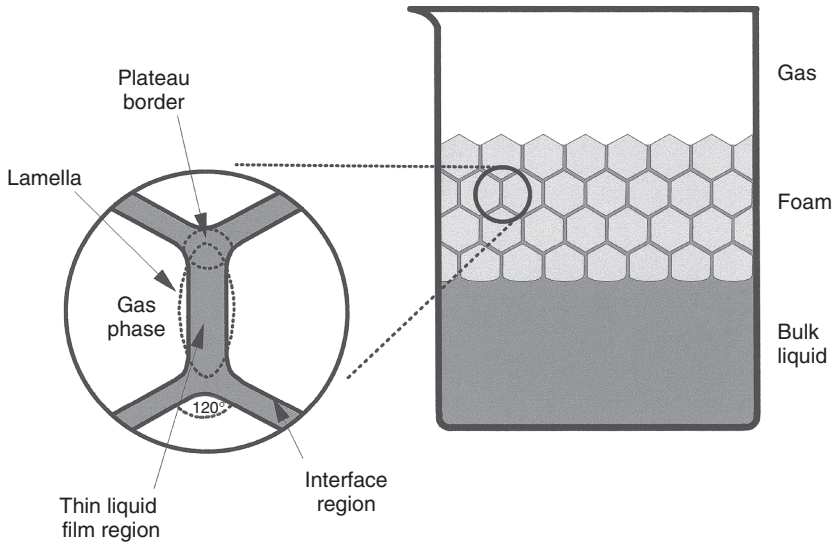


Figure 1.4 Illustration of a generalized foam system showing aspects of a foam lamella.

approximately 109° . Observations of dynamic foams show that any time more films happen to come together, a rearrangement immediately takes place to restore junctions of only three films at plateau borders in 2D and four lamellae in 3D. The three-dimensional foam bubbles are spherical in wet foams (i.e. those with gas volume fractions of up to $\phi = 0.74$, the maximum volume fraction possible for an internal phase made up of uniform, incompressible spheres), but the foam bubbles start to distort in drier foams, in the range $0.74 < \phi < 0.83$ (approximately). In still drier foams, the foam cells take on a variety of polyhedral shapes in drier foams ($\phi > 0.83$, approximately). There are many polyhedrons that can exist in foams and froths. One of the model shapes that may be the most stable, in terms of minimizing surface free energy, is the Kelvin's tetrakaidecahedron, which has eight non-planar hexagon faces and six planar quadrilateral faces [72]. It should be remembered, however, that most foams contain a distribution of shapes (and sizes) [73].

Foams may contain not just gas and liquid (and usually surfactant) but also dispersed oil droplets and/or solid particles. Figure 1.5 shows a practical aqueous foam that contains dispersed oil droplets within the foam lamellae. This can occur, for example, when a foaming solution is used for detergent action in a cleaning process (see Section 12.2) or when a foam is propagated through an underground oil reservoir as part of an enhanced oil recovery process [74] (see Section 11.2.2). Ferrofluid foams are liquid foams containing a stable suspension of magnetic particles (see Section 16.3). A foam can also contain an emulsion in its liquid phase. Whipped cream provides an example of a foam emulsion in that it consists of air bubbles dispersed in cream, and the cream is an emulsion (see Section 13.5). Foam emulsions are also termed *aerated emulsions*.

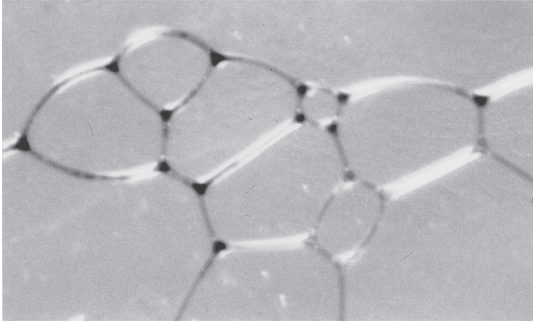


Figure 1.5 Example of a petroleum industry foam containing emulsified oil droplets. Photomicrograph by the author.

