Colloids and Colloidal Stability

ESS5855 Lecture
Fall 2010

Definition

- **Structure**
  - **In general, a colloid is a system consisting of one substance (the dispersed phase: a solid, liquid, or gas) finely divided and distributed evenly (relatively speaking) throughout a second substance (the dispersion medium or continuous phase: a solid, liquid, or gas)**

Examples of Commonly Encountered Colloidal Systems

System	Type	Dispersed Phase	Continuous Phase
Fog, mist	Liquid aerosol	Liquid	Gas
Smoke	Solid aerosol	Solid	Gas
Shave cream	Foam	Gas	Liquid
Styrofoam	Solid foam	Gas	Solid
Milk	Emulsion	Liquid (fat)	Liquid (water)
Butter	Emulsion	Liquid (water)	Solid (fat)
Paint	Dispersion	Solid	Liquid
Opal	Dispersion	Solid	Solid
Jello	Gel	Macromolecules	Liquid
Liquid soaps and detergents	Micellar solution	Micelles of detergent molecules	Liquid

Definition

- **Size**
    - **Experience over many years has shown that special "colloidal" properties are usually exhibited by systems in which the size of the dispersed phase falls in the range of 1 to 1000 nm**

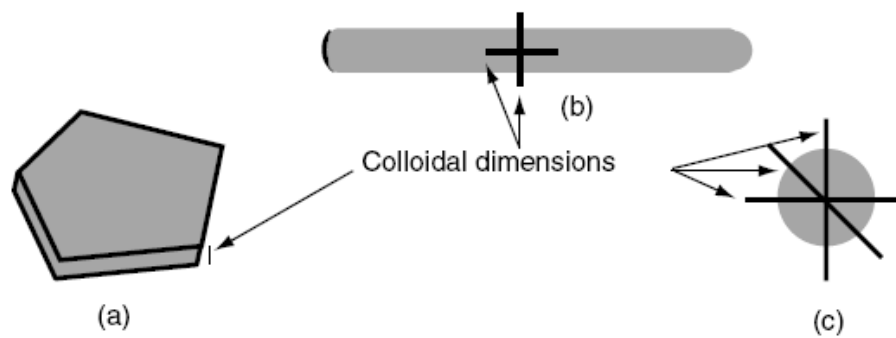- **If it looks like a colloid and acts like a colloid, it is a colloid**

FIGURE 10.1. A colloid is basically defined by its dimensions. While one may set a size limit of, for example, 0.01 mm as an arbitrary upper limit to what may be called a colloid, the reality is that many systems with larger dimensions are considered "classic" colloids (e.g., clays) because at least one dimension falls into the limiting size range. To be considered a colloid, then, a system may have one dimension in the range as in a flat plate (*a*), two dimensions as in a cylinder (*b*), or three dimensions as in a drop or particle (*c*).
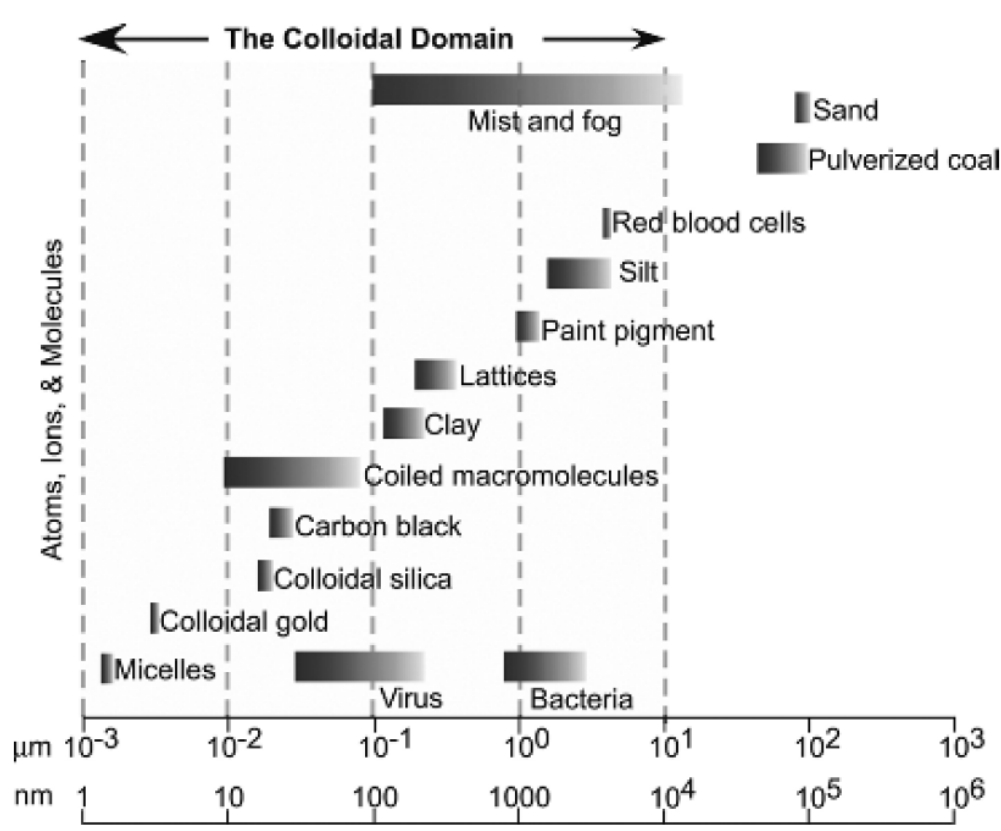

Figure 2.2. Typical particle size ranges in the colloidal domain.

