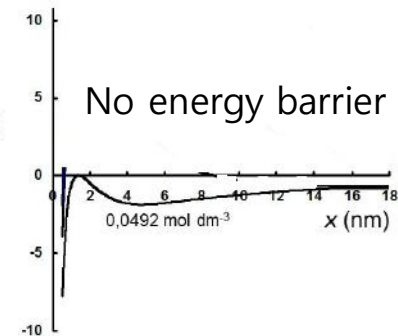


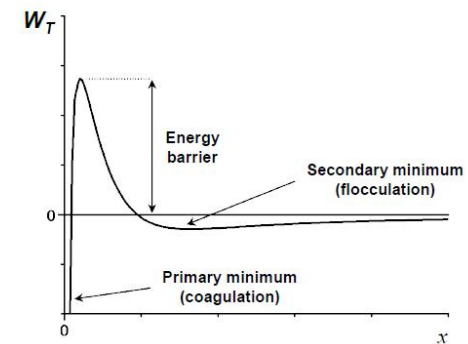
Kinetics of Coagulation

- Rate depends on
 - Collision Frequency
 - Collision Efficiency

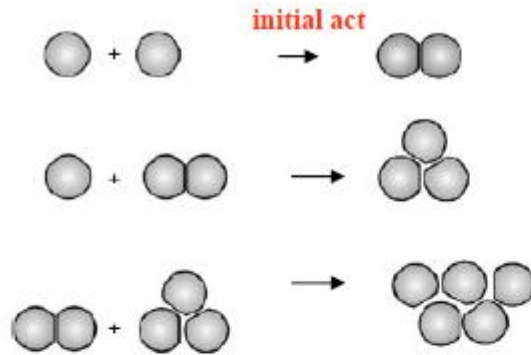
Fast coagulation (Smoluchowski): each collision leads to aggregation
(high electrolyte concentration, $V_{\min} \lesssim 0$, rate constant: k_f)



Slow coagulation (Fuchs): only part of the collisions leads to aggregation
(low/intermediate electrolyte concentration, $V_{\min} \sim kT$, rate constant: k_s)



Elementary acts of coagulation:



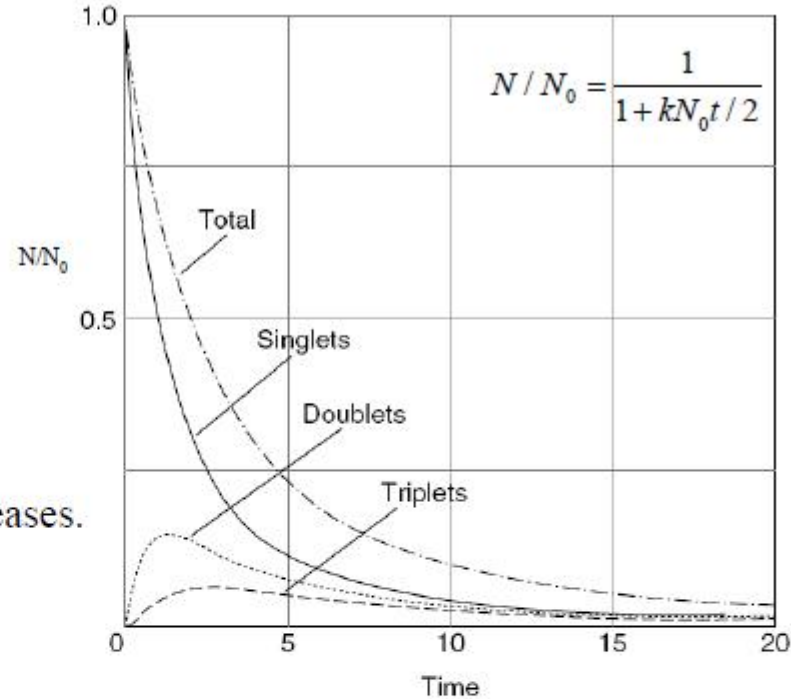
N decreases with time, while their size increases.

$$VN = \text{constant} = V_0 N_0 \quad V \sim 1/N$$

$$-\frac{dN}{dt} = k N^2 \quad \rightarrow \quad \frac{1}{N} - \frac{1}{N_0} = k t$$

If all flocculation rate constants are the same

$$N/N_0 = \frac{1}{1 + kN_0 t / 2}$$



The decrease in the normalized number of total particles, singlets, doublets, and triplets according to Smoluchowski theory as a function of time.

