Coagulation of Particles

Aerosol particles collide due to their random motions and coalesce to form larger chains of flocs made up of many particles. The Brownian (thermal) motion of particles, turbulence, presence of a shear field, and external forces such as gravity and electrical forces could cause coagulation.

Coagulation of Monodisperse Spheres

Smoluchowski was the first to develop a model for the coagulation of monodispersed spherical aerosols. He considered the reference particle to be fixed as shown in Figure 1. The other particles would then diffuse to the reference particle by the action of the Brownian motions. The concentration then satisfies the following diffusion equation:

\[
\frac{\partial c}{\partial t} = D \nabla^2 c = D \nabla^2 \frac{\partial^2 c}{\partial t^2} + \frac{2 \partial c}{\partial t} \]

subject to boundary conditions

\[
c = 0 \text{ at } r = d , \ \\
c = c_0 \text{ at } t = 0 , \text{ or } r \ \\
(1)
\]

Here, \( d \) is the diameter of the particle and \( c_0 \) is the concentration far away. Equation (2) assumes sticking of particles without rebound upon contact.

Figure 1. Schematic of Brownian coagulation of monodispersed particles.

Equation (1) may be restated as
\[
\frac{\partial (cr)}{\partial t} = D \frac{\partial^2 (cr)}{\partial r^2}.
\] (4)

The concentration field then is given by
\[
c = c_0 \left(1 - \frac{d}{r} + \frac{d}{r} \operatorname{erf} \left( \frac{r - d}{2 \sqrt{Dt}} \right) \right).
\] (5)

The flux to surface of the reference particle is given by
\[
I = J \Delta A = 4 \pi d^2 D \left. \frac{\partial c}{\partial r} \right|_{r = d},
\] (6)

where \( J = D \frac{\partial c}{\partial r} \) is the flux and \( I \) is the total flux to the surface of the reference particle per unit time. Using (5), it follows that
\[
I = 4 \pi d D c + \frac{d}{\sqrt{4 \pi D t}}.
\] (7)

For large \( t \gg \frac{d^2}{D} \),
\[
I = 4 \pi d D c.
\] (8)

In reality, the reference particle is not fixed and is diffusing itself. The relative diffusivity of two particles is sum of their diffusivities. That is according to Einstein's equation
\[
D_{ij} = \frac{\left( \overline{x_i x_j} \right)}{2t} = \frac{x_i^2}{2t} \left( \frac{2x_i x_j}{2t} + \frac{x_j^2}{2} \right),
\] (9)

\[
D_{ij} = D_i + D_j.
\]

In the derivation of (9) it is assumed that \( \overline{x_i x_j} = 0 \), because the motions of the two particles are independent. Therefore, in a time \( dt \), the reference particle collides with
\[
8 \pi d D c dt = \Delta c dt
\] (10)
particles. Here, $\Box$ is the collision frequency function. With $c$ particles per unit volume, there will be $\frac{c}{2}$ collisions if all the particles collide once. Assuming that the particles stick to each other upon collision, it follows that

$$\frac{dc}{dt} = \Box \frac{c^2}{2},$$  \hspace{1cm} (11)$$

where

$$\Box = 8\Box dD = \frac{8kT}{3\Box} c,$$  \hspace{1cm} (12)$$
is the collision frequency function of coagulation constant.

Equation (11) may be solved. i.e.,

$$\frac{1}{c} \frac{1}{c_0} = \frac{t}{2},$$  \hspace{1cm} (13)$$
or

$$c = \frac{c_0}{1 + \frac{t}{2}} = \frac{c_0}{1 + \frac{t}{t_h}}.$$  \hspace{1cm} (14)$$

Here, $t_h$ is the half-value time, which is the time that the concentration becomes half of its original value.

**Coagulation of Many Sizes**

Consider an aerosol, which initially consists of particles of different sizes. The concentration of the $k$th size particle then satisfies the following equation:

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{j \neq k} \Box_{kj} c_j c_k,$$  \hspace{1cm} (15)$$

where the first term on the right hand side is the generation rate of the $k$th particle by combination and the second term is the loss of $k$th particle due to coalescence. Here, $\Box_{kj}$ is the collision frequency function (coagulation parameter) for particles with diameters $d_j$ and $d_k$ shown in Figure 2 and is given by
\[ \Theta_{kj} = 2 \left( d_j + d_k \right) \left( D_j + D_k \right) \]  

(16)

The corresponding values of \( \Theta_{kj}(d_j, d_k) \) are listed in Table 1.