Roots of Colloidal Behavior

- **Atoms or molecules at a surface have properties distinct from those located in a bulk phase or in solution**

- **As the bulk phase is subdivided into finer and finer particles, the relative ratio of surface to bulk molecules will increase until the effect of specific surface properties will begin to become significant, or even dominate the characteristics of the system**

- **Particle size and shape**

- **Surface properties, both chemical and physical**

- **Continuous phase chemical and physical properties**

- **Particle–particle interactions**

- **Particle–continuous phase interactions**

Definition

- **Coagulum**
  - **An aggregate of colloidal particles having a relatively tight and dense structure formed as a result of the inability of the colloidal system to maintain its dispersed state**
  - **Such aggregates are normally formed irreversibly; that is, they cannot be returned to the colloidal state without significant input of work**
- **Coagulation**
  - **The process of forming coagulum**

Definition

- **Floc**
  - **An aggregate of individual colloidal particles related to a coagulum but generally having a rather loose, open structure**
  - **Flocs may sometimes be formed reversibly and returned to the dispersed state with minimal energy input**
- **Flocculation**
  - **The process of forming flocs**

Formation Mechanisms

- **Since colloids represent a range of unit sizes intermediate between molecules and macroscopic bulk phases, it seems reasonable to expect that the problem can be attacked from one of two directions**
  - **By breaking down large pieces to the size required, known generally as comminution**
  - **By starting with a molecular dispersion and build up the size by aggregation, that is, by condensation**
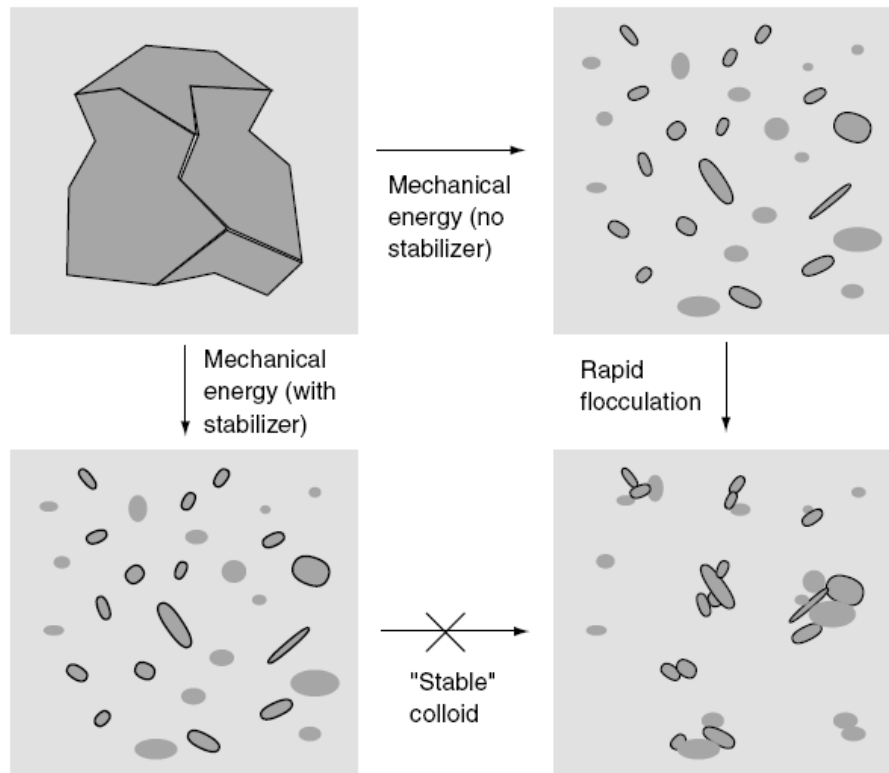
FIGURE 10.2. In the preparation of colloids by comminution, it is usually necessary to include a surfactant or polymeric stabilizer to inhibit the rapid flocculation of the newly formed particles.

Comminution

- **It is reasonable to assume that the work required to reduce a given material to colloidal size varies directly with the surface energy of the material; higher surface-energy materials require more work input**

- **The natural tendency of subdivided particles is to reduce the total surface area by some aggregation process, especially if produced in a vacuum or inert atmosphere**

Comminution

- **The attractive interaction between particles can be reduced by the introduction of an intervening medium, usually a liquid**
- **The liquid medium will have two positive effects on the process:**
    - **It will reduce the surface energy of the system by adsorption on the new surface**
    - **It will usually reduce the van der Waals attraction between the particles by averaging its Hamaker constant with that of the particulate material**

Comminution

- **The dispersed particles may begin to flocculate or coagulate rapidly once the comminution process is halted**
- **The solution is stabilized by the addition of new components (surfactant, polymer, small particles, etc.) that adsorb at the solid–liquid interface and provide an electrostatic or steric barrier that retards or prevents sticky collisions between particles, thereby making the dispersion more stable**
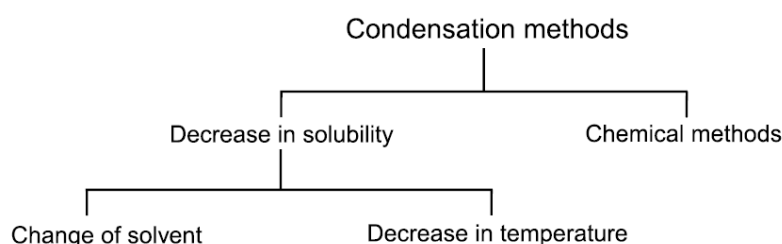

Figure 2.10. Types of condensation methods used for preparation of colloidal systems (sols).
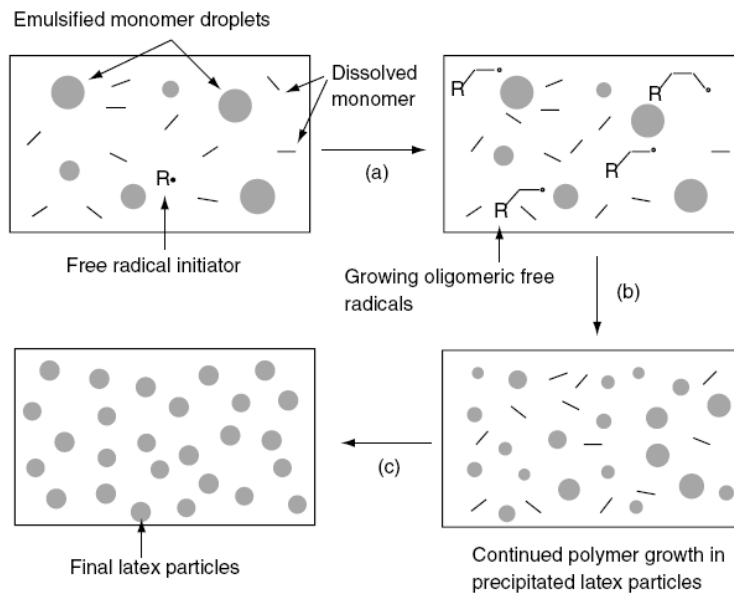
Condensation

FIGURE 10.3. In the process of emulsion polymerization, the incipient latex particle begins as a free-radical-initiated dimer or oligomer in solution (*a*). As polymerization proceeds, the growing chain precipitates and continues to grow, fed by new monomer taken from the reservoir of emulsified material (*b*). Polymerization continues until all available monomer is consumed (*c*).

