

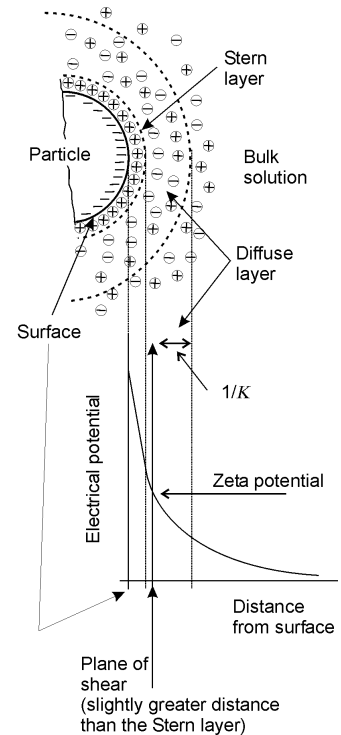
# 13 Colloids and agglomeration

The processing of fine particulate materials is becoming increasingly important and the term *nanotechnology* is typically used to describe any system with particle diameters less than 1 micron. In liquid systems, colloidal forces become significant when particle diameters are less than 40 microns and very significant below 10 microns. At higher particle sizes the liquid drag and particle weight forces are normally dominant. These thresholds are, of course, material dependent and the equations covered in this chapter should help in determining the relative importance of the various forces. In gas based systems, some of the forces appropriate to liquid systems may still be applied, such as van der Waal's attraction, but others will not: e.g. electrical double layer repulsion. Thus, this chapter covers the forces on fine particles (other than drag and inertia) in both systems separately.

In a gaseous continuous phase *agglomeration* may be performed, which is the process of sticking particles together, either relying on natural adherence forces to bring the particles together or by adding binding agents. Granulation is the process of forming particle granules that are usually large enough to flow readily and are easy to process. Industrial granulation relies upon the formation of strong agglomerates which are, usually, compressed or heated (or otherwise treated) to give granules that do not easily subsequently break. Hence, within a process it may be necessary to grind a powder to a small size, to intimately mix the small grain sizes with another powder, and then to agglomerate the resulting mixture into granules for the purpose of storage and further powder processing. The granules may, eventually, be made into tablets or a similar compressed compact. Another process worth mentioning is the formation of engineering components from very small particles, which after pressing form strong solid objects. Complex shaped objects with tailored physical properties, and composites, can be made by this technique. Hence, an understanding of fine particle processing, and forces, is important to many modern processing industries.

## 13.1 Forces on small particles – in liquid medium

Figure 13.1 illustrates a particle in water and the associated electric field around it. Most mineral particle surfaces are negatively charged, due to defects in the solid crystal lattice, chemical reactions at the surface, slightly soluble ions dissolving from the crystal and adsorption (and exchange) of ions from the surrounding solution. Some biological particles may be positively charged. The charge on the particle surface gives rise to ions of counter charge strongly bound to the surface. The total depth of strongly bound ions to the particle is called the *Stern layer*. At some distance further away from the particle there is the shear plane, which marks the start of the *diffuse layer*. It is



**Fig. 13.1** Electrical charge around a particle in an electrolyte solution

not possible to shear the ions off the particle that are closer to it than the shear plane. Thus, if the particle surface potential is measured using a device involving motion, the potential will be measured at the shear plane, and not the true potential on the particle. This is called the *Zeta potential*. So, a particle in an electrolyte solution contains a strongly bound layer and a diffuse layer of ions close to its surface. This is known as the *Double layer*. It is worth noting that ions are hydrated, often by several solvent (usually water) molecules, so the distance of these layers is not that of the ions alone, but is a distance dependent on the hydrated ion. The degree of hydration depends upon the ionic strength of the solution ( $I$ ), which is defined as follows