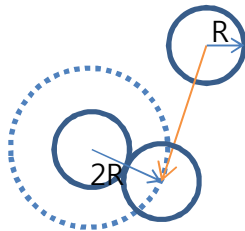
Rate can be measured through decreasing the total number $-dN/dt$ or increasing the average volume, dV/dt for example by turbidity as a function of time.

Turbidity $\sim V^2 N \sim V(VN) \sim V \text{ constant}$

<http://apricot.polyu.edu.hk/~lam/dla/>

Fast Coagulation

- Simple case: uniform spherical particles, Brownian motion only



Rate of coagulation: rate at which they diffuse across the dashed surface

After coagulation, a concentration gradient around the fixed particle \rightarrow cause diffusion

According to Fick's Law

$$J = -D \frac{dN}{dr}$$

D : diffusion coefficient, N : number of particle per unit volume

Total number of particles crossing a spherical surface of radius r and area A

$$JA = -(4\pi r^2)D \frac{dN}{dr}$$

At steady state, $JA = \text{const.}$, N_0 : initial no. concentration at $r = \infty$, $N = 0$ at $r = 2R$
integrating

$$JA = -8\pi RDN_0$$

- If both particles are moving

$$(JA)' = -16\pi RDN_0$$

- There are N_0 particles initially present as the 'reference' particles
- Therefore, total rate of coagulation

$$= -(16\pi RDN_0) N_0 = -k_f N_0^2$$

- Stokes-Einstein Eq. $D = \frac{k_B T}{6\pi\mu R} \rightarrow k_f = \frac{8k_B T}{3\mu}$

Eg) Initial conc. $N_0 = 10^9$ particles/cm³

Calculate the time required for the concentration of the dispersed units to drop to 90% of the initial value

$$k_f = \frac{8(1.38 \times 10^{-16})(293)}{3(0.01)} = \frac{1.08 \times 10^{-11} \text{ cm}^3}{\text{particle} \cdot \text{sec}}$$

$$\frac{1}{0.9N_0} - \frac{1}{N_0} = (1.08 \times 10^{-11})t \rightarrow t = 10.3 \text{ sec}$$

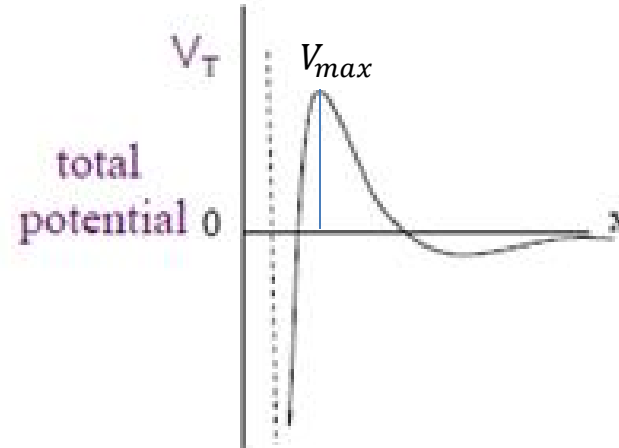
Slow Coagulation

$$k_s = \frac{k_f}{2R \int_{2R}^{\infty} \exp\left(\frac{V_T}{k_B T}\right) r^{-2} dr}$$

