

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:

$$\frac{\partial c}{\partial t} = D \nabla^2 c = D \left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right] \quad (1)$$

subject to boundary conditions

$$c = 0 \text{ at } r = d, \quad (2)$$

$$c = c_0 \text{ at } t = 0, \text{ or } r \rightarrow \infty. \quad (3)$$

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.

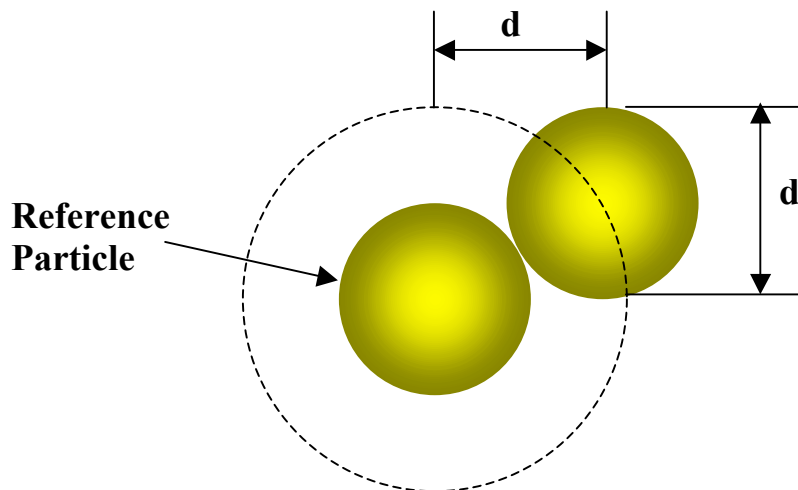


Figure 1. Schematic of Brownian coagulation of monodispersed particles.

Equation (1) may be restated as

$$\frac{\partial(cr)}{\partial t} = D \frac{\partial^2(cr)}{\partial r^2}. \quad (4)$$

The concentration field then is given by

$$c = c_0 \left[\frac{d}{r} + \frac{d}{r} \operatorname{erfc} \left(\frac{r-d}{2\sqrt{Dt}} \right) \right]. \quad (5)$$

The flux to surface of the reference particle is given by

$$I = JA = 4\pi d^2 D \left. \frac{\partial c}{\partial r} \right|_{r=d}, \quad (6)$$

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

$$I = 4\pi d D c_0 \left[\frac{d}{\sqrt{\pi Dt}} + \frac{d}{\sqrt{\pi Dt}} \right]. \quad (7)$$

For large $t \gg \frac{d^2}{D}$,

$$I = 4\pi d D c_0. \quad (8)$$

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

$$D_{ij} = \frac{\overline{(x_i - x_j)^2}}{2t} = \frac{\overline{x_i^2}}{2t} + \frac{\overline{x_j^2}}{2t} + \frac{2\overline{x_i x_j}}{2t}, \quad (9)$$

$$D_{ij} = D_i + D_j,$$

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

$$8\pi d D c dt = \pi c dt \quad (10)$$

particles. Here, Ω 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

$$\frac{dc}{dt} = -\Omega \frac{c}{2}, \quad (11)$$

where

$$\Omega = 8\pi D^2 = \frac{8kT}{3\mu} c_c, \quad (12)$$

is the collision frequency function of coagulation constant.

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

$$\frac{1}{c} \frac{dc}{dt} = -\frac{\Omega}{2}, \quad (13)$$

or

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

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:

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{j=1}^{k-1} \Omega_{j(k-j)} c_j c_{k-j} - \sum_{j=1}^{\infty} \Omega_{kj} c_k c_j, \quad (15)$$

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, Ω_{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

$$\Omega_{kj} = 2(d_j + d_k)(D_j + D_k) \quad (16)$$

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

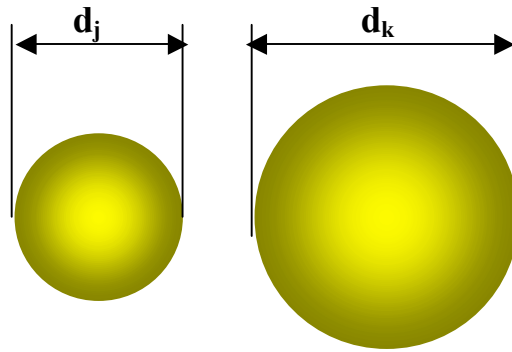


Figure 2. Brownian coagulation of dissimilar particles.