In industry, froth flotation processes are used to separate particles and/or droplets gas by attaching them to gas bubbles, which rise in a flotation vessel to form a product layer of foam termed *froth*. The most common type of froth flotation is induced gas flotation (also termed *scavenging flotation*), in which gas bubbles are injected (sparged) into the flotation medium. Variations include dissolved gas flotation, in which gas is dissolved in water after which microbubbles come out of solution, attach to the dispersed species of interest and cause them to float (see also Section 8.3 and Chapter 10).

1.2.3

Suspensions

A suspension is a colloidal dispersion in which a solid is dispersed in a continuous liquid phase (Figure 1.6). The dispersed solid phase is sometimes referred to as the *internal (disperse) phase* and the continuous phase as the external phase. Suspensions may be either aqueous or non-aqueous.



Figure 1.6 Suspension of amber particles. Photomicrograph by the author.

The classical size range for colloidal dispersions given earlier (1 nm to 1 μm) assumes that dispersed species have a spherical shape. When other shapes are considered, particles with diameters of up to 2 μm can be well described as colloids. Practical suspensions usually have diameters greater than 0.2 μm and often contain particles that exceed the classical size range limits given earlier, sometimes to 50–100 μm in diameter. The principles of colloid science are still important to the behaviour of such larger particles. The particle sizes can also fall below the classical size limit given earlier. Nanoparticle suspensions are increasingly being developed, for example, in some literature, the term *sol* is used to distinguish suspensions in which the particles are of such very small sizes, and suspensions of nanosized particles are sometimes referred to as *nanosuspensions* or *nanofluids*.

In addition, clay particles can exhibit widely contrasting particle dimensions: their ratio of particle diameter to thickness can range from 10:1 to 250:1, depending on the nature of the clay and its exchangeable ions [55]. Particles, which are frequently irregular in shape, are somewhat unique in the variety of associations that can take place in their dispersion. Figure 1.7 shows some of the modes of association among suspended clay mineral particles [75]. Such associations have a profound effect on the flow properties of these dispersions (see Section 6.5).

A suspension of particles in turbulent gas or liquid, or a mixture of both, behaves much like a fluid, hence the terms *fluidization* and *fluidized* beds.¹⁾ In the fluidized state, much larger particles can be maintained in suspension than would be possible under static or laminar flow conditions. This provides a means, for example, to make large particles flow like a fluid. The minimum fluidization velocity is the velocity of gas or liquid that is just needed to support the weight of the particles. At greater velocities, the particles are transported. When the fluidized bed is maintained by the flow of gas bubbles, there is also a critical, minimum bubble size. The principal difference between fluidized beds maintained by liquid and gas flow is that the former type, being stabilized by an integral continuous phase, is homogeneous. The latter type, being stabilized by bubbles, rather than a continuous phase, is not homogeneous. There are differences in density contrast between the phases, and there can also be differences in electrical charging. Fluidized beds involving solid particles have been used where efficient mixing, heat transfer and/or mass transfer are needed [76]. Examples include fluidized beds of catalyst particles, of coal particles for combustion and in deep bed filtration for water treatment. If the particles are less dense than the fluid, then the bed is fluidized by causing the continuous phase to flow downwards rather than upwards. This has been termed *inverse fluidization* [76].

An example of a particle size classification system is shown in Table 1.4. Subsequent chapters provide many examples of suspensions in industry and in everyday

1) In laminar flow, all elements of a fluid passing a certain point follow the same path or streamline. In turbulent flow, all components of a fluid passing a certain point do not follow the same path. The flow velocity corresponding to the transition from laminar to turbulent flow conditions, or vice versa, is called the *transition velocity*.