$$W = 2R \int_{2R}^{\infty} \exp\left(\frac{V_T}{k_B T}\right) r^{-2} dr$$

$$\approx \frac{1}{2\kappa R} \exp\left(\frac{V_{max}}{k_B T}\right)$$

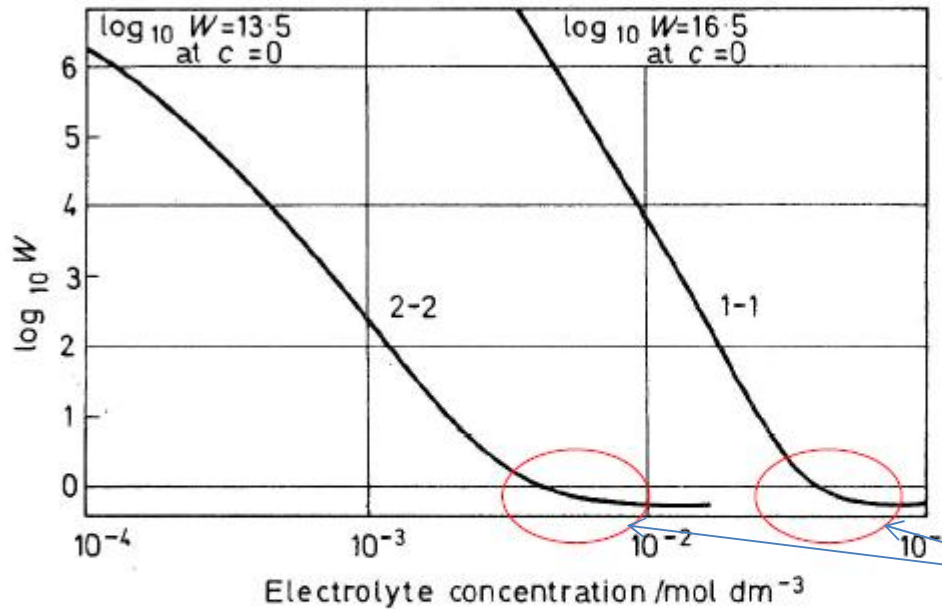
$$W = \frac{k_f}{k_s}: \textit{stability ratio}$$



If there is an **energy barrier**, V_{max} to coagulate then a fraction (α) of collisions is unsuccessful, so the rate of coagulation slower, k_s .

The stability of dispersion is increased by: increase in particle radius, increase in surface potential ($\zeta > 25\text{mV}$), decrease in Hamaker constant, decrease in the ionic strength, decrease in temperature.

Stability ratio vs. electrolyte conc.



the stability ratio: $W = \frac{k_f}{k_s}$

$$W \geq 1$$

$$\ln W \geq 0$$

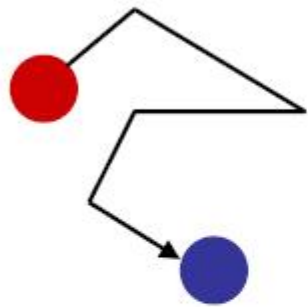
Fast Coagulation

Figure 8.5. Theoretical dependence of stability ratio on electrolyte concentration calculated from Equation (8.9) for $a = 10^{-8}$ m, $A = 2 \times 10^{-19}$ J and $\psi_0 = 76.8$ mV = $3kT/e$. At high electrolyte concentrations $W < 1$ owing to flocculation being accelerated by van der Waals attractive forces¹²⁵ (By courtesy of Elsevier Publishing Company)

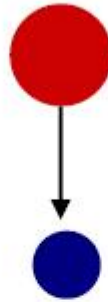
Collision Frequency

- depends on: 1) concentration of particles
2) relative motion of particles

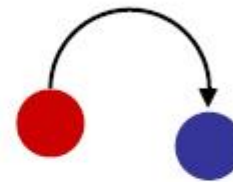
↓
Mechanisms of coagulation



perikinetic



differential
settling



orthokinetic
Mechanical agitation

perikinetic: collisions by Brownian motion
differential settling (polydisperse suspensions)
orthokinetic: induced collisions through stirring; shear

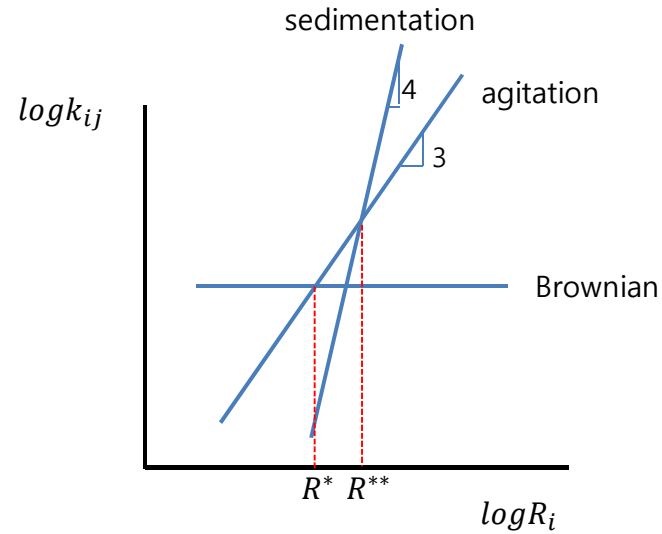
- In general, collision frequency between particles i and j (radius R_i, R_j)
 $= k_{ij}n_in_j$