![Figure 2. Brownian coagulation of dissimilar particles.](image)

Table 1. Collision frequency function \( \Theta(d_j, d_k) \times 10^{10} \text{ cm}^3 / \text{s} \).

<table>
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<th>( d_i (\text{m}) )</th>
<th>( 2 \times 10^{13} )</th>
<th>( 4 \times 10^{13} )</th>
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<th>.02</th>
<th>.04</th>
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**Effect of Particle Force Field**

The particle force field will modify the collision frequency. It may be shown that the collision distribution function is given as (Friedlander, 2000)
\[
\Phi_{ij} = \frac{2\phi(d_i + d_j)(D_i + D_j)}{W}
\]  

(17)

where

\[
W = \left(\frac{d_i + d_j}{2}\right) \phi \left(\frac{x}{kT}\right) \frac{\text{d}x}{x^3}.
\]  

(18)

Here, \(\phi(r)\) is the potential energy of the central force per unit mass with

\[
F(r) = \frac{\text{d}\phi}{\text{d}r}.
\]  

(19)

**Van der Waals Force**

The potential energy for the attractive van der Waals force is given by

\[
\Phi(r) = \frac{d_i d_j}{6} \left[ \frac{r^2}{d_i + d_j} + \frac{r^2}{d_i} + \ln \frac{r^2}{d_i} \right] + \frac{d_i d_j}{6} \left[ \frac{r^2}{d_i + d_j} + \frac{r^2}{d_i} + \ln \frac{r^2}{d_i} \right] + \frac{d_i d_j}{6} \left[ \frac{r^2}{d_i + d_j} + \frac{r^2}{d_i} + \ln \frac{r^2}{d_i} \right]
\]  

(20)

where \(r\) is the distance between the centers of the sphere and \(A\) is the Hamaker constant.

For monosize particles,

\[
\Phi = \frac{A}{6} \left[ \frac{d^2}{r} + \frac{d^2}{r d^2} + \ln \frac{d^2}{r} \right]
\]  

(21)

and

\[
W = \frac{\exp{\left(\frac{A\phi(x)}{6kT}\right)}}{\int_0^\infty dx},
\]  

(22)

where
\[ f(x) = \frac{x^2}{2} + \frac{x^2}{2(1 + x^2)} + \ln(1 + x^2) \]  \hspace{1cm} (23)

The increase of collision frequency with \( \frac{A}{kT} \) is shown in the figure:

(Diagram Here)

**Coulomb Forces**

For charged particles, the Coulomb force potential is given as

\[ \Phi = \frac{z_i z_j e^2}{\epsilon} \], \hspace{1cm} (24)

where \( z_i \) is the number of charges, \( e \) is the electronic charge, and \( \epsilon \) is the dielectric constant of the medium.

The expression for \( W \) then is given by

\[ W = \frac{1}{y} \left( e^y \Phi + 1 \right) \], \hspace{1cm} (25)

where

\[ y = \frac{2z_i z_j e^2}{kT(d_i + d_j)} \] \hspace{1cm} (26)

is the ratio of the electrostatic potential energy at contact to the thermal energy \( kT \).

For \( y = 0 \), \( W = 1 \). For charges of opposite sign, \( y \) is negative and \( 0 < W < 1 \) and hence collision rate increases. When charges have the same sign, \( y > 0 \) and \( W > 1 \) and the collision rate decreases.
For large numbers of charged particles, the coulomb potential must be modified to account for Debye shielding effects. Accordingly, equation (26) is replaced by

\[
y = \frac{1}{2} \left( \frac{1}{kT} \right)^{\frac{2}{3}} \left( \frac{e^2}{kT} \right)^{\frac{2}{2}}.
\]

(27)

**Shear Flows**

The collision frequency function due to shear flow is given as

\[
\tau_{ij} = \frac{1}{6} \left( d_i + d_j \right) \frac{dU}{dy}.
\]