Droplet Control for Microfluidics
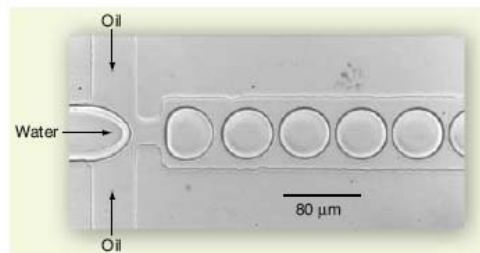
Monodisperse Double Emulsions Generated from a Microcapillary Device
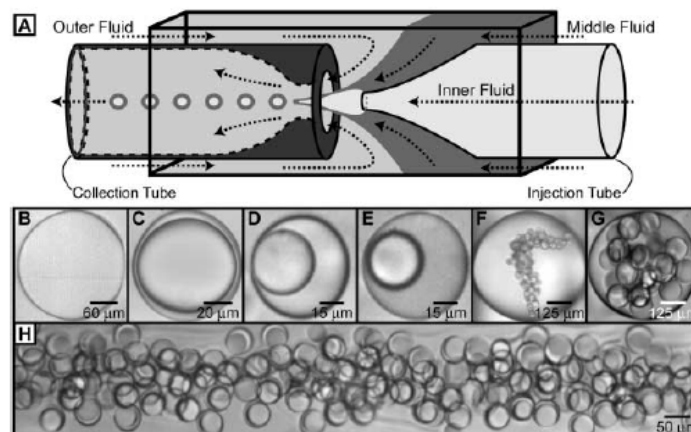
Miniaturizing Chemistry and Biology in Microdroplets
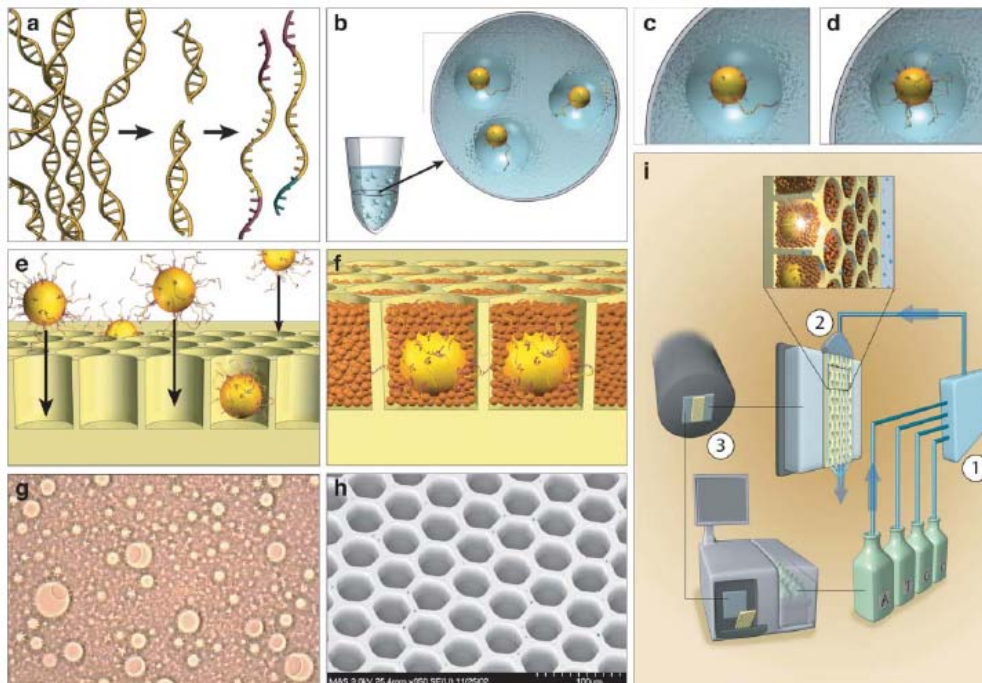
DLVO Theory

- **The study of colloidal stability is based on the DLVO theory, in honor of Derjaguin, Landau, Verwey, and Overbeek**

- **The theory describes the force between charged surfaces interacting through a liquid medium: it combines the effects of the van der Waals attraction and the electrostatic repulsion due to electrical double layers**

- **We use the DLVO theory to examine the dependence of colloid stability on the various parameters that determine the shapes and the magnitudes of interaction energies between particles**

Colloidal Stability

• Electrostatic repulsion between EDLs

$$\Delta G_{\text{total}} = - \Delta G_{\text{att}} + \Delta G_{\text{rep}}$$

A general expression for the repulsive interaction between the electrical double layers around two spherical particles is quite complex and does not warrant discussion here. A simple and relatively good approximate equation derived by Reerink and Overbeek is

$$\Delta G_{\text{rep}} = \frac{Bek^2T^2a\gamma^2}{z^2} \exp\left(-\kappa H\right) \qquad \kappa^2 = \frac{4\pi e^2}{\epsilon kT} \sum_i n_i z_i^2$$

where H is the distance between spheres of radius a, B is a constant, z is the charge on the counterion, e in the unit electrical charge, and

$$\gamma = \frac{\exp\left(ze\psi_s/2kT\right) - 1}{\exp\left(ze\psi_s/2kT\right) + 1}$$