- Also

$$k_{ij} = k_m R_i^m P_m(R_i/R_j) : m \text{ depends on the mechanism}$$

mechanism	m	k_m	P_m	$P_m/R_i = R_j$
Brownian	0	$\frac{2k_B T}{3\mu}$	$2 + \frac{R_i}{R_j} + \frac{R_j}{R_i}$	4
agitation	3	$\frac{4G}{3}$	$\left(1 + \frac{R_j}{R_i}\right)^3$	8
sedimentation	4	$\frac{2\pi(\rho_s - \rho_l)g}{9\mu}$	$\left(1 + \frac{R_j}{R_i}\right)^3 \left(1 - \frac{R_j}{R_i}\right)$	-

$$G = \text{mean velocity gradient } \overline{\left(\frac{dv}{dx}\right)}$$



$R < R^* : \textit{Brownian}$

$R^* < R < R^{**} : \textit{Agitation}$

$R > R^{**} : \textit{Sedimentation}$

Typically, $R^* \sim 1 \mu m$, $R^{**} \sim 50 \mu m$

assume $k_{ijeff} = k_{ijBr} + k_{ijagitation}$

agitation interrupt settling, so it is not desirable to add sedimentation term

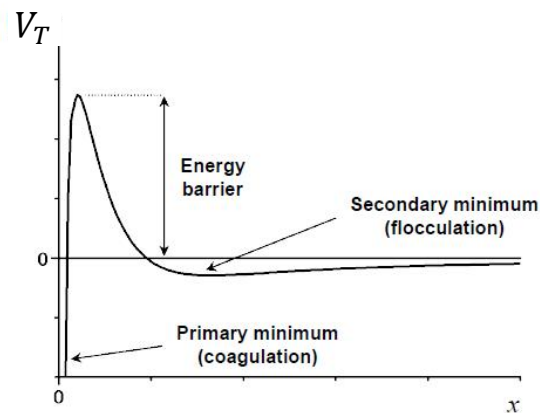
Collision Efficiency

- Brownian

$$\text{coagulation rate} = \frac{k_{ij}n_i n_j}{W_{ij}}$$

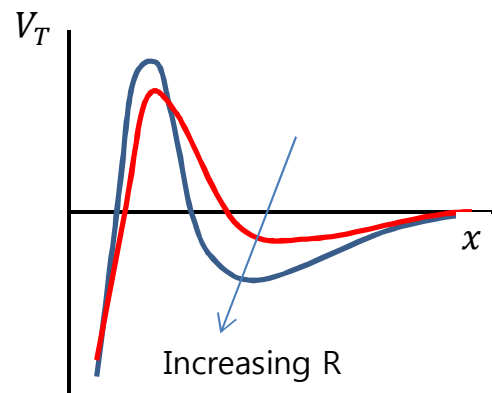
$$W_{ij} = (R_i + R_j) \int_{(R_i+R_j)}^{\infty} \exp\left(\frac{V_T}{k_B T}\right) r^{-2} dr$$

Stability depends on interaction force and external force



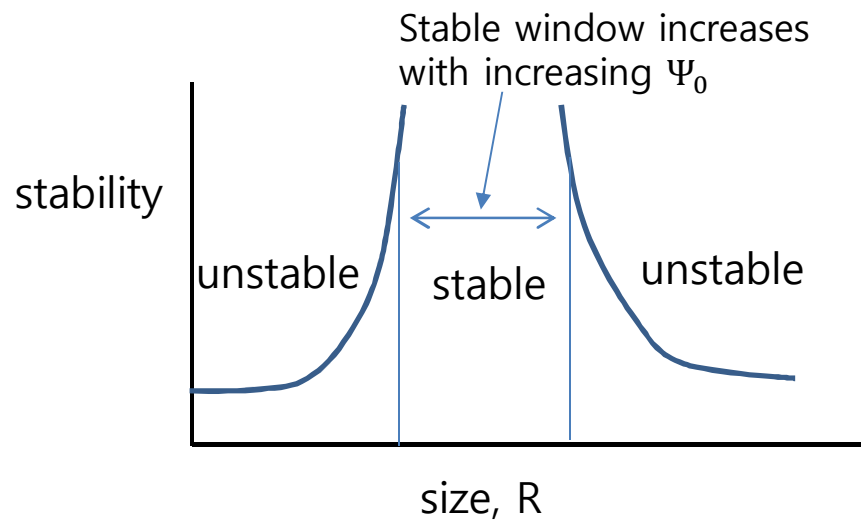
Primary coagulation: particles must pass over the energy barrier