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (13.1)$$

where  $c_i$  is the molar concentration of an ion and  $z_i$  is the ionic charge, or valency; i.e. the ionic strength is based on the sum of contributions for all ions in solution. The electrical potential at the particle surface ( $\psi_0$ ) can be deduced from the Nernst equation, based on the concentration (or more correctly solution activity) difference between the particle surface and bulk solution. The potential at the Stern layer ( $\psi_d$ ) will be less, and can even have a different charge value (i.e. negative or positive) to the potential at the surface, if the counter ions bound to the surface are polyvalent. The diffuse layer potential ( $\psi$ ) diminishes exponentially, as first derived by Gouy-Chapman, giving

$$\psi = \psi_d \exp(-K\Delta z) \quad (13.2)$$

where  $\Delta z$  is distance from the surface and  $K$  is the Debye-Hückel function. For a simple electrolyte consisting of a cation of concentration  $c_1$  and anion of concentration  $c_2$ , this function is

$$K = \left( \frac{c_1 z_1^2 e^2}{\epsilon_p k_B T} + \frac{c_2 z_2^2 e^2}{\epsilon_p k_B T} \right)^{1/2} \quad (13.3)$$

where  $e$  is the charge on an electron,  $n_0$  is the concentration of ions present,  $\epsilon_p$  is the electrical permittivity,  $k_B$  is the Boltzmann's constant and  $T$  is the temperature in degrees absolute. However, in SI units it is usual to calculate the permittivity from the dimensionless permittivity ( $\epsilon_d$ ) and the permittivity of a vacuum ( $\epsilon_0$ )

$$\epsilon_p = 4\pi\epsilon_d\epsilon_0 \quad (13.4)$$

The inverse Debye-Hückel function has the units of length and it is convenient to assume that this is the diffuse layer thickness for practical use. However, the real diffuse layer extends to infinity. Equations (13.2) to (13.4) can be used to predict the electrical potential with separation distance from a particle surface. Clearly, on bringing two particles together the electric fields will overlap and this could cause the particles to repel each other. This is known as electrical double layer repulsion.

At the same time, and if the particles are in close enough proximity, the London-van der Waal's attractive force will tend to pull the

#### Dimensions

There is some confusion in colloid chemistry with units and dimensions. The recommended system for equation (13.3) is:

$c_i$  in number of ions  $\text{m}^{-3}$ ,

$e$  is  $1.6 \times 10^{-19}$  Coulombs

$\epsilon_0$  is  $8.85 \times 10^{-12}$  Farad  $\text{m}^{-1}$

$\epsilon_d$  is typically 81 for water

$k_B$  is  $1.38 \times 10^{-23}$  J  $\text{K}^{-1}$

so

$c_i$  is  $1000 \times \text{Molarity} \times$

Avagadro's number

#### Potential and energy

The potential is defined as work done in moving a unit charge of the same sign as the surface from infinity to that point; i.e. if a charge of  $ze$  is moved from infinity to a point within the electric field surrounding the particle the work done is  $ze\psi$

which is the potential energy possessed by the charge at that position.

particles together. This is a short range force between particles that arises because of electrical dipole fluctuation between neighbouring particles. In particle force terms, the van-der Waal's force is short ranged: up to 0.1  $\mu\text{m}$ . The potential due to van-der Waal's attraction ( $\psi_A$ ) may be deduced from

$$\psi_A = -\frac{A_H}{12} \left[ \frac{2(1+H_s)}{H_s(2+H_s)} + \ln\left(\frac{H_s}{2+H_s}\right) \right] \quad (13.5)$$

where  $A_H$  is the Hamaker constant for a given system and  $H_s$  is the ratio of the separation distance ( $\Delta z$ ) between the particles and the particle radius. So, in terms of particle diameter

$$H_s = \frac{2\Delta z}{x} \quad (13.6)$$

The Hamaker constant varies with material, but is about  $5 \times 10^{-20}$  J for water. In systems containing two different types of particles and a liquid, the constant may be estimated by

$$H_{s:132} = (H_{s:1}^{0.5} - H_{s:3}^{0.5})(H_{s:2}^{0.5} - H_{s:3}^{0.5}) \quad (13.7)$$

where the liquid Hamaker constant is  $H_{s:3}$  and the other two subscripted constants refer to the two particles. Thus,  $H_{s:132}$  represents the resulting mean constant value for use in equation (13.5), etc.

Equation (13.5) is just one form of the London-van-der Waal's equation; there are many others depending on the assumptions made in the solution, such as surface geometry. When the separation distance is very small, in comparison to particle diameter, equation (13.5) simplifies to

$$\psi_A = -\frac{A_H}{12H_s} \quad (13.8)$$

Molecular forces and valence energy are only applicable for separations between particles in the order of less than 10  $\text{\AA}$ , which may be applicable to particles only after the application of very high pressures. In most instances the particle separation will be in excess of 10  $\text{\AA}$  due to surface roughness.