$$\Delta G^{\text{total}} = \left[\left(\frac{Bek^2T^2a\gamma^2}{z^2}\right) \exp\left(-\kappa H\right)\right] - \left[\frac{A_H}{(12\pi H^2)}\right]$$
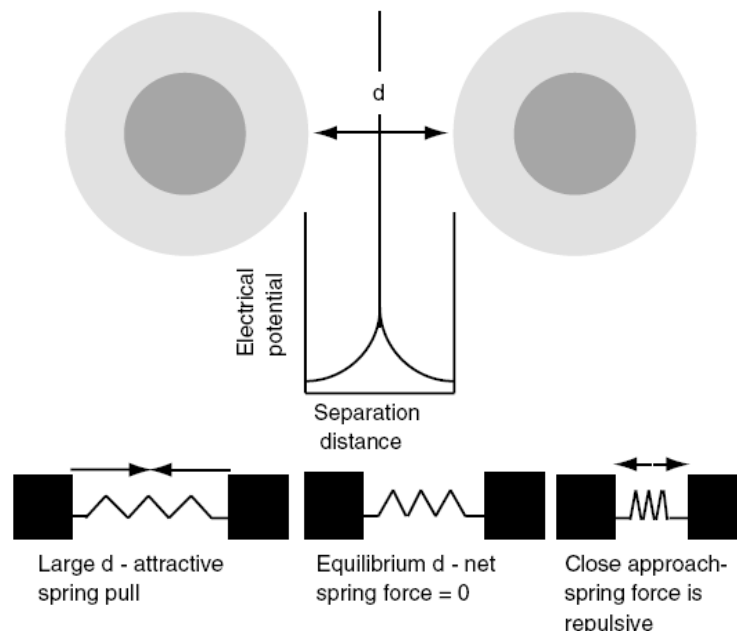
The interactions between two colloidal particles with electrical double layers can be visualized as two blocks connected by a spring. At large distances of separation the spring is stretched and applies a net force pulling the blocks together (attractive van der Waals interactions). At close approach, the spring is compressed producing a net repulsive force pushing the blocks apart (electrostatic repulsion). At some intermediate distance, the forces will be in equilibrium.

Repulsion between EDLs

- **The key element in determining the height of the energy barrier imposed by the electrical double layer is the concentration and valence of electrolyte in the system**

- **An increase in the electrolyte concentration reduces the repulsive electrostatic interaction, reducing the energy barrier and facilitating effective particle collisions - the system is less stable**

- **A good approximation to the point at which the system will begin to undergo rapid coagulation (indicating a loss of stability) is that at which**

$$\Delta G_{\text{total}} = 0 \text{ and } d\,\Delta G_{\text{total}}/dH = 0$$

Steric Stabilization

- **If two colloidal particles have an adsorbed layer of a lyophilic polymer, as they approach each other, those layers must begin to interpenetrate**

- **Such interpenetration can have two effects**
  - **An osmotic effect due to an increase in the local concentration of the adsorbed species between the two particles**
  - **An entropic or volume restriction effect because the interacting species begin to lose certain degrees of freedom due to crowding**
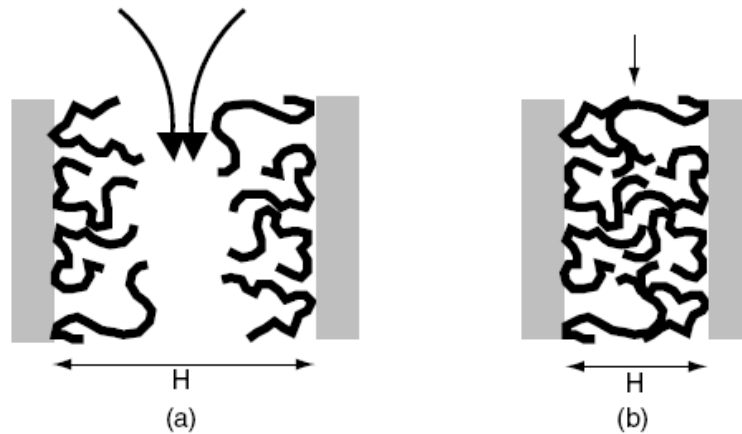
FIGURE 10.8. As two surfaces having adsorbed polymer approach, two phenomena occur that produce a net <u>repulsive</u> force between the surfaces. (*a*) At relatively close approach, but before actual interpenetration of the layers, the local concentration of polymer chains (between particles) increases above the "normal" equilibrium value giving rise to an <u>osmotic pressure effect</u>; solvent molecules move into the area between the surfaces and pushes them apart. (*b*) At distances where layer interpenetration occurs, the polymer chains begin to lose degrees of freedom (an entropy decrease) and <u>thermodynamic factors</u> introduce a second repulsive term.

Steric Stabilization

- **In both cases, the local system will experience a decrease in entropy, which will, of course, be unfavorable, while the osmotic effect may be accompanied by an unfavorable enthalpic effect due to desolvation of the more closely packed units**
- **In order to regain the lost entropy, the particles must move apart allowing them more freedom of movement, while solvent moves in to resolvate the units**
- **The result is an energy barrier retarding the approach of particles and providing an effective mechanism for stabilization (another spring so to speak)**

$$\Delta G_{total} = \Delta G_{steric} - \Delta G_{att}$$

Solvent Effects

- **The solvent plays a critical roles in determining the effectiveness of a given stabilizer–colloid–solvent system**
- **In a good solvent, the polymer chains will be extended in relatively open, random-coil configurations, giving optimum protective layer thickness**
- **As the temperature is changed, the quality of the solvent may decrease, at some point becoming poor, and the polymer chains will collapse into a more compact configuration**
- **The point at which the transition from good to poor solvent properties occurs is termed the θ point**

TABLE 13.2   Electrostatic and Steric Stabilization: A Comparison

Electrostatic stabilization	Steric stabilization
Addition of electrolytes causes coagulation.	Insensitive to electrolytes in the case of non-ionic polymers.
Usually effective in aqueous systems.	Equally effective for both aqueous and non-aqueous dispersions.
More effective at low concentrations of the dispersion.	Effective at both low and high concentrations.
Coagulation is not always possible.	Reversible coagulation is more common.

Source: Hunter, 1987.

Coagulation Kinetics

- **Due to random Brownian motion**
- **Whether there exists some barrier to coagulation between two approaching particles**
- **Fast Coagulation**
- **Slow Coagulation**

Fast Coagulation

Let us now consider coagulation of particles in the absence of any repulsive barrier. In addition, we assume that, although there are no inter-particle forces that contribute to the transport of particles toward each other, there is sufficient attraction between the particles on contact for them to form a permanent bond. As early as 1917, Smoluchowski formulated the equations for the collision rate for particles transported by diffusion alone, and we develop the same idea here.