(28)

For \( d_i = d_j = d \),

\[
\tau = \frac{4}{3} d^3 \frac{du}{dy}.
\]

(29)

**Turbulence**

Saffman and Turner suggested that

\[
\tau_{ij} = 1.3 \left( \frac{d_i + d_j}{2} \right)^{\frac{1}{3}}.
\]

(30)

where \( \tau \) is the dissipation rate and \( \nu \) is the kinematic viscosity. For pipe flows (core region),

\[
\tau = \frac{2}{R} \left\{ \frac{f}{R} \right\}^{\frac{3}{2}} V^3,
\]

(31)

where \( V \) is the mean velocity, \( f \) is the friction factor, and \( R \) is the pipe radius. Average dissipation rate for the pipe is given as

\[
\bar{\tau} = \frac{f V^3}{4 R}.
\]

(32)
**Differential Motion by Gravitational Force**

For particles falling according to Stokes settling velocity, the collision frequency function is given by

\[
\Theta_{ij} = \frac{d_i^p g}{\Theta} d_j^4 (1 + \Theta)^2 \left[ \frac{3}{2(l + \Theta)} + \frac{1}{2(l + \Theta)^2} \right] (l + \Theta)^2
\]  

(33)

where

\[
\Theta = \frac{d_i}{d_j} < 1
\]

*(Diagram Here)*
Electrical Double Layer Interactions for Colloidal Systems

Most colloidal particles carry electrostatic charges. Since the dispersion as a whole is neutral, there must be an excess of ions of opposite charge in the solution. These excess ions are found near the surface of suspended colloidal particles and form what is called a "diffused electrical double layer." The double layer has a profound effect on interactions of colloidal particles.

Ion Distribution Near a Colloidal Particle

Consider the diffusion of ions near a charged surface. The convective diffusion equation for the number concentration, \( n_i \), of ion \( i \) is given as

\[
\nabla \cdot (D_i \nabla n_i) = \nabla \cdot (u_i n_i),
\]

where \( D_i \) is the diffusivity and \( u_i \) is the velocity due to the electric field. Force balance of a single ion gives

\[
\frac{3 \zeta \eta d_i u_i}{c_c} = z_i e E,
\]

where \( \eta \) is the viscosity, \( d_i \) is the diameter, \( c_c \) is the slip correction, \( e \) is the unit electric charge, \( z_i \) is the valency of ion \( i \) and \( E \) is the electric field strength given as

\[
E = \phi
\]

and \( \phi \) is the electric field potential.

Equation (2) leads to

\[
u_i = \frac{z_i e E}{3 \zeta \eta d_i} = \frac{z_i e E d_i}{kT c_c}
\]

where

\[
D_i = \frac{kT}{3 \zeta \eta d_i c_c}
\]

is used. Using (3) and (4) in (1), we find
\[ \mathbf{D} \cdot (\nabla \mathbf{n}_i) = \mathbf{D} \cdot \left( \frac{n_i \mathbf{z}_i e \mathbf{D}}{kT} \right) \]  \tag{6}

or

\[ \ln n_i = \frac{n_i - \mathbf{z}_i e \mathbf{n}_i}{kT} \]  \tag{7}

Integrating (7), one finds

\[ n_i = n_{i0} \exp \left( \frac{\mathbf{z}_i e \mathbf{n}_i}{kT} \right) , \]  \tag{8}

the well-known Boltzmann distribution. Note that the potential \( \phi = \phi (\mathbf{x}) \).

Using Coulomb's law and equation (3), we find

\[ \nabla^2 \phi = \frac{\mathbf{z}_i e}{\epsilon} \]  \tag{9}

where \( \epsilon \) is the permittivity (dielectric constant times permittivity of free space), and \( \mathbf{z}_i e \) is the charge density given as

\[ \mathbf{z}_i e = \mathbf{z}_i n_i \]  \tag{10}

Using (10) in (9), the Poisson-Boltzmann equation follows, i.e.

\[ \nabla^2 \phi = \epsilon \nabla \mathbf{z}_i n_i e + \frac{\mathbf{z}_i e}{kT} \]  \tag{11}

Solution of (11) gives \( \mathbf{n}_i \) and \( n_i \). Equation (11) is restricted to low electrolyte concentrations, since ions are treated as point charges.