### 13.2 DLVO and applications

There is enormous difficulty in measuring the appropriate Hamaker constant. In recent years, Atomic Force Microscopy (AFM) has been used for his purpose, but ensuring pure components with no surface adsorption of ions still makes this a difficult task. In many cases the Hamaker constant has been used as an empirical variable in order to reconcile measured data and theory. Nevertheless, the equations described above can still be used for a very useful semi-quantitative analysis of observed phenomena. The theory first expounded by Deryagin and Landau, and separately by Verwey and Overbeek (DLVO) was to use the potential field around the particles, as determined by equation (13.2) and calculate the repulsive potential formed when overlapping the potential fields for each particle. This

#### Hamaker coefficient

It is convenient to use a Hamaker constant, but in colloid chemistry it has been known for some time that the value is a variable dependent on the separation distance. Thus, it is sometimes referred to as the Hamaker coefficient, which is a function of separation distance. A true analysis of this coefficient requires a consideration of quantum mechanics,

#### Atomic Force Microscopy

Is a device that uses a tip mounted on a cantilever to move over a solid surface. It is possible to keep the tip and surface apart by providing a constant force - hence constant distance apart. The deflection on the cantilever is a measure of the surface contours. The AFM can also be used to measure force whilst the tip approaches the surface from a distance away.

provides the electrical double layer repulsion between two particles, adding the van-der Waal's attraction potential, or force, provides the total interaction potential ( $\psi_T$ ). At constant potential, the double layer repulsion potential is

$$\psi_R = \frac{\epsilon_p x}{8} \left( 2\psi_{z:1}\psi_{z:2} \ln \left[ \frac{1 + \exp(-K\Delta z)}{1 - \exp(-K\Delta z)} \right] + (\psi_{z:1}^2 + \psi_{z:2}^2) \ln [1 - \exp(-2K\Delta z)] \right) \tag{13.9}$$

and at constant charge the repulsion potential is

$$\psi_R = \frac{\epsilon_p x}{8} \left( 2\psi_{z:1}\psi_{z:2} \ln \left[ \frac{1 + \exp(-K\Delta z)}{1 - \exp(-K\Delta z)} \right] - (\psi_{z:1}^2 + \psi_{z:2}^2) \ln [1 - \exp(-2K\Delta z)] \right) \tag{13.10}$$

where  $\psi_{z:1}$  and  $\psi_{z:2}$  are the Zeta potentials on particles one and two respectively, see Figure 13.1. Simpler forms of equations (13.9) and (13.10) exist, depending on the assumptions made in their derivation and application. The total interaction energy, by DLVO theory, is

$$\psi_T = \psi_A + \psi_R \tag{13.11}$$

The potential energy curves are illustrated in Figure 13.2. Often, the total interaction energy is normalised (divided) by the kinetic energy due to thermal motion: this is called the dimensionless interaction energy and may be represented by

$$\frac{\psi_T}{k_B T} \tag{13.12}$$

or more correctly

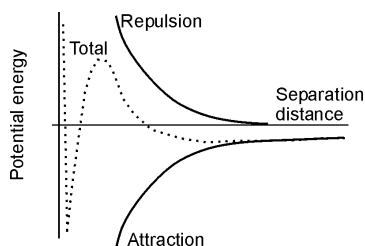
$$\frac{e\psi_T}{k_B T} \tag{13.13}$$

The potentials described above can be converted into forces on a particle by differentiation with respect to separation distance

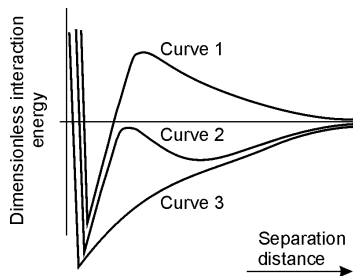
$$F = \frac{d\psi}{dz} \tag{13.14}$$

hence a comparison of the forces influencing a particle is possible.