We begin by considering an array of spherical particles with motion that is totally governed by Brownian movement. Let us assume that there are particles of two different radii, $R_{s,1}$ and $R_{s,2}$. We assume the spheres interact on contact, in which case they adhere, forming a doublet. Although this is a highly oversimplified picture, it provides a model from which more realistic models can be developed in subsequent stages of the presentation.

Radius, $R_{s,2}$

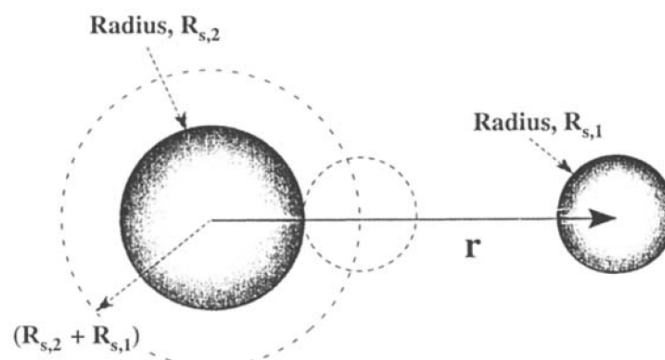Radius, $R_{s,1}$

r

$(R_{s,2} + R_{s,1})$

Figure 13.9 shows a schematic illustration of the formation of a doublet. We have fixed the origin of the coordinate system (i.e., $r = 0$, with r the center-to-center distance between two particles) at the center of a particle of type 2, that is, a particle with radius $R_{s,2}$. Since the particles adhere on contact, the rate at which these particles disappear equals the rate at which they diffuse across the dashed surface in the figure. This surface corresponds to a spherical surface of radius $(R_{s,1} + R_{s,2})$ inscribed around one of the spheres, which, for the present, is assumed to be stationary. After coagulation the number of independent kinetic units is locally decreased in the neighborhood of this coagulation site. Therefore we may imagine a concentration gradient around the fixed particle as responsible for the diffusion toward it.

According to Fick's first law, J, the number of particles crossing a unit area toward the reference particle per unit of time is given by

$$J = -D_1(dN_1/dr)$$

where D_1 is the diffusion coefficient of the spheres of radius $R_{s,1}$, and N_1 is their total number of particles of type 1 per unit volume. This flux can be combined with a number or mass balance equation on a thin spherical shell to obtain the unsteady-state diffusion for the particles:

Continuity equation: $\quad \dfrac{\partial N_1}{\partial t} = D_1 \dfrac{1}{r^2} \dfrac{\partial}{\partial r}\left(r^2 \dfrac{\partial N_1}{\partial r}\right)$

The diffusion coefficient D_1, is given by the Stokes-Einstein relation

$$D_1 = k_B T/6\pi\eta R_{s,1}$$

where T is the temperature of the dispersion (in K), η is the viscosity of the fluid (mass/(length · time)), and k_B is the Boltzmann constant. The diffusion equation for N_1 given above assumes that the spatial variation N_1 is spherically symmetric and depends on the radial distance only.

We restrict our attention to steady-state diffusion, for which the left-hand side of Equation (13) is zero. The resulting equation can be integrated easily, and one gets

$$N_1(r) = -B\frac{1}{r} + C$$

The flux at any distance r is obtained simply from the above solution using the Fick's law for flux:

$$J(r) = \text{Flux} = -D_1 \frac{dN_1}{dr}$$

Number of particles arriving at r per unit area per unit time

$$J(r) = -BD_1 \frac{1}{r^2}$$

Now, let us evaluate the constants B and C; for this we use the usual boundary conditions

    (i) As $r \to \infty$, $N_1(r) \to N_{b1}$,   the bulk concentration of particles (of type 1)   (18)

    (ii) At $r = R_{s,1} + R_{s,2}$, $N_1(r) = 0$ (19)

where we have assumed that particles of radius $R_{s,1}$ are diffusing relative to particles of radius $R_{s,2}$. The reference point $r = 0$ is fixed at the center of a particle of radius $R_{s,2}$ (see Fig. 13.9). The second boundary condition states that the "concentration" of particles of radius $R_{s,1}$ at the contact point $r = R_{s,1} + R_{s,2}$ is zero.

From the above conditions one sees that $C = N_{b1}$ and $B = N_{b1}(R_{s,1} + R_{s,2})$. Therefore, the flux at the contact point $r = (R_{s,1} + R_{s,2})$ becomes

$$J \text{ (at } r = R_{s,1} + R_{s,2}) = -D_1 N_{b1}(R_{s,1} + R_{s,2})^{-1} \tag{20}$$

The negative sign indicates that the particles of radius $R_{s,1}$ are transported toward the particle of radius $R_{s,2}$ (which has been assumed to be fixed in its position at $r = 0$). The magnitude of the collision rate Z_1, that is, the number of collisions of type 1 particles with a stationary particle of type 2 per unit time, is then

$$Z_1 = |J| 4\pi(R_{s,1} + R_{s,2})^2 = 4\pi(R_{s,1} + R_{s,2})D_1 N_{b1} \tag{21}$$

In general, particles of radius $R_{s,2}$ will also be executing random Brownian motion (i.e., diffusion). In such a case, D_1 should be replaced by $D_{12} = (D_1 + D_2)$. The collision rate Z_{12} (where the second subscript now reminds us that particle 2 is also executing diffusive motion) is then

$$Z_{12} = 4\pi(R_{s,1} + R_{s,2})D_{12}N_{b1} \tag{22}$$

The above result implies that the collision rate is of the form

$$Z_{12} = \alpha_r N_{b1} \tag{23}$$

where

$$\alpha_r = 4\pi(R_{s,1} + R_{s,2})D_{12} \tag{24}$$

with the subscript r indicating that the result is for rapid coagulation. One can now use this result to determine the reduction in N_{b1} as a result of the formation of 1-2 pairs (doublets). In particular, the rate of reduction of the bulk concentration N_{b1} with time t can be written as

$$dN_{b1}/dt = -\alpha_r N_{b1} N_{b2} \tag{25}$$

where we have multiplied Equation (23) by (a) N_{b2} since there are N_{b2} number of type 2 particles (used as reference particles in solving the diffusive collisions by particles of type 1) per unit volume of the dispersion and (b) -1 to indicate the reduction in the particles of type 1 due to coagulation. Note that the same equation with subscript 1 in place of 2 and vice versa describes the reduction in concentration N_{b2}.