Secondary coagulation: valley must be deep enough to prevent escape

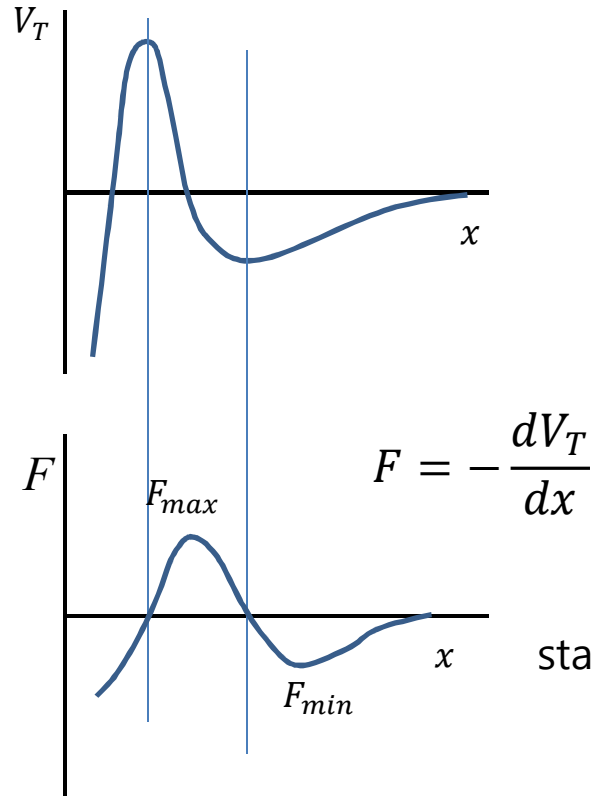


Primary coagulation: stability $\propto V_{max}$, and $\propto R$

Secondary coagulation: stability $\propto \frac{1}{R}$



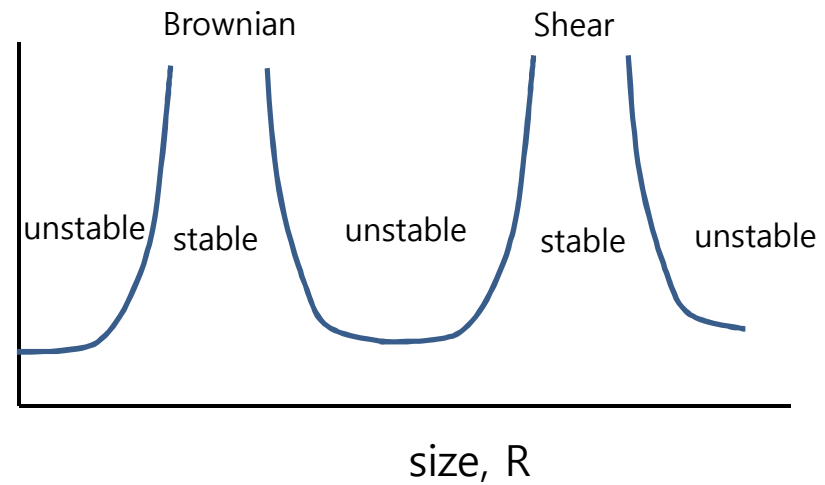
- Shear Coagulation



Stability depends on force of interaction relative to "hydrodynamic" force

Primary: stable if $F_{max} > F_{hydro}$

Secondary: stable if $F_{min} < F_{hydro}$

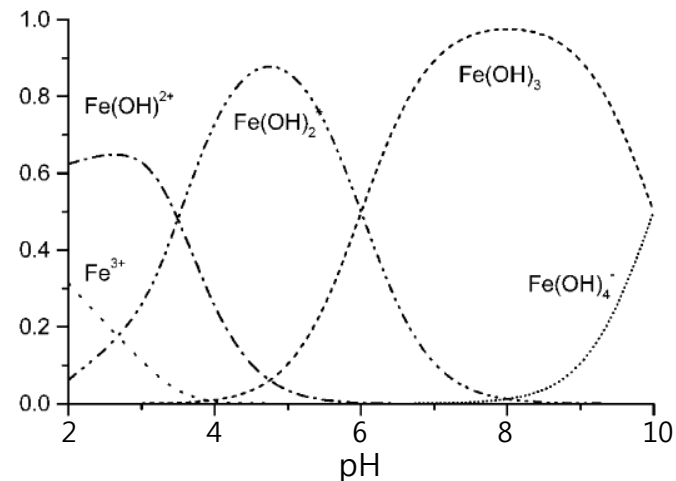
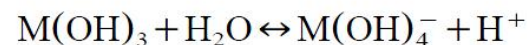
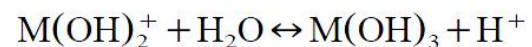
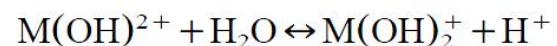
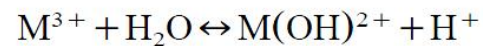
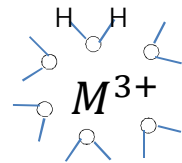


Flocculants

a) **Ions:** Schultz-Hardy Rule $ccc \propto \frac{1}{z^6}$

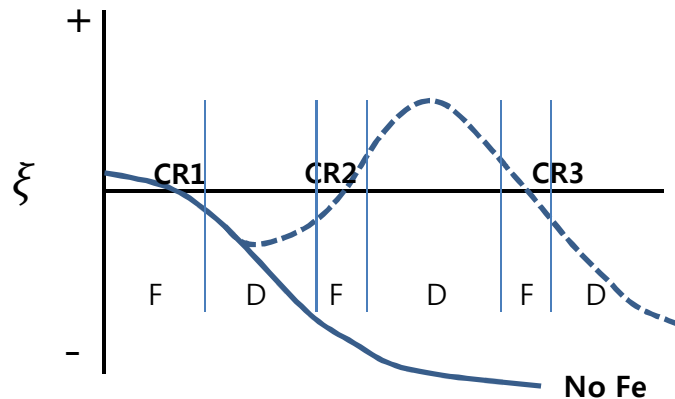
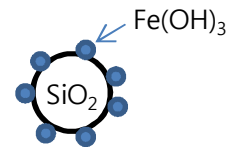
b) **Hydrolyzing cations** (Al^{3+} , Fe^{3+})

- Al(III) and Fe(III) accomplish destabilization by two mechanisms:
 - (1) Adsorption and charge neutralization.
 - (2) Enmeshment in a sweep floc.
- Hydrolysis: a progressive deprotonation of water molecules in the primary hydration shell



