

Introduction

Dispersions of particles in liquids are commonly encountered in a wide range of process industries. Dispersed particles can have sizes ranging from fractions of a millimetre down to macromolecular dimensions (a few nanometres). Figure 1.1 gives an overview of typical particle size ranges, together with some related information. Traditionally, a distinction has been drawn between *colloidal* and *suspended* particles, with the former taken as having at least one dimension with a size less than about $1\text{ }\mu\text{m}$. This boundary is rather arbitrary, but can be broadly justified for a number of reasons:

- (a) dispersed particles are very often examined by optical microscopes and it is difficult to resolve particles smaller than the wavelength of ordinary light (say, less than $0.5\text{ }\mu\text{m}$). Thus colloidal particles, as defined above, would be largely 'invisible' to the optical microscopist. Suspended particles are more easily observed

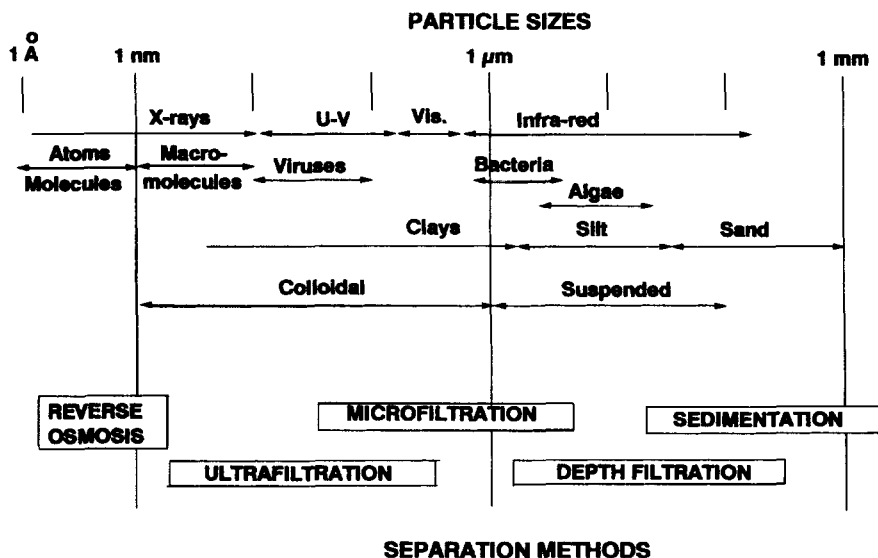


Figure 1.1 Typical size ranges of particulate material and the wavelengths of different forms of electromagnetic radiation. The conventional boundary between colloidal and suspended matter is at $1\text{ }\mu\text{m}$. Appropriate solid-liquid separation processes for different particle sizes are also shown

- (b) sedimentation rate is dependent on the square of particle size, and particles smaller than about $1\text{ }\mu\text{m}$ tend to settle very slowly. Thus colloidal particles remain in a dispersed state for long times, whereas suspended particles are fairly rapidly removed by sedimentation under normal gravity
- (c) the specific surface of particles (i.e. the surface area per unit mass or volume) depends inversely on particle size. Spherical particles with a diameter of $1\text{ }\mu\text{m}$ have a surface area of about $6\text{ m}^2\text{ cm}^{-3}$ or $3\text{ m}^2\text{ g}^{-1}$ for a material with a specific gravity of 2. Processes occurring at surfaces, notably adsorption, become more significant with smaller particles, and $1\text{ }\mu\text{m}$ is a size below which surface effects begin to predominate
- (d) certain interactions between particles, often referred to as colloid interactions or surface forces (to be discussed in Chapter 3), are proportional to the first power of particle size. 'External' forces such as those arising from gravitational and hydrodynamic effects depend more strongly on particle size. For instance, the gravitational attraction force is proportional to the mass of a particle and hence on the cube of its size. Hydrodynamic forces, as a result of flow, depend roughly on the square of particle size. It follows that, as particle size decreases, colloid interactions become increasingly significant relative to external forces. Again, $1\text{ }\mu\text{m}$ is a convenient dividing line.

In natural waters, an operational distinction between 'suspended' and 'dissolved' impurities is often drawn on the basis of particle size. Impurities which are retained on a standard membrane filter ($0.45\text{ }\mu\text{m}$) are defined as 'suspended', whereas those which are small enough to pass through the membrane are 'dissolved'. Clearly, much of the 'dissolved' fraction would be classed as 'colloidal' on the basis of the previous definition.

However, it must not be supposed that there is a sudden change from one type of behaviour to another at a given particle size. In most cases there is a gradual transition, and for this reason the terminology that we employ will not usually imply anything about particle size. We shall refer to particles, colloids, colloidal dispersions and colloidal suspensions, rather indiscriminately.

In this book we shall be concerned with two related aspects of the behaviour of suspended particles – *aggregation* and *deposition*. These processes have many features in common and some important differences. Aggregation involves the association of particles to form clusters. Deposition is the process whereby particles are transported to a surface, where they become attached. These processes are illustrated schematically in Figure 1.2.