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

d_2 (μm) \backslash d_1 (μm)	2×10^3	4×10^3	.01	.02	.04	0.1	0.2	0.4	1	2	4	10	20
0.002	2.25												
0.004	3.75	3											
.01	15	7.5	4.5										
.02	45	20	7.5	6									
.04	150	55	17.5	8.5	5.5								
0.1	800	275	60	20	7.5	3.6							
0.2	2500	700	135	40	12.5	4	2.6						
0.4	6500	2050	300	85	23.5	5.5	2.65	2					
1	18500	4750	800	210	57.5	12	4.5	2.35	1.7				
2	38500	10000	1600	420	115	22.5	8	3.55	1.85	1.6			
4	80000	20000	3300	850	225	45	15	6	2.6	1.75	1.5		
10	200000	50000	8000	2150	550	110	36	14	5.15	2.8	1.85	1.5	
20	400000	100000	15000	4250	1100	215	70	27	8.5	4.8	2.75	1.65	1.5

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)

$$\rho_{ij} = \frac{2(d_i + d_j)(D_i + D_j)}{W} \quad (17)$$

where

$$W = \frac{(d_i + d_j)}{2} \int_{\frac{d_i+d_j}{2}}^{\infty} e^{-\frac{\phi(x)}{kT}} \frac{dx}{x^2}. \quad (18)$$

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

$$F(r) = -\frac{d\phi}{dr}. \quad (19)$$

Van der Waals Force

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

$$\phi(r) = \frac{A}{6} \frac{d_i d_j}{r^2 \left(\frac{d_i + d_j}{2}\right)^2} + \frac{d_i d_j}{r^2 \left(\frac{d_i + d_j}{2}\right)^2} + \ln \frac{r^2 \left(\frac{d_i + d_j}{2}\right)^2}{r^2 \left(\frac{d_i + d_j}{2}\right)^2}, \quad (20)$$

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

For monosize particles,

$$\phi = \frac{A}{6} \frac{1}{2} \frac{d^2}{r^2} + \frac{d^2}{r^2 d^2} + \ln \frac{d^2}{r^2 d^2} \quad (21)$$

and

$$W = \int_0^1 \exp\left[-\frac{Af(x)}{6kT}\right] dx, \quad (22)$$

where

$$f(x) = \frac{x^2}{2} + \frac{x^2}{2(1-x^2)} + \ln(1-x^2) \quad (23)$$

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

$$\phi = \frac{z_i z_j e^2}{\epsilon r}, \quad (24)$$

where z_i is the number of charges, e is the electronic charge, and ϵ is the dielectric constant of the medium.

The expression for W then is given by

$$W = \frac{1}{y} (e^y - 1), \quad (25)$$

where

$$y = \frac{2z_i z_j e^2}{\epsilon kT (d_i + d_j)} \quad (26)$$

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

$$y = \frac{1z_i z_j e^2 e^{-\frac{\kappa(d_i+d_j)}{2}}}{\kappa T (d_i + d_j)}. \quad (27)$$