For particles of identical radius R_s, one has

$$Z = 16\pi D R_s N_b = \alpha_r N_b \tag{26}$$

with

$$\alpha_r = 16\pi D R_s \tag{27}$$

Note that we no longer need the subscripts 1 and 2 on Z and N_b.

The coagulation rate for identical particles is then given by

$$\frac{dN_b}{dt} = -\frac{\alpha_r}{2} N_b^2 = -k_r N_b^2 \tag{28}$$

with $(\alpha_r/2)$ written as k_r, the *rate constant for rapid coagulation*. Notice that the factor (1/2) appears in this case to avoid counting the same particle twice in the total collision rate; that is, collision of particle i with particle j accounts also for collision of j with i. Equations (25) and (28) correspond to the rate expressions for bimolecular "reactions" and, in this sense, the above description of coagulation is analogous to two reactant particles forming a doublet as the product of the reaction.

Equation (28) can be solved easily to obtain the concentration N_b as a function of time. If N_{b0} is the overall (bulk) concentration at $t = 0$, one gets from the above equation

$$N_b(t)/N_{b0} = (1 + t/t_{1/2})^{-1} \tag{29}$$

where

$$t_{1/2} = \frac{2}{\alpha_r N_{b0}} = \frac{1}{k_r N_{b0}} \tag{30}$$

is the so-called *half-life* for coagulation, that is, the time it takes for the overall concentration to reduce to half the initial concentration N_{b0}. Equation (29) can also be written as

$$\frac{1}{N(t)} - \frac{1}{N_{b0}} = k_r t \tag{31}$$

One should keep in mind the restrictions or limitations implicit in this development. It has been assumed, in effect, that only binary collisions occur. The result obtained is therefore strictly applicable to dilute dispersions, for which the probability of the formation of triplets, quadruplets, and so on, is negligible.

The most reliable way to evaluate a rate constant for coagulation, therefore, is to measure N_b as a function of time. Although this is an easy statement to make, it is not an easy thing to do experimentally. One technique for doing this is literally to count the particles microscopically. In addition to particle size limitations, this is an extraordinarily tedious procedure. Light scattering (Chapter 5) is particularly well suited to kinetic studies since, in principle, experimental turbidities can be interpreted in terms of the number and size of the scattering centers. A variety of additional techniques for following the rate of particle disappearance has been developed for specific systems. We do not pursue these, but merely note that experimental rate constants for coagulation can be determined.

Now, substituting the Stokes-Einstein equation (Equation (14)) for the diffusion coefficient in the expression for k_r leads to

$$k_r = 4k_B T/3\eta \tag{32}$$

Note that the size of the particles drops out of the final expression for k_r; therefore the expression is equally valid for small molecules or colloidal particles so long as the various assumptions of the model apply. This constant describes the rate of diffusion-controlled reactions between molecules of the same size. In Example 13.2 we examine the numerical magnitude of the rate for the process we have been discussing.

EXAMPLE 13.2 *Variation of Particle Concentration Due to Rapid Coagulation.* An aqueous dispersion initially contains 10^9 particles cm^{-3}. Assuming rapid coagulation, calculate the time required for the concentration of the dispersed units to drop to 90% of the initial value. The viscosity of water is 0.010 P at 20°C, which may be used for the temperature of the experiment.

Solution: First we evaluate k_r, using Equation (32). It is convenient to use cgs units for this calculation; therefore we write $k_r = 4 \cdot (1.38 \cdot 10^{-16}) \cdot (293)/(3)(0.010) = 0.54 \cdot 10^{-11}$ cm^3 s^{-1}. Recall that the coefficient of viscosity has units (mass length^{-1} time^{-1}), so the cgs unit, the poise, is the same as (g cm^{-1} s^{-1}). As a second-order rate constant, k_r has units (concentration^{-1} time^{-1}), so we recognize that the value calculated for k_r gives this quantity per particle, or $k_r = 0.54 \cdot 10^{-11}$ cm^3 particle^{-1} s^{-1}. Note that multiplication by Avogadro's number of particles per mole and dividing by 10^3 cm^3 per liter gives $k_r = 3.25 \cdot 10^9$ liter mole^{-1} s^{-1} for the more familiar diffusion-controlled rate constant.

The 90% time is analogous to the half-life of the reaction. By considering a smaller extent of reaction, the assumptions of the model are more apt to remain valid. Substituting $N_b = 0.90$ N_{b0} into Equation (31), we obtain $(0.90 N_{b0})^{-1} - (N_{b0})^{-1} = k_r t_{0.90}$ or $t_{0.90} = (1.00 - 0.90)/0.90$ $k_r N_{b0} = 0.10/(0.90)(10^9)(0.54 \cdot 10^{-11}) = 20.6$ s. Note the cancellation of concentration units in this last step. ∎

$$k_r = 4k_B T/3\eta \qquad \frac{1}{N(t)} - \frac{1}{N_{b0}} = k_r t$$

$$\frac{1-0.9}{0.9 N_{b0} k_r} = \frac{0.1}{0.9 \times 10^9 \times 0.54 \times 10^{-11}} \qquad T_{0.5} = 185 \text{ s}$$

Slow Coagulation

We saw above, from Fick's first law of diffusion, that the flux at a distance r from the central particle is given by

$$J(r) = -D_1 \frac{dN_1}{dr} \tag{33}$$

at steady state (when only diffusion is the transport mechanism). We must now add the flux due to the interparticle interaction energy $\Phi_{12}(r)$ between particles of type 1 and type 2 to the above expression. The interaction energy exerts a force given by $(-d\Phi_{12}/dr)$ on the diffusing particle. This force imposes on the particle an effective *drift velocity* v_{eff}, given by

$$v_{eff} = -\frac{1}{f}\frac{d\Phi_{12}}{dr} \tag{34}$$

where f is the *friction factor* (and $1/f$ is the *mobility* of the particle; see Atkins 1994). Note that for a spherical particle of radius $R_{s,1}$ in Stokes flow, $f = 6\pi\eta R_{s,1}$ as we introduced in Chapter 2 and used in the last section. The velocity v_{eff} can therefore be written as

$$v_{eff} = -D_1 \frac{d(\Phi_{12}/k_BT)}{dr} \qquad D_1 = k_BT/6\pi\eta R_{s,1} \tag{35}$$

by using the Stokes-Einstein relation. Equation (33) for the diffusive flux can now be modified to include the flux $v_{eff} N_1$ caused by the drift velocity of the particles in the direction of the force due to interparticle energy:

$$J(r) = -D_1 \left| \frac{dN_1}{dr} + N_1 \frac{d(\Phi_{12}/k_BT)}{dr} \right| \tag{36}$$