- Interrelations between pH, coagulant dosage, and colloid concentration determine mechanism responsible for coagulation.
- Charge on hydrolysis products and precipitation of metal hydroxides are both controlled by pH. The hydrolysis products possess a positive charge at pH values below iso-electric point of the metal hydroxide. Negatively charged species which predominate above iso-electric point, are ineffective for the destabilization of negatively charged colloids.
- Precipitation of amorphous metal hydroxide is necessary for sweep-floc coagulation.

Eg) SiO_2 in presence of Fe^{3+}



3 charge reversals

CR1: PZC of mineral (pH 1)

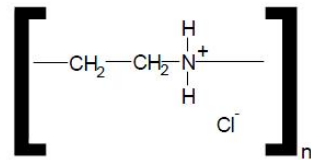
CR3: PZC of metal hydroxide (pH 8)

CR2: formation of first hydroxy complex (Fe(OH)^{2+})

c) **Polymers**

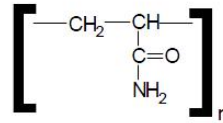
- natural: starch
- synthetic (MW: 10^5 - 10^7)

Cationic



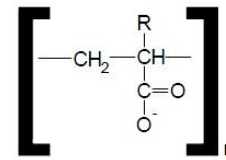
Polyethylenimine

Nonionic



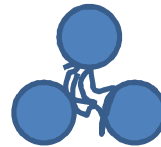
Polyacrilamide

Anionic



Poly(meth)acrylic acid

- mechanism: 1) charge neutralization
- 2) Bridging



- 3) enmeshment