**Debye-Huckel Approximation**

For low potential \( z_i e \mathbf{\phi} \ll kT \) and

\[ e^{\frac{\mathbf{z}_i e \mathbf{\phi}}{kT}} = 1 \left( \frac{\mathbf{z}_i e \mathbf{\phi}}{kT} \right) \]  \tag{12}

Using (12) in (11) and noting the neutrality condition of the burk suspension,
\[ n_{i_0} Z_i e = 0, \]  
\( (13) \)

it follows that
\[ \bar{\Phi}^2 \bar{\Phi} = \bar{\Phi}^2 \bar{\Phi} \]  
\( (14) \)

where
\[ \bar{\Phi} = \sqrt{\frac{e^2}{kT n_{i_0} Z_i^2}} \]  
\( (15) \)

is the Debye-Huckel parameter.

The solution of (14) for double layer adjacent to a flat plate is given as
\[ \bar{\Phi} = \bar{\Phi}_0 e^{\bar{\Phi}_0 y}. \]  
\( (16) \)

For double layer near a spherical particle of radius \( a \),
\[ \bar{\Phi} = \bar{\Phi}_0 e^{\bar{\Phi}_0 (r/a)}. \]  
\( (17) \)

In (16) and (17), \( \bar{\Phi}_0 \) is the potential at the surface, and \( \bar{\Phi} \) decays with distance from the surface. The characteristic length is \( \bar{\Phi}_0 \) (Debye length) double layer thickness. The concentration of electrolyte is related to \( n_{i_0} \) by
\[ n_{i_0} = 1000 N_A c_{i_0}, \]  
\( (18) \)

where \( c_{i_0} \) is the bulk concentration of ions of species \( i \) (in mol/L) and \( N_A = 6.02 \times 10^{23} \) is Avogadro's number. Typically, \( \bar{\Phi}_0 \) varies from less than 1 nm to about 100 nm.

**Gouy-Chapman Theory**

An exact solution of Poisson-Baltzmann equation for symmetric electrolytes for which
\[ z^*_+ = \bar{\Phi} Z_i = z \]  
\( (19) \)

and
\[ n^0_+ = n^0_- \]  \hspace{1cm} (20)

was found by Gouy-Chapman for double layer near a place. In this case, equation (11) reduces to

\[ \frac{d^2 \phi}{dx^2} = \frac{2en_0z}{\phi} \sinh \left( \frac{ze\phi}{kT} \right) \]  \hspace{1cm} (21)

The solution to (21) is

\[ \phi = \frac{2kT}{ze} \ln \left( 1 + \frac{\phi_0 e^{k\phi_0} \phi}{1 + \phi_0 e^{k\phi_0}} \right), \]  \hspace{1cm} (22)

where

\[ \phi_0 = \tanh \left( \frac{ze\phi_0}{kT} \right). \]  \hspace{1cm} (23)

The surface charge density, \( \phi \), may be related to surface potential \( \phi_0 \), i.e.

\[ \phi = \int_0^\infty dy = \int_0^{\phi_0} \frac{d\phi}{dx} \bigg|_{x=0} = \frac{2kT}{ze} \sinh \left( \frac{ze\phi_0}{kT} \right) \]  \hspace{1cm} (24)

for \( \phi \) given by (22) and

\[ \phi = \phi_0 \]  \hspace{1cm} (25)

for \( \phi \) given by (16). This means that the double layer may be considered as a capacitor consisting of two plates a distance of \( \phi_0 \) apart.

For spherical particles, the surface charge density is

\[ \phi = \frac{1 + \frac{\phi}{a}}{a} \phi_0, \]  \hspace{1cm} (26)

and the total surface charge of the sphere becomes

\[ Q_e = 4\pi a \frac{1 + \phi_0}{a} \phi_0. \]  \hspace{1cm} (27)
Electrostatic Double Layer Interactions

Colloidal particles carrying the same surface charges cause double layer repulsion.