The magnitude of the number of particles transported through the spherical cross section of area $4\pi r^2$ is then equal to the collision rate Z_1, which at steady state becomes

$$Z_1 = -4\pi D_1 r^2 \left| \frac{dN_1}{dr} + N_1 \frac{d(\Phi_{12}/k_BT)}{dr} \right| = \text{Constant} \tag{37}$$

This equation can be simplified by defining

$$y(r) = \exp[\Phi_{12}(r)/k_BT]N_1(r) \tag{38}$$

to

$$\frac{Z_1}{4\pi D_1} \exp[-\Phi_{12}(r)/k_BT] \frac{dr}{r^2} = dy \tag{39}$$

On integration one has

$$N_1(r) = e^{-\Phi_{12}(r)/k_BT}\left[N_{b1} - \frac{Z_1}{4\pi D_1} \int_r^{\infty} e^{\Phi_{12}(r)/k_BT}\frac{dr}{r^2} \right] \tag{40}$$

Lennard-Jones Potential

where the conditions that $N = N_{b1}$ and $\Phi_{12} \to 0$ as $r \to \infty$ have been used.

The second boundary condition (i.e., $N_1 = 0$ at $r = R_{s,1} + R_{s,2}$, which also implies that $\{\exp[\Phi_{12}(r)/k_BT]N_1(r)\}$ is also equal to zero at $r = R_{s,1} + R_{s,2}$) can now be used to get the collision rate Z_1 (with a stationary reference particle of radius $R_{s,2}$):

$$Z_1 = 4\pi D_1 N_{b1} \div \int_{R_{s,1}+R_{s,2}}^{\infty} e^{\Phi_{12}(r)/k_BT} \frac{dr}{r^2} \tag{41}$$
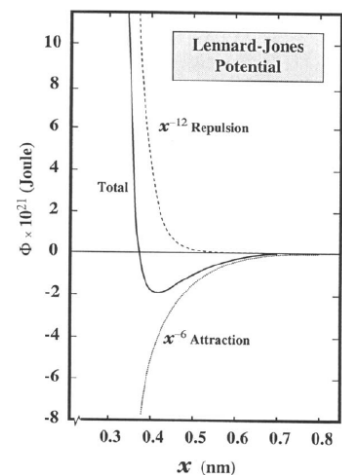
As discussed in the previous section, D_1 will have to be replaced with D_{12} for two mutually diffusing particles of radii $R_{s,1}$ and $R_{s,2}$:

$$Z_{12} = 4\pi D_{12} N_{b1} \div \int_{R_{s,1}+R_{s,2}}^{\infty} e^{\Phi_{12}(r)/k_B T} \frac{dr}{r^2} \qquad (42)$$

The total rate of collision (and, hence, the coagulation rate) is now given by

$$\frac{dN_{b1}}{dt} = -Z_{12} N_{b2} = -\left\{ 4\pi D_{12} N_{b1} \div \int_{R_{s,1}+R_{s,2}}^{\infty} e^{\Phi_{12}(r)/k_B T} \frac{dr}{r^2} \right\} N_{b2} \qquad (43)$$

in analogy with Equation (25).

Equation (43) can be written as

$$dN_{b1}/dt = -\alpha_s N_{b1} N_{b2} \qquad (44)$$

analogous to the case of rapid coagulation. The subscript s on the rate coefficient α_s draws attention to the fact that our focus here is slow coagulation:

$$\alpha_s = \left\{ 4\pi D_{12} \div \int_{R_{s,1}+R_{s,2}}^{\infty} e^{\Phi_{12}(r)/k_B T} \frac{dr}{r^2} \right\} \qquad (45)$$

For identical particles of radius R_s, with $D_{12} = D_1 + D_2 = 2D$, one gets from Equation (42)

$$Z = 8\pi D R_s N_b \div \int_0^{\infty} e^{\Phi(s)/k_B T} \frac{ds}{(s+2)^2} \qquad (46)$$

where s is the dimensionless surface-to-surface distance defined by $s = [(r/R_s) - 2]$. The corresponding coefficients α_s and k_s become

$$\alpha_s = 8\pi D R_s \div \int_0^{\infty} e^{\Phi(s)/k_B T} \frac{ds}{(s+2)^2} = 2 k_s \qquad (47)$$

where the fact that $k_s = (\alpha_s/2)$ has been used.

When there is no interaction force between the particles (i.e., $\Phi(r) \equiv 0$), the above result reduces to α_r, corresponding to the rapid coagulation rate given by Equation (27) in the previous section. When there is a strong repulsive barrier, the integral in Equation (47) leads to a large value, thereby reducing the rate of coagulation.

Stability Ratio W

Equations (27) and (47) show that

$$k_s = k_r/W \tag{48}$$

where W is the stability ratio defined in Equation (11). Thus

$$W = 2 \int_0^\infty e^{\Phi(s)/k_B T} \frac{ds}{(s+2)^2} = \frac{\text{Rate of diffusion-controlled interparticle collision}}{\text{Rate of interaction-force-controlled interparticle collision}} \tag{49}$$

As we noted above, the evaluation of W for given values of dispersion properties such as surface potential, Hamaker constant, pH, electrolyte concentration, and so on, forms the goal of classical colloid stability analysis. Because of the complicated form of the expressions for electrostatic and van der Waals (and other relevant) energies of interactions, the above task is not a simple one and requires numerical evaluations of Equation (49). Under certain conditions, however, one can obtain a somewhat easier to use expression for W. This expression can be used to understand the qualitative (and, to some extent, quantitative) behavior of W with respect to the barrier against coagulation and the properties of the dispersion. We examine this in some detail below.