Plots of the dimensionless interaction energy are useful for assessing the *stability* of colloid suspensions. Figure 13.3 illustrates three cases: curve 1 has a primary minimum and a maximum, curve 2 has a primary minimum and maximum together with a secondary minimum, and curve 3 only has a primary minimum. To destabilise a colloid, such as in effluent treatment, the requirement is to bring the particles together so that they form a bigger aggregate that will settle faster and be easier to remove from suspension. Thus, the particles need to closely approach each other for the attractive forces to stabilise the aggregate. A high repulsion force provides a stable colloidal suspension. The DLVO theory uses plots like Figure 13.3 to explain colloid stability as follows. The explanation considers the potential curve based on one particle surface whilst bringing the second particle towards that surface, from right to left on Figure 13.3. In the case of



**Fig. 13.2** Potential energy curves for attraction and repulsion as well as total interaction energy curve



**Fig. 13.3** Dimensionless interaction energy curves to illustrate colloidal behaviour by DLVO theory

curve 3, the primary well is close to the particle surface and from equation (13.14) the force is attractive (positive gradient) until the approaching particle sits in the primary well, which is at a low enough separation distance for settling as an aggregate to take place. Thus, in case 3 the colloid is unstable as the two particles will settle as an aggregate. For curve 2, there is a mildly attractive force until the particle sits in the secondary minimum. In order to approach further the particles must have sufficient energy to overcome the maximum – and to overcome the repulsive force at separation distances less than this maximum. Once over the secondary maximum there is a strong force pulling the particle into the primary well. Hence, this situation could be a stable colloid (because of the repulsive force preventing the approaching particle from reaching the primary minimum), or it may be unstable because the maximum to be overcome is fairly low in height. In curve 1 the maximum is very significant and the force, equation (13.14), is strongly repulsive: this is a very stable colloid.

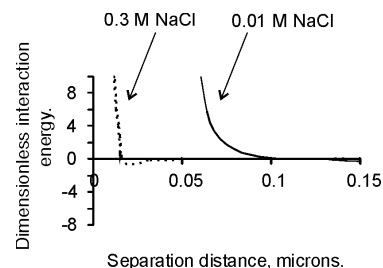
One practical application of this theory is to explain the occurrence of silting within estuaries. Colloidal clay is carried down a river in stable suspension because rivers are freshwater and have a low ionic concentration, the electrical double layer extends to a large distance around the particles providing a strong repulsion force. This is illustrated in Figure 13.4, the 0.01 M NaCl curve. However, on meeting the saline seawater the ionic concentration increases, and may reach 0.3 M, which reduces the distance that the electrical repulsion acts over, equation (13.3), and the particles can approach each other. This is illustrated as the 0.3 M NaCl curve on Figure 13.4. The colloidal particles, therefore, aggregate together and settle out into the estuary causing silting.

The DLVO theory is a useful approach to explaining observed phenomena, but many of the equations are difficult to apply and have different forms depending upon the assumptions made in their derivation. Also, colloidal stability, or instability, may be due to adsorption of solutes and ions onto the particle surface. So, the above description is not a complete model of colloidal behaviour.

### 13.3 Coagulation

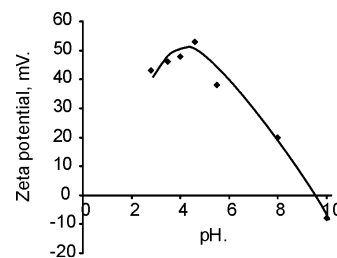
In the silting of estuaries example given above particles were brought together to form an aggregate that is easier to remove from suspension than the primary particles. This is an example of the process of coagulation, and the resulting aggregate is called a *coagula* which is formed by adding a *coagulant* (usually a metal salt) in solution. The process of coagulation forms coagula that may be broken by the application of shear, such as during pumping, but they will usually reform when the shear field is removed.

Consideration of equation (13.3) results in the conclusion that the distance over which the electrical double layer repulsion acts is strongly dependent on the valency of the electrolytes in solution. Thus, a tertiary valent salt is more effective at causing coagulation than a

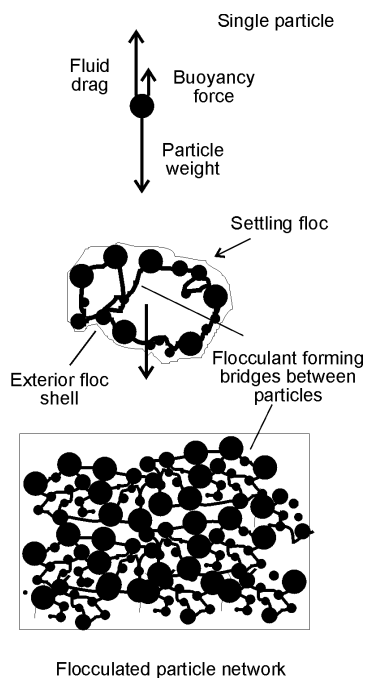


**Fig. 13.4** Clays in freshwater and estuary water salinities and stability – conditions:  
 Zeta potential -30 mV  
 particle size 4 μm  
 Hamaker water  $5 \times 10^{-20}$  J  
 Hamaker particle  $6 \times 10^{-20}$  J  
 ion valencies 1  
 temperature 298 K  
 dimensionless dielectric 81  
 also:

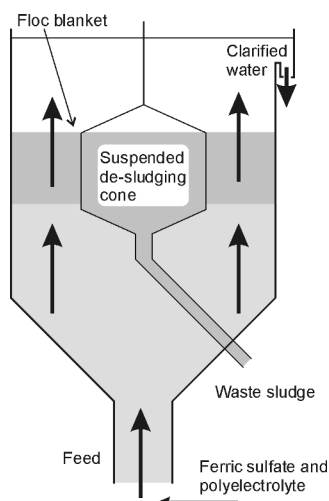
permittivity of a vacuum  
 $8.85 \times 10^{-12}$  F m<sup>-1</sup>  
 Boltzmann constant  
 $1.38 \times 10^{-23}$  J K<sup>-1</sup>  
 electron charge  
 $1.6 \times 10^{-19}$  Coulombs  
 Avagadro's number  $6 \times 10^{23}$



**Fig. 13.5** Zeta potential of iron oxide colloid particles



**Fig. 13.6** A floc is much bigger than a particle and is easier to remove from suspension, but a floc network settles slowly



**Fig. 13.7** Floc bed clarifier

secondary, or monovalent salt. In water treatment, ferric (iron III) sulfate, and aluminium salts, are often used for this reason. They are also inexpensive chemicals to apply. By the addition of a salt solution, or by the adjustment of the pH, it may be possible to effectively reduce the electrical potential at the shear plane (Zeta potential) to zero. Thus, the double layer repulsion term in equations (13.9) and (13.10) becomes zero and the particles will have no repulsion force on them to prevent aggregation by van-der Waal's attraction. This is illustrated in Figure 13.5, for iron oxide at various pH values. The point at which the Zeta potential is zero is often referred to as the *iso-electric point*. Thus, in the example of Figure 13.5 adjusting the pH to 9.5 should result in a less stable colloid than is found at other pH values. Conversely, at a pH of 5 a very stable colloidal suspension would be expected by DLVO theory.

### 13.4 Flocculation

Another means by which primary particles are brought together to form aggregates, that is easier to remove from suspension than primary particles, is by flocculation, see Figure 13.6. In this process the aggregation is caused by bridges from one particle to another, usually formed by high molecular weight polymers in solution. The polymers may be man-made, or they can be naturally occurring; examples of the latter are found with several biological compounds. The resulting aggregate is called a *floc* which is formed by adding a *flocculant* (usually a polymer) in solution. The process of flocculation forms flocs that may be broken by the application of shear, such as during pumping, and the physical bridges linking the particles do *not* usually reform when the shear field is removed. Thus, unlike coagulation, the process of flocculation is shear sensitive. So, when flocculants are used in high shear applications, such as to assist dewatering in a scroll discharge decanter centrifuge (Figure 8.3) a special shear resistant flocculant is required. These are normally very high molecular weight polymers. However, the higher the molecular weight the more difficult it is to dissolve the polymer and it may be more difficult to disperse the flocculant within the feed suspension to be treated.

Synthetic polymer flocculants (*polyelectrolyte*) are supplied in three forms: non-ionic, anionic and cationic. The first has no net charge, the second is negatively charged in solution and the latter is positively charged. Hence, when treating mineral suspensions cationic flocculants are preferred because they can more easily bind on to the negatively charged mineral surface. For similar reasons anionic flocculants are applied to biological suspensions. There are many instances when flocculation follows a primary coagulation stage. The coagulation is designed to destabilise the suspension and the flocculation stage to then form aggregates that are even easier to settle, filter, etc. Hence, anionic polymers may be applied to mineral systems after coagulation and cationic to biological systems. So, the optimum flocculant and coagulant dose, and strategy, is one that can only be

determined by experimental testing. The quickest way to achieve this is by the simple settling jar test, illustrated in Figure 6.2: fast settling times are desired. However, the optimum dose is usually provided by the cost of flocculant purchase, rather than any physical consideration, as these chemicals constitute a significant recurrent cost.

Conventionally coagulants and flocculants are added to the feed launder to the thickener, however, in the *floc blanket clarifier* (popular in the potable water industry) the feed is introduced, with flocculant, into the flocculated and settling bed of solids, see Figure 13.7. Likewise the *high rate thickener* applies the same principle; the clarifier is used for dilute feeds and the thickener at higher concentrations usually found in the minerals industry.