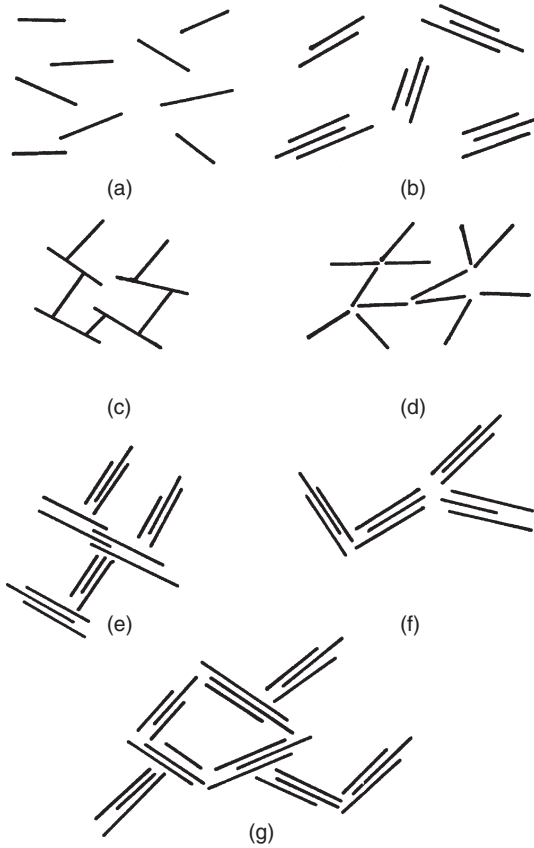


Figure 1.7 Modes of platelet associations in clay suspensions: (a) dispersed, (b) FF aggregated, (c) EF flocculated and dispersed, (d) EE flocculated and dispersed, (e) EF flocculated and aggregated, (f) EE flocculated and aggregated, and (g) EF and EE flocculated and aggregated. FF, face-to-face; EF, edge-to-face; and EE, edge-to-edge. (Adapted from Schramm [75]. Copyright (1980), reproduced with permission of Laurier L. Schramm.)

life. Solid suspensions, dispersions of one solid in another solid, are not, in general, covered in this book.

Just as with emulsions and foams, suspensions can exist with additional dispersed phases present. They may contain, in addition to solid particles and a continuous liquid phase (and possibly a stabilizing agent), emulsified droplets and/or gas bubbles. Figure 2.4 (in Section 2.2.1) shows photomicrographs of a practical suspension that contains suspended oil droplets in addition to the particles. The terminology used to describe such systems can become confusing. Consider an aqueous dispersion of solid particles and emulsion droplets. If the solid particles are adsorbed on the emulsion droplets, then it is an emulsion that also contains solids. If, however, the particles and droplets are not mutually associated, then the system is at once a suspension and an emulsion. Which term is used becomes a

Table 1.4 Classifications for particle sizes above the classical colloidal domain.

| Classification | Wentworth | Soil Science Society America |
|------------------|-----------|------------------------------|
| Clays | 0–3.9 | 0–2.0 |
| Silt | 3.9–62.5 | 2.0–50 |
| Very fine sand | 62.5–125 | 50–100 |
| Fine sand | 125–250 | 100–250 |
| Medium sand | 250–500 | 250–500 |
| Coarse sand | 500–1000 | 500–1000 |
| Very coarse sand | 1000–2000 | 1000–2000 |
| Gravel–granule | 2000–4000 | 2000–80 000 |

All values are lower and upper size limits in micrometres.

Adapted from References [77, 78].

matter of choosing the most appropriate context; frequently one or the other is considered to be the primary dispersion while the other phase is considered to be an additive or a contaminant.

1.2.4

Aerosols

Aerosols are colloidal dispersions in which either a solid or a liquid is dispersed in a continuous gas phase. Some examples are given in Tables 1.3, 9.1, 10.1, 11.1, 12.1, 13.1, 13.3, 14.1 and 15.1. Two principal types of aerosols are distinguished in colloid science and nanotechnology, which are as follows:

- solid aerosols (aerosols of solid particles), for solid particles dispersed in a gas (some examples and size ranges are given in Tables 1.5), and
- liquid aerosols (aerosols of liquid droplets), for liquid droplets dispersed in a gas (some examples and size ranges are given in Tables 1.6).

These are the meanings that will be used in most of this book. An exception is where it is appropriate to refer to the common use of the term *aerosol* as the formulated aerosol spray products that are packaged under pressure, and released through a fine orifice to produce either an aerosol or a foam (see Sections 13.7.2 and 15.4.1).