An extremely important aspect of the behaviour of dispersed particles is their colloidal stability, which determines whether they remain in a dispersed state or form larger aggregates. The process by which small particles aggregate is known by various terms depending on the type of system involved and on specific conventions. These include coagulation, flocculation, agglomeration and agglutination. In this book, the generic term aggregation is used for the most part, but there will be cases where more specific terminology is needed.

Aggregation depends essentially on two distinct influences:

- (a) particles must move in such a way that collisions occur. This may be achieved by Brownian diffusion, fluid motion or sedimentation

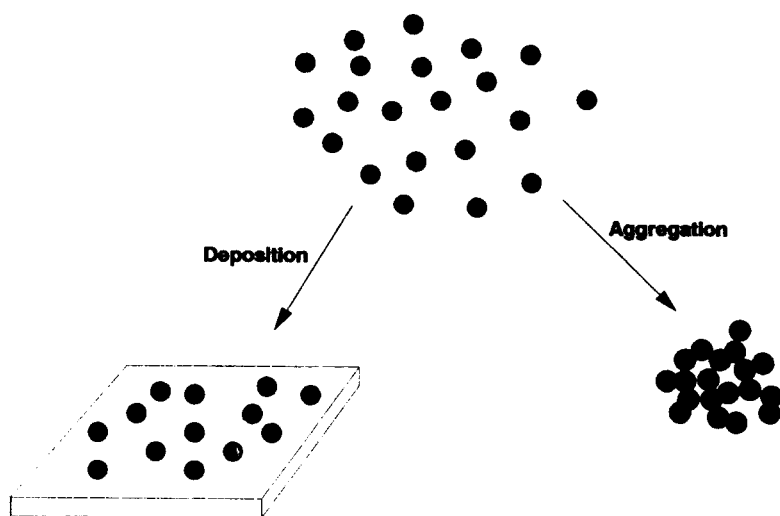


Figure 1.2 *Schematic illustration of the processes of aggregation and deposition of particles*

- (b) interactions between colliding particles must be such that permanent contacts can be formed. Particles which repel each other are said to be stable, since they do not form aggregates.

These two processes, transport and attachment, can, to a good approximation, be treated independently in most practical cases. The reason is that colloid interactions (Chapter 3) are of very short range, usually much less than the particle size, so that particles have to approach very close to each other before any significant interaction is felt. The interaction may be attractive (e.g. van der Waals or hydrophobic attraction) or repulsive (e.g. electrical or steric repulsion). The nature of the interaction is greatly dependent on the nature of the particle surfaces and on the solution chemistry. The transport step (Chapters 4 and 6) has to bring particles together from comparatively large distances, over most of which colloid interactions play no role.

Deposition also involves transport and attachment steps, which, again, can be treated separately to a large extent. In fact, deposition has several features in common with aggregation and could be regarded as an extreme case of *heteroaggregation* (which normally involves particles of different types). An important feature of deposition is that particles which are colloidally stable, by virtue of, say, electrical repulsion, may readily deposit on a surface of a different type, with which there is no repulsion.

Aggregation and deposition are extremely important in the process industries and in the natural environment. The aggregation of aquatic colloids is of major importance in determining the transport and ultimate fate of many pollutants in natural waters. Particulate impurities in lakes and oceans settle at rates which depend greatly on the nature of aggregates formed.

Particle separation processes such as sedimentation, flotation and filtration are significantly influenced by particle size, and the process chosen can depend greatly on the size of the particles to be removed (see Figure 1.1). For most operations there is an optimum particle size and in very many practical cases the actual particles are in a smaller size range. Consequently, separation can be greatly enhanced by increasing the particle size and this is achieved by some form of aggregation process. An obvious example is sedimentation, where colloidal particles would have too low a settling rate for practical purposes. Aggregation (flocculation) of such particles is often essential in order to give more rapid settling.

The process of *microfiltration* involves filtration of suspensions through media with pores finer than the particle size (e.g. membranes). The separated particles may form a filter cake, which plays an important role in the removal of further particles. Small particles, especially those in the colloidal size range, give filter cakes of very low permeability and hence low filtration rates. Again, aggregation can give a marked improvement.

With *depth filtration* (or *packed-bed filtration*) particles are removed during passage through beds of granular or fibrous filter media, where the pores are considerably larger than the particle size. Removal depends on particle size and flow rate in a complicated manner (see Chapter 12), but there is usually a minimum efficiency for particles a few micrometres in size. Aggregation of small particles can greatly enhance the capture efficiency.

The deposition of particles from suspension onto solid surfaces is a subject of great significance in many industries. In some cases, deposition is desirable, as in filtration and various processes in which a coating of deposited particles needs to be formed. In many other instances deposition needs to be prevented as far as possible. These include detergency, mineral processing (where 'slime coating' of colloidal particles onto larger grains can be a serious problem) and the fouling of heat exchanger surfaces. A number of biological examples could be mentioned, such as the deposition of bacteria on the tooth surface and thrombus formation associated with artificial organs.