When the repulsion barrier is large (i.e., Φ_{max} is about $10\,k_B T$ or larger), one can evaluate the integral in the expression for W using what are known as asymptotic techniques and obtain the following expression (Derjaguin 1989, p. 162):

$$W \approx 2\left(\frac{2\pi k_B T}{-\Phi''(s_m)}\right)^{1/2} \frac{e^{\Phi(s_m)/k_B T}}{(s_m + 2)^2} \tag{50}$$

where s_m is the value of s corresponding to the maximum in Φ [i.e., $\Phi(s_m) = \Phi_{max}$] and $\Phi''(s_m) = d^2\Phi/ds^2$ evaluated at $s = s_m$. Note that because $\Phi(s_m)$ is the maximum in the potential, the second derivative of Φ at $s = s_m$ is negative and $[-\Phi''(s_m)]$ is positive. Typically, the location of the maximum in $\Phi(s)$ occurs at distances of the order of a few nanometers. Therefore, for particle radii of the order of 100 nm or larger, $s_m \ll 1$, and the above equation simplifies to

$$W \approx \frac{1}{2}\left(\frac{2\pi k_B T}{-\Phi''(s_m)}\right)^{1/2} e^{\Phi_{max}/k_B T} \tag{51}$$

Equation (51) shows that W is a sensitive function of Φ_{max}, the maximum in the interaction potential, which in turn is a very sensitive function of properties such as ψ_0, electrolyte concentration, and so on. As a consequence, the stability ratio decreases rapidly with, for example, added electrolyte, and the dispersion coagulates beyond a threshold value of electrolyte concentration known as the critical coagulation concentration, as we saw in Section 13.3b.1.

Stability Ratio and Critical Coagulation Concentration

$$\log W = K_1 \log c + K_2$$

where K_1 and K_2 are constants and c is the concentration of the ions in moles per liter. For water at 25°C the value of K_1 has been calculated as $[-2.15 \cdot 10^9 \, \Upsilon_0^2 R_s/z^2]$ where Υ_0 is given by Equation (11.65) with ψ_0 in place of ψ, z is the valence of the counterions, and R_s (in m) is the radius of the particles. Notice that because of the way Equation (53) has been written, the value of K_2 depends on the units used for c, although taken together the right-hand side is dimensionless since $\log W$ is dimensionless. We shall not go into this further since our primary objective here is to use Equation (53) to examine the dependence of W on c and its agreement with experimental results.

log c (c in mmoles 1iter^{-1})
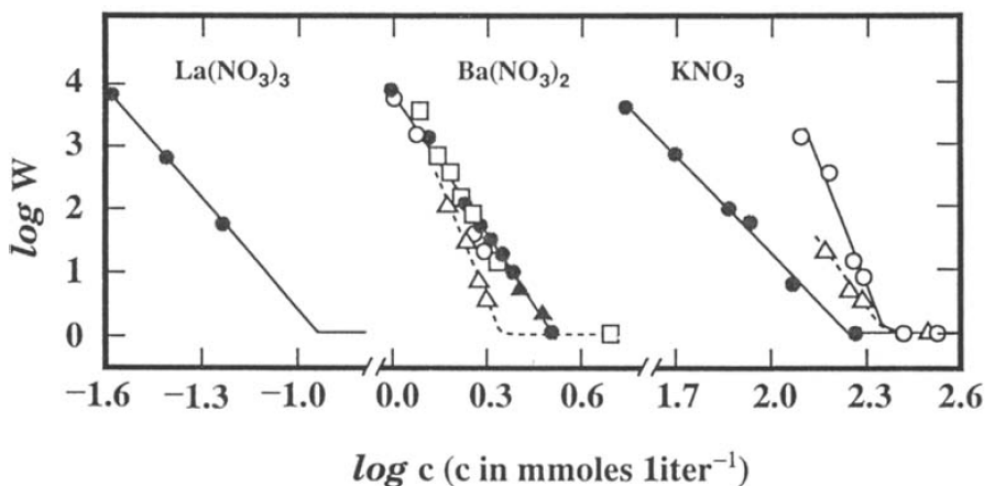
1. A plot of $\log W$ versus $\log c$ is linear as required by Equation (53).
2. The concentrations at which $W = 1$ (where the breaks in the curves appear) measure the CCC values for the electrolyte involved. The CCC values for mono-, di-, and trivalent ions are about 0.199, $2.82 \cdot 10^{-3}$, and $1.3 \cdot 10^{-4}$ mole liter^{-1}, respectively. These are in the ratio $1 : 1.42 \cdot 10^{-2} : 0.7 \cdot 10^{-3}$. These figures compare very favorably with the other experimental data for AgI and the theoretical values presented in Table 13.1.
3. Slow coagulation is observed for $\log W < 4$ or $W \approx 10^4$. For a typical potential energy curve, this corresponds to a value of Φ_m of about $15 \, k_B T$. From this we may conclude that the height of an energy barrier must be at least $15 \, k_B T$ if the colloid is to have any appreciable stability. Likewise, we may assume that unless the secondary minimum is approximately this deep, particles will be able to "escape" from it. In view of the general shape of the potential energy curves, the retardation effect, and this assessment of what constitutes a "high" barrier or a "deep" well, it seems likely that *rigid* aggregates are not formed in the secondary minimum.
4. Equation (53) can be used to analyze the slopes of the curves in Figure 13.10 since the mean size of the AgI particles is known. In this way, Reerink and Overbeek (1954) found ψ_0 values in the range 12 to 53 mV and A values in the range $0.2 \cdot 10^{-20}$ to 10^{-19} J. Both of these are of the proper order of magnitude—no minor accomplishment in itself in light of the diverse assumptions required to get to this point.
5. The values of A and ψ_0 obtained from this analysis are slightly less satisfying in detail: The values of A show a lot of scatter and ψ_0 appears to be too low. Recall that the variation of the CCC with z^{-6} implies large values of ψ_0 (see Section 13.3b.2); for lower ψ_0 values a different dependence on z is expected.
6. Least satisfactory of all is the correlation with particle size. The results shown in Figure 13.10 were determined for AgI sols covering a 10-fold range of particle sizes.

Complete Interaction

$$\Delta G_{\text{total}} = \Delta G_{\text{elec}} + \Delta G_{\text{steric}} + \Delta G_{\text{misc}} - \Delta G_{\text{att}}$$

- **Proteins, for example, are excellent protective colloids. They are polymeric and tend to adsorb on various surfaces, providing good steric stabilization, and may also be charged (depending on the pH), providing electrostatic stabilization as well. Such a dual nature can have certain practical advantages.**