Shear Flows

The collision frequency function due to shear flow is given as

$$\nu_{ij} = \frac{1}{6} (d_i + d_j) \frac{dU}{dy}. \quad (28)$$

For $d_i = d_j = d$,

$$\nu = \frac{4}{3} d^3 \frac{du}{dy}. \quad (29)$$

Turbulence

Saffman and Turner suggested that

$$\nu_{ij} = 1.3 \frac{d_i + d_j}{2} \frac{\epsilon^3}{\nu^2}, \quad (30)$$

where ϵ is the dissipation rate and ν is the kinematic viscosity. For pipe flows (core region),

$$\epsilon = \frac{2}{R} \frac{f}{2} \frac{\nu^3}{2} V^3, \quad (31)$$

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

$$\epsilon = \frac{f V^3}{4 R}. \quad (32)$$

Differential Motion by Gravitational Force

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

$$\Omega_{ij} = \frac{\rho_p g}{\mu} d_j^4 (1 + \Omega)^2 \left[\frac{3}{2(1 + \Omega)} + \frac{1}{2(1 + \Omega)^3} \right] \Omega^2 (1 + \Omega)^2 \quad (33)$$

where

$$\Omega = \frac{d_i}{d_j} < 1$$

(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

$$\nabla \cdot (D_i \nabla n_i) = \nabla \cdot (\mathbf{u}_i n_i), \quad (1)$$

where D_i is the diffusivity and \mathbf{u}_i is the velocity due to the electric field. Force balance of a single ion gives

$$\frac{3\eta d_i \mathbf{u}_i}{c_c} = z_i e E, \quad (2)$$

where η 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

$$E = -\nabla \phi \quad (3)$$

and ϕ is the electric field potential.

Equation (2) leads to

$$\mathbf{u}_i = \frac{z_i e E}{\frac{3\eta d_i}{c_c}} = \frac{z_i e E D_i}{kT} \quad (4)$$

where

$$D_i = \frac{kT}{\frac{3\eta d_i}{c_c}} \quad (5)$$

is used. Using (3) and (4) in (1), we find

$$\nabla \cdot (D_i \nabla n_i) = \nabla \cdot \left[\frac{n_i z_i e D_i}{kT} \right] \quad (6)$$

or

$$\nabla \ln n_i = \frac{\nabla n_i}{n_i} = \nabla \frac{z_i e \psi}{kT}. \quad (7)$$

Integrating (7), one finds

$$n_i = n_{i0} \exp \left[\frac{z_i e \psi}{kT} \right], \quad (8)$$

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

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

$$\nabla^2 \psi = \frac{\rho_e}{\epsilon} \quad (9)$$

where ϵ is the permittivity (dielectric constant times permittivity of free space), and ρ_e is the charge density given as

$$\rho_e = \sum_i n_i z_i e. \quad (10)$$

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

$$\nabla^2 \psi = \frac{e}{\epsilon} \sum_i n_{i0} z_i e^{\frac{z_i e \psi}{kT}}. \quad (11)$$

Solution of (11) gives ψ and n_i . Equation (11) is restricted to low electrolyte concentrations, since ions are treated as point charges.

Debye-Huckel Approximation

For low potential $z_i e \psi \ll kT$ and

$$e^{\frac{z_i e \psi}{kT}} \approx 1 + \frac{z_i e \psi}{kT} \quad (12)$$

Using (12) in (11) and noting the neutrality condition of the bulk suspension,

$$\sum_i n_{i0} z_i e = 0, \quad (13)$$

it follows that

$$\nabla^2 \psi = -\kappa^2 \psi \quad (14)$$

where

$$\kappa = \sqrt{\frac{e^2}{\epsilon_0 kT} \sum_i n_{i0} z_i^2} \quad (15)$$

is the Debye-Huckel parameter.

The solution of (14) for double layer adjacent to a flat plate is given as

$$\psi = \psi_0 e^{-\kappa x}. \quad (16)$$

For double layer near a spherical particle of radius a ,

$$\psi = \psi_0 \frac{e^{-\kappa(r-a)}}{\frac{r}{a}}. \quad (17)$$

In (16) and (17), ψ_0 is the potential at the surface, and ψ decays with distance from the surface. The characteristic length is κ^{-1} (Debye length) double layer thickness. The concentration of electrolyte is related to n_{i0} by

$$n_{i0} = 1000 N_A c_{i0}, \quad (18)$$

where c_{i0} 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, κ^{-1} varies from less than 1 nm to about 100 nm.