There is considerable interest in the transport of colloidal contaminants (including bacteria and viruses) in ground water and this depends greatly on the deposition behaviour of such particles in soils and aquifers. This topic is the subject of Chapter 13.

Particle deposition is of great importance in depth filtration since particles must be deposited on collectors, such as filter grains or fibres, in order to be captured in the filter. In the early stages of a filtration process particles deposit on essentially clean collector surfaces. This aspect has been studied most extensively in model investigations (see Chapter 5). Particles may also become attached to previously deposited particles and extensive deposits may build up. This would depend greatly on the nature of the particle-particle interactions and should only occur when the particles are colloiddally unstable. In such cases aggregation of particles may also occur *before* deposition, depending on kinetic factors.

Fundamental studies of deposition and aggregation have been undertaken with different perspectives and with various objectives. Hydrodynamic factors

and colloidal interactions play very important roles, but in many studies only one aspect has been emphasized. For instance, deposition on the rotating disc (Chapter 5) has been investigated primarily because the hydrodynamic conditions are easily controlled and are well understood. Deposition rates are then used to gain insight into the colloid interactions between the disc surface and suspended particles. Similarly, many investigations of filtration through packed beds (Chapter 10) have been concerned primarily with colloidal aspects.

In such cases, the effect of colloid interactions is often expressed as a collision efficiency factor, which is the ratio of the actual rate of aggregation or deposition to the transport-limited rate. A collision efficiency of unity implies that every collision leads to permanent attachment. This condition should be achieved when surface-chemical conditions are adjusted to eliminate repulsion. Repulsive forces can reduce the collision efficiency by many orders of magnitude, such that practically no aggregation or deposition occurs. Attractive interactions can, in principle, give a rate higher than the transport-limited value, but the increase is usually quite small, as a result of the short-range nature of colloid interactions. Interaction between particles, especially electrical interaction, can be changed by adjustments to solution chemistry (ionic strength, pH) and the collision efficiency can be controlled in this way. Comparison between measured and computed collision efficiencies can give very useful information on colloid interactions. There are still some major discrepancies between theoretical predictions and measured collision efficiencies (Chapter 11), which are the subject of continuing debate.

Because of the central role played by colloid interactions in aggregation and deposition processes, Chapters 2 and 3 are devoted to a discussion of charged interfaces and surface interaction potentials.

Most 'real world' problems involving aggregation and deposition are very complex and the systems cannot be described in sufficient detail to enable a complete analysis to be undertaken. The emphasis in this book is on 'ideal' systems, which may be somewhat remote from practical processes.

Modelling and simulation studies inevitably have to make simplifying assumptions, such as uniform spherical particles and smooth collector surfaces, constant surface-chemical conditions and laminar flow. Without such simplification, computational and theoretical difficulties would be insurmountable with present techniques. Experimental studies have very often used ideal systems, such as monodisperse latex particles and spherical collectors, so that comparisons with theoretical predictions can be made.

Nevertheless, model studies, providing systematic information on well-defined systems, can usefully contribute to greater practical understanding of real processes. The influence of certain parameters, such as particle size and flow rate, can be thoroughly investigated and the results will often enable, at least, a qualitative interpretation to be made of similar phenomena in real systems.

Although the distinction is not entirely clear-cut, it is worth pointing out the essential differences between modelling and simulation approaches to problems of particle aggregation and deposition, before detailed discussion of these topics in later chapters.

Modelling is an essentially *macroscopic* process, which seeks to provide functional relationships between important variables. It deals with suspensions in terms of overall properties such as particle concentrations, size distributions and shear rates, using either analytical or numerical methods of analysis. Examples of modelling of colloid transport, deposition and aggregation are given in Chapters 4–6. Depending on the nature of the assumed model and on the level of approximation used, quite simple analytical results can be derived in some cases, which give an immediate indication of the effect of key variables on the process being considered. In many instances, however, the results can only be obtained by numerical techniques. The motivation for most modelling studies is to predict the response of a process, such as packed-bed filtration (Chapter 12), to changes in certain variables, such as flow rate and particle size.

By contrast, *simulation* is performed at a *microscopic* level, dealing with individual particles and based on a stochastic approach. A typical simulation process involves a detailed consideration of particle interactions and hydrodynamics and starts from basic principles. Details are given in Chapters 7 and 8 and applications to filtration processes and colloidal dispersions are discussed in Chapters 14 and 15. One of the major advantages of simulation is that information on the *structure* of aggregates or deposits may be derived. Some of the earliest applications were in the field of particle aggregation, from which fundamental ideas on the fractal, self-similar nature of aggregates emerged (Chapter 6). Conventional analytical models of aggregation and deposition give no idea of structure.

While the major emphasis in this work is on theoretical aspects, relevant experimental techniques are described briefly in Chapters 9 and 10. The methods covered are mainly appropriate to fundamental studies, based on ideal systems. Results from such studies are especially useful for comparison with theoretical predictions, e.g. of particle deposition kinetics (Chapter 11).