Constant Potential Interactions

The interaction energy for two spheres of radii $a_1$ and $a_2$ and potentials $\varphi_{01}$ and $\varphi_{02}$ at infinite separation is given as

$$V = \frac{h^2 a_1 a_2}{4(a_1 + a_2)} \left[ 2\varphi_{01} \varphi_{02} \ln \frac{1 + \exp(h)}{1 - \exp(h)} \right] + \ln \left[ \frac{e^{-2\varphi_{01} h}}{e^{-2\varphi_{02} h}} \right] \quad \text{(28)}$$

where $\varphi$ is the dielectric constant of the medium, $h$ is the distance of minimum approach and $2\varphi$ is the double layer thickness. Equation (28) holds for $\varphi < 25 \text{ mV}$ and $2\varphi << a_1, a_2$.

For sphere-plate the interaction energy is twice that of sphere-sphere, i.e.,

$$V_{\text{sp}} = 2V_{\text{ss}}. \quad \text{(29)}$$

The corresponding force (repulsion) is

$$F_{\text{sp}} = -\frac{dV_{\text{sp}}}{dh} = \frac{h}{2} \left( \frac{2\varphi_{01} \varphi_{02}}{1 - \exp(h)} \right) \left[ 2\varphi_{01} \varphi_{02} \ln \frac{1 + \exp(h)}{1 - \exp(h)} \right] \quad \text{(32)}$$

For materials with $\varphi_{01} = \varphi_{02} = \varphi_0$, equation (30) becomes

$$F_{\text{sp}} = \frac{h \varphi_0^2 x e^{-\varphi_0 h}}{1 + e^{-h}} \quad \text{(31)}$$

Constant Charge Interactions

The repulsion interaction energy of two colloidal particles with constant surface charge density is given as

$$V = V \frac{h^2 a_1 a_2}{2(a_1 + a_2)} \ln \left[ \frac{e^{-2\varphi_{01} h}}{e^{-2\varphi_{02} h}} \right] \quad \text{(32)}$$

The corresponding sphere-plate force is
\[ F_{s\|b}^{\|} = \frac{h}{2} \left( \bar{\phi}_{01}^2 + \bar{\phi}_{02}^2 \right) \frac{e^{\bar{\phi}_{01}\hbar}}{1 + e^{\bar{\phi}_{01}\hbar}} \left( \bar{\phi}_{01}^2 + \bar{\phi}_{02}^2 \right) + e^{\bar{\phi}_{01}\hbar} \]  
(33)

When \( \bar{\phi}_{01} = \bar{\phi}_{02} = \bar{\phi}_0 \),

\[ F_{s\|b}^{\|} = \frac{h}{2} \bar{\phi}_0^2 e^{\bar{\phi}_0\hbar} \frac{1}{1 + e^{\bar{\phi}_0\hbar}} . \]  
(34)

In practice, \( \bar{\phi}_0 \) is not known and usually it is assumed that

\[ \bar{\phi}_0 = \bar{\phi} \text{ potential } = \text{Elecrokinetic potential} . \]  
(35)

(Diagram Here)

Two Spheres Interactions

Constant Potential (Deryaguin)

\[ V_{s\|b}^{\|} = 2 \bar{\phi}_0^2 \ln \left( 1 + e^{\bar{\phi}_0\hbar} \right) \]  
(36)

\[ F_{s\|b}^{\|} = 2 \bar{\phi}_0^2 \frac{e^{\bar{\phi}_0\hbar}}{1 + e^{\bar{\phi}_0\hbar}} \]  
(37)

Linear Superposition (Debye-Huckel)

\[ V_{s\|b}^{\|} = 4 \bar{\phi}_0^2 \frac{a^2}{2a + h} \bar{\phi}_0^2 e^{\bar{\phi}_0\hbar} \]  
(38)

\[ F_{s\|b}^{\|} = \bar{\phi}_0^2 \frac{1 + \left( h + 2a \right)}{2a} e^{\bar{\phi}_0\hbar} \]  
(39)

Superposition (thin double layer)

\[ V_{s\|b}^{\|} = 32 \bar{\phi}_0^2 kT \frac{a \tanh^2 \frac{\bar{\phi}_0 ze}{4kT}}{ze} \]  
(40)

\[ F_{s\|b}^{\|} = 32 \bar{\phi}_0^2 kT \frac{a \tanh^2 \frac{\bar{\phi}_0 ze}{4kT}}{ze} \]  
(41)
**Electrokinetic Phenomena**

Electrokinetic phenomena occur when there is relative motion between the charged interface and the adjacent electrolyte solution so that part of the double layer charge moves with the liquid. The "plane of shear" separates the mobile part of the double layer from the fixed part. The electrical potential at the shear plane is the electrokinetic potential or the zeta potential (\( \zeta \)-potential).