Gouy-Chapman Theory

An exact solution of Poisson-Boltzmann equation for symmetric electrolytes for which

$$z_+ = -z_- = z \quad (19)$$

and

$$n_+^0 = n_-^0 \quad (20)$$

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

$$\frac{d^2\psi}{dx^2} = -\frac{2en_0z}{\epsilon} \sinh\left(\frac{ze\psi}{kT}\right) \quad (21)$$

The solution to (21) is

$$\psi = \frac{2kT}{ze} \ln \frac{1 + \psi_0 e^{\kappa x}}{1 - \psi_0 e^{\kappa x}}, \quad (22)$$

where

$$\psi_0 = \tanh \frac{ze\psi_0}{kT}. \quad (23)$$

The surface charge density, σ , may be related to surface potential ψ_0 , i.e.

$$\sigma = -\epsilon \left. \frac{d\psi}{dx} \right|_{x=0} = \frac{2\epsilon kT}{ze} \sinh\left(\frac{ze\psi_0}{kT}\right), \quad (24)$$

for ψ given by (22) and

$$\psi = \psi_0 \quad (25)$$

for ψ given by (16). This means that the double layer may be considered as a capacitor consisting of two plates a distance of λ_D^{-1} apart.

For spherical particles, the surface charge density is

$$\sigma = \frac{1 + \kappa a}{a} \psi_0, \quad (26)$$

and the total surface charge of the sphere becomes

$$Q_e = 4\pi a(1 + \kappa a)\psi_0. \quad (27)$$

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 ψ_{01} and ψ_{02} at infinite separation is given as

$$V^{\psi} = \frac{\epsilon a_1 a_2 (\psi_{01} + \psi_{02})}{4(a_1 + a_2)} \frac{2\psi_{01}\psi_{02}}{\psi_{01}^2 + \psi_{02}^2} \ln \frac{1 + \exp(\kappa h)}{1 - \exp(\kappa h)} + \ln \left(1 - \exp(-\kappa 2kh) \right) \quad (28)$$

where ϵ is the dielectric constant of the medium, h is the distance of minimum approach and κ^{-1} is the double layer thickness. Equation (28) holds for $\psi_0 < 25\text{mV}$ and $\kappa^{-1} \ll a_1, a_2$.

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

$$V_{s|p}^{\psi} = 2V_{s|s}^{\psi} \quad (29)$$

The corresponding force (repulsion) is

$$F_{s|p}^{\psi} = \epsilon \frac{dV_{s|p}^{\psi}}{dh} = \frac{\epsilon a}{2} (\psi_{01}^2 + \psi_{02}^2) \frac{\kappa e^{\kappa h}}{1 - e^{\kappa h}} \frac{2\psi_{01}\psi_{02}}{\psi_{01}^2 + \psi_{02}^2} \kappa e^{\kappa h} \quad (32)$$

For materials with $\psi_{01} = \psi_{02} = \psi_0$, equation (30) becomes

$$F_{s|p}^{\psi} = \frac{\epsilon a \psi_0^2 \kappa e^{\kappa h}}{1 + e^{\kappa h}} \quad (31)$$

Constant Charge Interactions

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

$$V^{\sigma} = V_{\psi} \frac{\epsilon a_1 a_2 (\psi_{01}^2 + \psi_{02}^2)}{2(a_1 + a_2)} \ln \left[1 - \exp(-\kappa 2kh) \right] \quad (32)$$