### 13.5 Forces on particles – gaseous medium

Forces on particles in a gaseous continuous phase, or medium, are important in the understanding of particle behaviour during many operations, such as powder flow during hopper discharge and for the process of granulation. It is useful to compare the forces on a particle in a gaseous medium to that of the weight of the particle; i.e. gravitational force. Thus, if the particle has a mass of  $m_p$  the particle weight ( $F_w$ ) is

$$F_w = m_p g$$

and when considering the simple aggregate situation represented by Figure 13.8, if  $m_p g > F$  then no permanent bond is formed, whereas when  $m_p g < F$  a permanent bond may be formed, where  $F$  represents the force under consideration.

The van-der Waal's attractive force is applicable to a gaseous continuous phase as well as in liquids. Table 13.1 compares the ratio of the van-der Waal force to the particle weight for particles 0.01 to 10 microns in diameter and at separation distances of 0.01 and 0.1 microns between the particles. For a separation of 0.1  $\mu\text{m}$  this ratio is 1 when the particle diameter is 3  $\mu\text{m}$ . In general, the force may be important for particles less than 10  $\mu\text{m}$ .

In a gaseous continuous phase an *electrostatic force* exists, but not the double layer repulsion discussed earlier. The electrostatic force can be calculated from

$$F_{es} = \frac{q_1 q_2}{\pi \epsilon_p x^2} \tag{13.15}$$

where  $q$  represents charge on the particles (1 and 2) and  $\epsilon_p$  is the electrical permittivity of the fluid medium (normally quoted relative to a vacuum). This force is difficult to quantify because a particle may only pick up a fraction of its equilibrium charge. Typical values of particle diameter, when the ratio of this force to the particle weight is 1, are: 0.3  $\mu\text{m}$  at 0.1% of the equilibrium charge attained, and 30  $\mu\text{m}$  for 1% of equilibrium charge attained. Hence, this force may be significant for particles in the *sub-sieve* range (less than 45  $\mu\text{m}$ ).

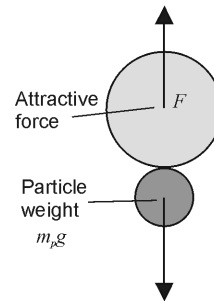


Fig. 13.8 Simple aggregate used to compare forces

Table 13.1 van-der Waal's force compared with gravity

$\Delta z$ ( $\mu\text{m}$ )	Particle diameter in $\mu\text{m}$ :			
	0.01	0.1	1	10
0.01	$7 \times 10^6$	$1.7 \times 10^5$	2000	20
0.1	700	220	8	0.1

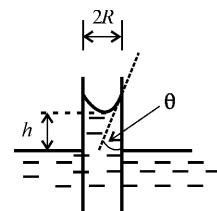


Fig. 13.9 Capillary rise due to surface tension

The *moisture force* is very strong between particles. You may notice this when riding a bike on a fine gravel path after rain: the gravel sticks together better than when dry.

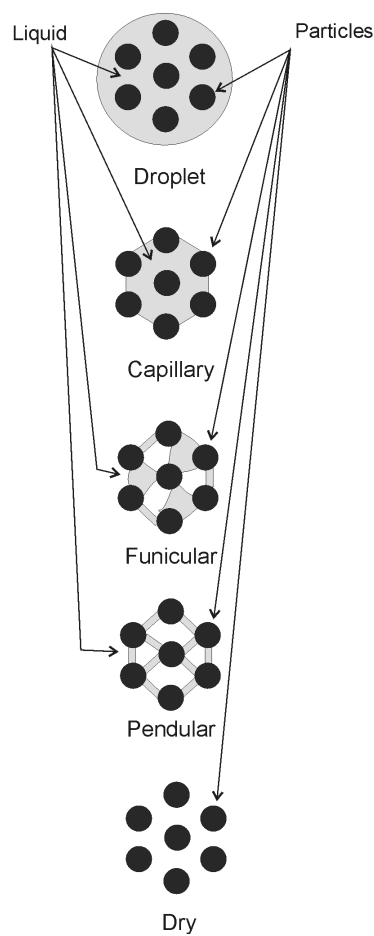


Fig. 13.10 Stages during the formation of a granule as liquid is removed

The *surface tension force*, or *moisture force*, arises from the well-known capillary pressure effect (see Figure 13.9). There is a *contact angle* ( $\theta$ ), which is the equilibrium angle of a liquid on a surface in the presence of another phase such as air (i.e. three phases are required: two fluids and a solid); e.g. as with the meniscus illustrated here. The Young-Laplace equation is