Aerosols of solid particles or liquid droplets are sometimes distinguished by their general mechanism of creation as

- primary aerosols, those created by the dispersion of particles, aggregates or droplets (dust, mist), or by chemical reactions (soot), and emitted from sources, or
- secondary aerosols, those created in the atmosphere, such as by condensation of gases to solids or liquids (e.g. smoke, fume, mist).

Table 1.5 Some approximate sizes for atmospheric aerosols of solid particles.

| Classification | Approximate lower–upper sizes (μm) |
|--|---|
| <i>By size range (modern literature)</i> | |
| Ultrafine range | 0–0.1 |
| Nanoparticles | 0.001–0.1 |
| Nuclei mode | 0.005–0.1 |
| Fine particles, $\text{PM}_{2.5}$ | 0–2.5 |
| Accumulation mode | 0.1–2 or 2.5 |
| PM_{10} | 0–10 |
| Total suspended particles | 0–35 or ∞ |
| Coarse mode | 2 or 2.5– ∞ |
| <i>By size range (older literature)</i> | |
| Aitken | 0–0.1 |
| Large | 0.2–2 |
| Giant | 2–40 |
| Precipitable | 40– ∞ |
| <i>By industrial type</i> | |
| Fume, smoke | 0–1 |
| Dust | 0.5–100 |
| Ash | 1–500 |
| Mist | 1–10 |
| Spray | 2–50 |
| <i>By health effect</i> | |
| Inhalable | 0–100 |
| Thoracic | 0–10 |
| Respirable | 0–4 or 5 |
| <i>Some bioaerosols</i> | |
| Viruses | 0.01–0.3 |
| Bacteria | 0.5–50 |
| Plant pollens | 5–100 |
| Mould spores | 2–200 |

Adapted from References [10, 11, 59, 60, 79].

Table 1.6 Some approximate sizes for atmospheric aerosols of liquid droplets.

| Classification | Approximate lower–upper size limit (μm) |
|----------------|--|
| Fog | 0.5–30 |
| Mist | 0.5–2 |
| Cloud | 2–200 |
| Drizzle | 200–500 |
| Rain | 500 to ~5000 |

Adapted from References [80–82].

In general, coarse aerosol particles, such as soil dust, cloud droplets and biological particles, are those produced by mechanical processes. Aerosol particles or droplets formed from the gas phase are usually the smallest in size and are often less than $1\ \mu\text{m}$ in diameter [59]. Such fine aerosol particles generally come from industrial emission sources or are formed in the atmosphere. Since these terms are defined by mechanisms of formation or type of occurrence (see Section 9.7), and although there are characteristic peaks (or modes) in the size distributions, the particle size ranges for the two ranges overlap and cannot be separated by specific size range numbers (see Tables 1.5 and 1.6).

Practical aerosols exhibit size ranges from molecular clusters in the nanoscale ($1\ \text{nm}$ and larger) to dusts and clouds containing aerosol droplets that exceed the classical colloidal size range limits given earlier, easily ranging to about $100\ \mu\text{m}$ (see Tables 1.5, 9.4 and 9.5). Section 7.1 describes the preparation of aerosols. Subsequent chapters (especially Chapters 8, 9, 13, and 15) provide many examples of aerosols in industry and everyday life.

Quite commonly distinguished in practical aerosol science are the following types of aerosols:

- *Dust*: Aerosols of solid particles (greater than about $0.5\ \mu\text{m}$ in diameter²⁾ that have resulted from the mechanical disintegration of larger matter.
- *Fume*: Aerosols of solid particles (less than $1\ \mu\text{m}$ in diameter) that arise from the condensation of vapours from a chemical reaction or physical reaction (such as evaporation and condensation).
- *Fog*: Aerosols of liquid droplets. In some definitions, fog is characterized by a particular droplet size range, whereas in others, fog refers to mist having a high enough droplet concentration to obscure visibility.
- *Smog*: Aerosols of liquid droplets or solid particles comprising air pollution (having diameters less than about $2\ \mu\text{m}$).
- *Smoke*: Aerosols of liquid droplets or solid particles that result from thermal processes like combustion or thermal decomposition.
- *Bioaerosols*: Airborne particles that are biological in origin, such as dispersed bacterial cells and fungal spores, fragments of insects or other animals, and particles carrying viruses.