The corresponding sphere-plate force is

$$F_{s\text{p}} = \frac{a}{2} (\psi_{01}^2 + \psi_{02}^2) \frac{e^{\psi h}}{1 + e^{2\psi h}} \frac{2\psi_{01}\psi_{02}}{\psi_{01}^2 + \psi_{02}^2} + e^{\psi h} \quad (33)$$

When $\psi_{01} = \psi_{02} = \psi_0$,

$$F_{s\text{p}} = \frac{a\psi_0^2 e^{\psi h}}{1 + e^{2\psi h}} \quad (34)$$

In practice, ψ_0 is not known and usually it is assumed that

$$\psi_0 = \text{zeta potential} = \text{Electrokinetic potential} \quad (35)$$

(Diagram Here)

Two Spheres Interactions

Constant Potential (Deryaguin)

$$V_{s\text{s}} = 2\pi a\psi_0^2 \ln(1 + e^{\psi h}) \quad (36)$$

$$F_{s\text{s}} = 2\pi a\psi_0^2 \frac{e^{\psi h}}{1 + e^{2\psi h}} \quad (37)$$

Linear Superposition (Debye-Huckel)

$$V_{s\text{s}} = 4\pi a^2 \frac{a^2}{2a + h} \psi_0^2 e^{\psi h} \quad (38)$$

$$F_{s\text{s}} = \pi a^2 \frac{1 + \psi(h + 2a)}{\psi + \frac{h}{2a}} e^{\psi h} \quad (39)$$

Superposition (thin double layer)

$$V_{s\text{s}} = 32\pi a^2 \left(\frac{kT}{ze}\right)^2 a \tanh^2 \left(\frac{\psi_0 ze}{4kT}\right) e^{\psi h} \quad (40)$$

$$F_{s\text{s}} = 32\pi a^2 \left(\frac{kT}{ze}\right)^2 a \tanh^2 \left(\frac{\psi_0 ze}{4kT}\right) e^{\psi h} \quad (41)$$

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 (ζ -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 ρ_e , it follows that

$$\rho \frac{d^2 u}{dy^2} = \rho_e E \quad (42)$$

(Diagram Here)

Using (9) to replace ρ_e in term of $\psi(y)$, ($\rho_e = -\epsilon \frac{d^2 \psi}{dy^2}$), we find

$$\rho \frac{d^2 u}{dy^2} = \epsilon E \frac{d^2 \psi}{dy^2} \quad (43)$$

or

$$u_{e0} = \frac{E \psi}{\rho} \quad (44)$$

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

$$u = 0, \quad \psi = \psi_0. \quad (45)$$

Particle Electrophoresis

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

$$u^p = \frac{E \psi}{\rho} \quad (46)$$

which may be restated in terms of the electrophoretic mobility, U (velocity for unit field) as

$$U = \frac{\zeta \eta}{4 \pi \epsilon_0 \epsilon_r a^2} \quad (47)$$

This is known as Smoluchowski equation.

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

$$6 \pi \eta a U = EQ = E(4 \pi \epsilon_0 \epsilon_r a^2 \kappa \zeta)$$

where equation (27) is used for total charge and ϵ_0 is replaced by ϵ .

It then follows that

$$U = \frac{2 \zeta \eta}{3 \epsilon_0 \epsilon_r \kappa} \quad (48)$$

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

$$U = \frac{2 \zeta \eta}{3 \epsilon_0 \epsilon_r \kappa} f_1(\kappa a) \quad (49)$$

where $f_1(\kappa a)$ varies from 1 to 1.5 for κa varying between 0 to ∞ .

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

$$V_B = \frac{A \epsilon_c^6}{7560} \left[\frac{8a + h}{(2a + 7)^2} + \frac{6a \epsilon_c h}{h^7} \right] \quad (50)$$

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

DLVO Theory of Colloidal Stability

The theory of colloidal stability was developed by Deryaguin, Landau (1941), Verway, and Overbeek (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.

$$V_T = V_A + V_R + V_B \quad (51)$$

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.