$$\Delta P = \frac{2\gamma \cos \theta}{R} \quad (13.16)$$

where  $\gamma$  is the surface tension of the liquid and  $R$  is the radius of the capillary. The height of rise of the fluid ( $h$ ) to balance this pressure is

$$h = \frac{2\gamma \cos \theta}{R\rho g} \quad (13.17)$$

From a consideration of the Young-Laplace equation Newitt and Conway-Jones (1958, Trans. IChemE) deduced the following equation for the force due to the *pendular* liquid between particles:

$$F_{\text{pend}} = \frac{2\pi\gamma r}{1 + \tan(\theta/2)} \quad (13.18)$$

where  $r$  is particle radius. However, the angle formed by the meniscus will change as liquid is lost from the agglomerate (it dries out). When  $\theta \rightarrow 0$  the particle diameter with the ratio of force divided by particle weight of one, is 4200  $\mu\text{m}$ . Hence, this force is more significant than van-der Waal's, or electrostatic, forces for bringing particles together in the agglomeration purposes; i.e. for particle diameters less than 4 mm the moisture force is greater than the force due to gravity. However, equation (13.18) is for pendular liquid bridges between the particles, other bridges are not so strong, so some consideration of the states of dehydration within a particle assemblage is required, see Figure 13.10.

Initially, as a droplet, the strength of the agglomerate is due only to the liquid surface tension; this forms a weak agglomerate that may be deformed or broken easily. As some moisture is lost the capillary agglomerate state is achieved, in which all the interstices are filled, but the agglomerate strength comes from curvature of the liquid alone. As more moisture is lost the funicular state is achieved, which still forms only a weak structure; followed by the pendular state of agglomerate. In the pendular state the liquid bridges are all independent of each other and the liquid cannot move between bridges, but draws particles together by the capillary pressure effect. It is a very strong force. Finally, it is possible to form a dry agglomerate, possibly bound together by van-der Waal's or electrostatic forces but, in the absence of solid bridges between constituent particles, the agglomerate will be weak. However, if solid bridges have been formed, caused by precipitation from solution, or drying of a binder, the agglomerate can be very strong. Such dry granules may be formed when a soluble binding agent, such as starch dries out to chemically bind the particles together, or if the particles have been sintered together: a high temperature causing some of the particle surface to melt and form the bridge between particles after cooling. Strong bonds are also formed



from chemically reacting species, crystallising solids or suspended colloidal material that dries out between the particles. Granules with a large number of bonds per particle are strongest.

During granulation using a liquid binder it is possible to identify several stages during the process. Initially, *nucleation* takes place when a particle plus liquid meets a second particle and sticks. This is followed by *nuclei growth* as other particles stick together on the nuclei. The nuclei themselves may then stick together during a *nuclei coalescence* stage. At this point the aggregate has many dendritic (i.e. spiky) parts to its shape and these may break off during *densification*, which will leave a stronger granule. Finally, *layering* or *snowballing* may occur, during which small fragments and fresh powder now coat granules to form new strong dense particles.

### 13.6 Agglomeration and granulation equipment

Agglomeration is the process of bringing particles together to form agglomerates and it may be performed in a liquid medium as well as gaseous. Granulation is a term usually applied to the formation of granules and is, therefore, restricted to particle agglomeration in the gaseous phase. Granulation is required for many reasons including: to improve powder flow properties within a process, to avoid dust explosions and physiological hazards from fine particles, to increase bulk density in storage, to prevent segregation, to meter a dose (e.g. tablets) and to achieve specified particle properties such as size and specific surface. Hence, there are many industries that use granulation and a variety of different equipment is employed. In the mineral industries a simple pan granulator, see Figure 13.11, open to the environment, may be sufficient but this would not be the case for pharmaceutical production. Enclosed granulation equipment includes fluidised bed granulators and high shear mixers, fitted with rotating blades that provide an optimum granule size for a given shear input with the addition of a binding agent.