**Electro-Osmosis**

Electro-osmosis is the flow of liquid due to influence of an applied electric field. Assume an electric field \( E \) is applied parallel to a surface. If the charge density is \( \varrho_e \), it follows that

\[
\varrho \frac{d^2u}{dy^2} = \varrho_e E
\]

**(Diagram Here)**

Using (9) to replace \( \varrho_e \) in term of \( \varrho(y) \), \( \varrho \varrho_e = \varrho \varrho_e \), we find

\[
\varrho \frac{d^2u}{dy^2} = \varrho E \frac{d^2\varrho}{dy^2}
\]

or

\[
u_{e0} = \frac{E \varrho}{\varrho}
\]

where \( u_{e0} \) is the electro-osmosis velocity and we assumed that at \( y = 0 \),

\[
 u = 0, \quad \varrho = \varrho_0
\]

**Particle Electrophoresis**

Particle electrophoresis is the movement of charged particles in an electric field. For thin double layer (\( \kappa a \gg 1 \)),

\[
u^p = \frac{E \varrho}{\varrho}
\]
which may be restated in terms of the electrophoretic mobility, \( U \) (velocity for unit field) as

\[
U = \frac{m_{ex}}{a}.
\]  

(47)

This is known as Smoluchowski equation.

For small particles with \( a \ll 1 \), the viscous drag must be balanced by the Coulomb force, i.e.

\[
6m_{ex}aU = EQ = E\left(4\pi a \right)
\]

where equation (27) is used for total charge and \( a_0 \) is replaced by \( a \).

It then follows that

\[
U = \frac{2m_{ex}}{3a},
\]

(48)

which is known as the Huckel equation. More generally, then

\[
U = \frac{2m_{ex}}{3a} f_i(\alpha a)
\]

(49)

where \( f_i(\alpha a) \) varies from 1 to 1.5 for \( \alpha a \) varying between 0 to \( a \).

**Born Repulsion**

At very short distances, the interpenetration of electron shells leads to the strong repulsive force known as the Born repulsion. The corresponding interaction energy is given as

\[
V_B = \frac{A_{cc}}{7560} \left( \frac{8a + h}{2a + 7} \right) + \frac{6a \, m_{ex} h}{h^7}
\]

(50)

for sphere-plate where \( a_c \) is the collision diameter (typical of the order of 5 Å).

**DLVO Theory of Colloidal Stability**

The theory of colloidal stability was developed by Deryaguin, Landau (1941), Verway, and Overbeak (1948) and is now known as the DLVO theory.
The interaction potential between particles is composed as the sum of van der Waals, $V_A$, electrical double layer, $V_R$, and Born, $V_B$, i.e.

$$V_T = V_A + V_R + V_B$$  \hspace{1cm} (51)\]

Depending on the magnitude of van der Waals and electrical double layer potential energies, the suspension could be stable or could rapidly aggregate.

Figure (a) shows a stable suspension where a strong energy barrier (EB) is formed. There is a deep primary minimum (SM). The secondary minimum could lead to weak aggregation which will break easily.

(Diagram Here)

Figure (b) shows the total potential for a colloidal system for which the electrical double layer is weak or absent. The particles will attract each other and the suspension will aggregate quickly.

(Diagram Here)

**Steric Interaction**

A colloidal suspension could remain stable when the particles absorb polymeric chains.

**Hydrophobic Interaction**

There is an attraction between hydrophobic surfaces as a result of water molecules migrating from the gap to the bulk.

**Hydration Effects**

At very short distances, hydrophilic surfaces may experience hydration repulsion. This is because of the need for the surfaces to become dehydrated for the particles to come in contact.