Figure 1.8 shows an example of an indoor aerosol of solid particles (dust aerosol).

Aerosols are not thermodynamically stable but, as a practical matter, some aerosols occur that may be stable for days to a few weeks, such as in the atmosphere. Most metastable aerosols that will be encountered in practice contain extremely small particle or droplet sizes, and the particles or droplets may carry significant electric charges, such as the charged particles or droplets in thunderclouds.

2) A common size range definition for dust aerosol particles is greater than $0.5\ \mu\text{m}$ as stated; however, in practise, dust aerosols such as desert dust storm aerosols, exhibit particles ranging from about $1\ \text{nm}$ to over $100\ \mu\text{m}$ in diameter.



Figure 1.8 An example of an indoor aerosol of solid particles (dust aerosol). The whorl on the fibre in the foreground (upper right) is about $25\ \mu\text{m}$ in diameter. Photomicrograph by the author.

1.2.5

Hybrids

Some complex dispersions do not fit neatly into the earlier classical distinctions. For example, anti-bubbles are dispersed species of liquid-in-gas-in-liquid wherein a droplet of liquid is surrounded by a thin layer of gas that in turn is surrounded by bulk liquid. In an air–aqueous surfactant solution system, such a dispersion would be designated as water-in-air-in-water, or W/A/W, in fluid film terminology. Some examples are provided in Reference [83].

Colloidal liquid aphrons are a kind of emulsion in which micrometre-size dispersed droplets have an unusually thick stabilizing film and exist clustered together as opposed to either separated, nearly spherical droplets. The stabilizing aqueous film, sometimes called a *soapy shell*, is thought to have inner and outer surfactant monolayers. Taking this a step further, vesicles are droplets characterized by the presence at their surface of a lipid bimolecular film (bilayer) or series of concentric bilayers. A vesicle can be single or multilamellar and stabilized by natural or synthetic surfactants. Vesicles made from lipid or fat (e.g. phospholipid) bilayers are called *liposomes* (or, sometimes, *polysomes*).

1.3

Characterization and Stability

For lyophobic dispersions, which are not thermodynamically stable, the degree of kinetic stability is very important (see Section 5.5). A complete characterization of colloid stability requires consideration of the different processes through which dispersed species can encounter each other: sedimentation (creaming), aggregation and coalescence. Sedimentation results from a density difference between the

dispersed and continuous phases and produces two separate layers of dispersions that have different dispersed phase concentrations. One of the layers will contain an enhanced concentration of dispersed phase, which may promote aggregation. Aggregation is when any of Brownian motion, sedimentation or stirring causes two or more dispersed species to clump together, usually touching at some points, but with virtually no change in total surface area. In aggregation, the species retain their identity but lose their kinetic independence since the aggregate moves as a single unit. Aggregation of droplets may lead to coalescence and the formation of larger droplets until the phases become separated. In coalescence thin film drainage occurs, leading to rupture of the separating film, and two or more particles, droplets or bubbles fuse together to form a single larger unit, reducing the total surface area. In this case, the original species lose their identity and become part of a new species. Kinetic stability can thus have different meanings. A colloidal dispersion can be kinetically stable with respect to coalescence, but unstable with respect to aggregation. Or, a system could be kinetically stable with respect to aggregation but unstable with respect to sedimentation. In summary, although lyophobic colloids are thermodynamically unstable they may be relatively stable in a kinetic sense, and it is crucial that stability be understood in terms of a clearly defined process.

Chapters 2–5 provide an introduction to the concepts and techniques needed to study and understand dispersion stability. Some approaches to the characterization of emulsions, foams, suspensions and aerosols, and of their dispersed species (droplets, bubbles and particles) are described in Chapter 2. The concepts of surface tension, wettability and surface activity, which are important to the stability and properties of all types of dispersion, are described in Chapter 3. To this is added the nature of electrically charged surfaces in Chapter 4. All of these aspects are brought together in Chapter 5 in an introduction to the stability of dispersions. This sets the stage for an introduction to dispersion flow properties in Chapter 6, control of stability in Chapter 7 and then applications in Chapters 8–16.

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