In most cases the binding agent is a liquid added to a powder in a granulating machine (pan, drum, fluidised bed, etc.) and agglomeration is induced to form the granules. This is the process of wet granulation. However, granulation can also be achieved by the action of heat and pressure on powder compacts due to sintering and this is called dry granulation. A brief summary of the main types of equipment, and their characteristics follows. A dish or pan granulator has been used for many years in metallurgical industries: a tilted pan rotates and fresh powder and solution (if required) are added, it may be run continuously and gives consistent 5 mm spherical granules. Fluidised bed granulators have powder injection into a granule forming bed, together with solution sprayed on the bed. Granules overflow from the bed. However, there may be problems with explosion risk, loss of fines and weak granules. High shear mixers, both vertical and horizontal axes machines, are available with high power input. A rotating drum (slightly tilted for continuous use with

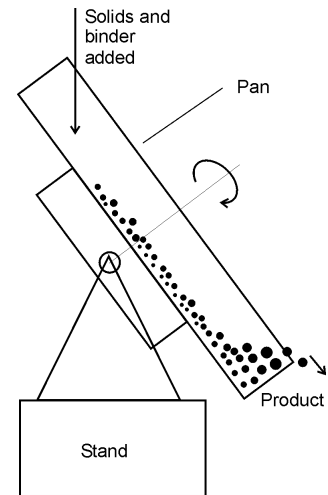


Fig. 13.11 Pan granulator

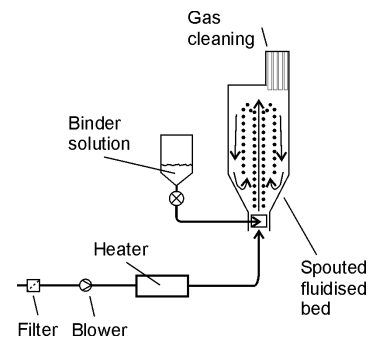


Fig. 13.12 Fluidised bed granulator

**Capillary pressure and pore size**

Equation (3.16) can be rearranged to give a method to determine the pore size ( $d$ ) of a membrane, cloth or porous medium:

$$d = \frac{4\gamma \cos \theta}{\Delta P}$$

Hence, immersing a membrane, in a filter holder, within a liquid and slowly increasing air pressure in the holder until air flow is observed can be used to determine the biggest pore size from the above equation. This is known as the *bubble point* test.

an outlet weir) may be used for wet and dry granulation; the latter just using the moisture associated with the powder mix.

Powder compacts are also formed by pressing and tableting and by extrusion of pastes. The forces considered earlier in this chapter can again be used to assist in the understanding of these processes, but in these instances very high pressures and, sometimes, shear fields are also employed. The equipment required for tableting, for example, is a highly specialised mould and punch system; generating considerable compaction pressure to compress and form the tablet. Usually, many punches are used simultaneously, to provide high throughput.

Another important consideration in the pharmaceutical and food related industries is an ability to comprehensively clean the machinery, possibly using a *Cleaning In Place* (CIP) strategy. In many instances it may be possible to clean the granulator and additional processing equipment at the same time. However, in highly regulated production environments it is usual for agreed procedures and protocols to be in place, under the remit of *Good Manufacturing Practice* (GMP), which might restrict the alteration of existing operating strategies, or adoption of new equipment, or techniques. Thus, when considering granulation equipment for these industries both GMP and CIP are factors that need to be considered carefully.

### 13.7 Summary

Forces on particles, in both gases and liquids, exert important influences on their behaviour in processes and processing equipment. Particles less than 10  $\mu\text{m}$  in diameter are considerably influenced by the colloidal forces described in this chapter and, towards the lower end of this size range, the weight force may become insignificant in determining the particle's behaviour. In wastewater and potable water treatment, coagulation and flocculation are extensively used processes for the removal of unpalatable and dangerous finely dispersed materials. The processing of fine particles is becoming increasingly important, but fine particles tend to stick, arch in hoppers, cause safety hazards and are generally difficult to process. Thus, it may be important to create fine particles for a processing stage, such as solid/solid mixing, but this may need to be followed by granulation in order to provide acceptable later processing performance.

Advances in laboratory analytical equipment, such as the Atomic Force Microscope, is leading to better direct experimental measurement of colloidal forces, which will help to refine the theoretical models and lead to a better understanding of particle-particle interaction.

### 13.8 Problems

- Using the data supplied with Figure 13.4, write a computer spreadsheet to investigate the influence of salt concentration and ion valency on the separation of two particles with the Zeta potentials, and other physical properties, assumed to remain constant.