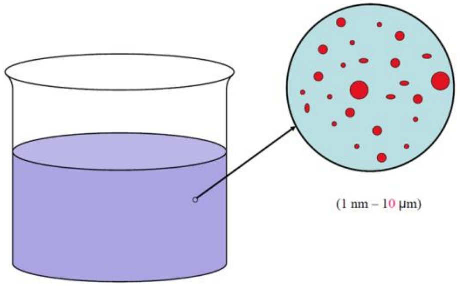
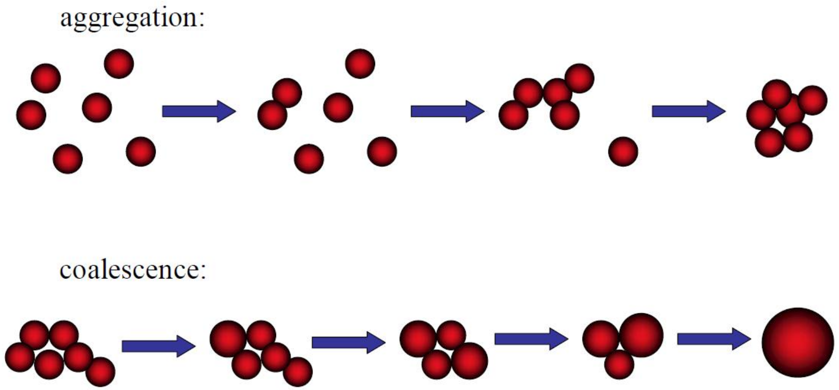
Colloidal Systems - Stability

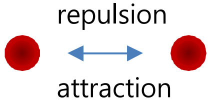
- Stable colloid – remain dispersed
- 2 classes of colloids
  - Lyophilic (hydrophilic) colloids
    - Dispersion occurs spontaneously
    - Polymers, bio-colloids
  - Lyophobic
    - Coagulation is spontaneous
    - Most inorganic (minerals) systems



Instability of liophobic colloids

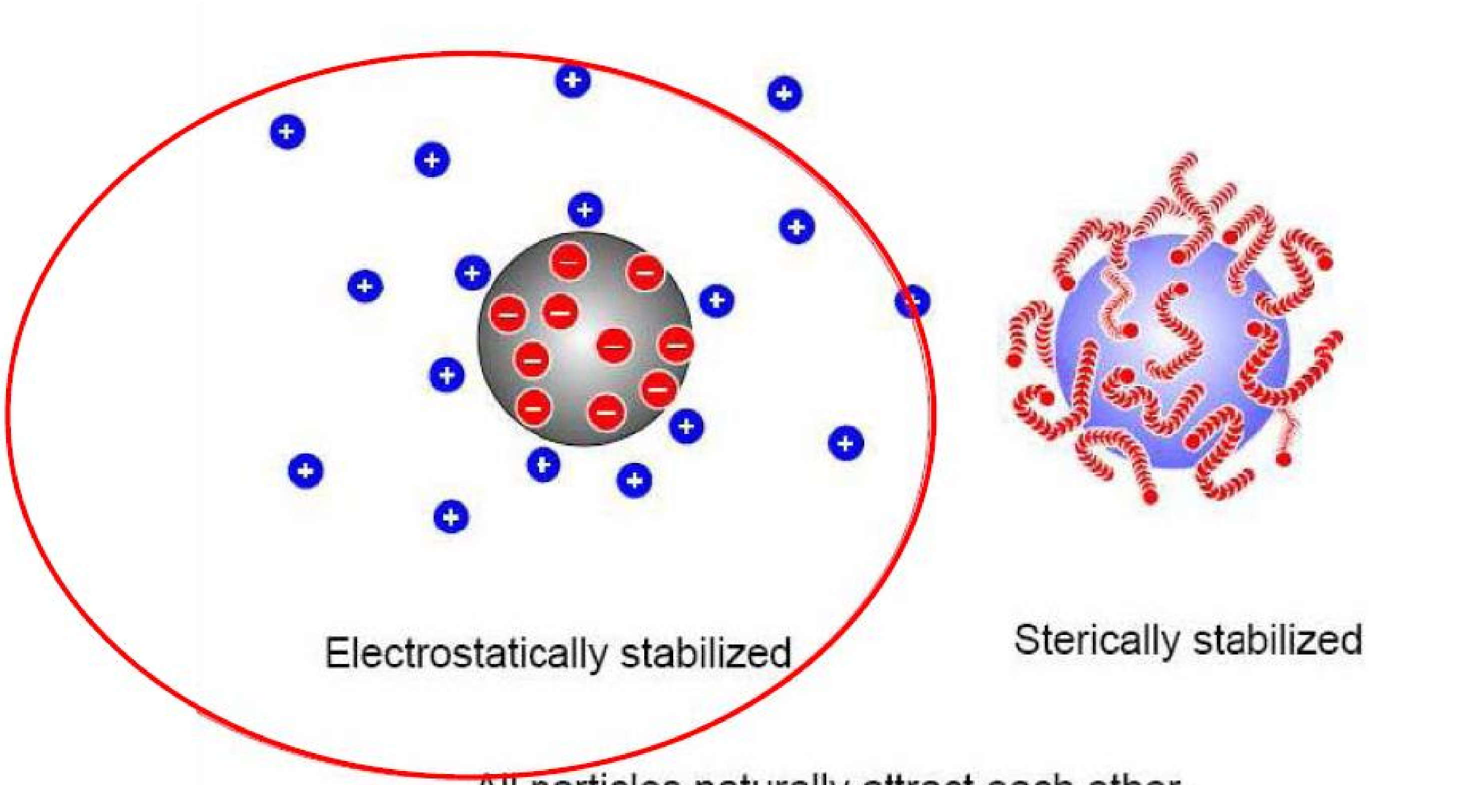


- Stability depends on forces of interaction between particles



  - Kind of forces: electrostatic, van der Waals, chemical etc

Colloid stability requires repulsive forces between colliding particles



Electrostatically stabilized

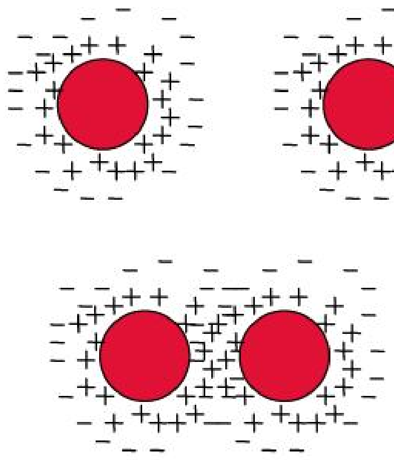
Sterically stabilized

All particles naturally attract each other.

Electrical charges or attached polymer layers screen the attraction.

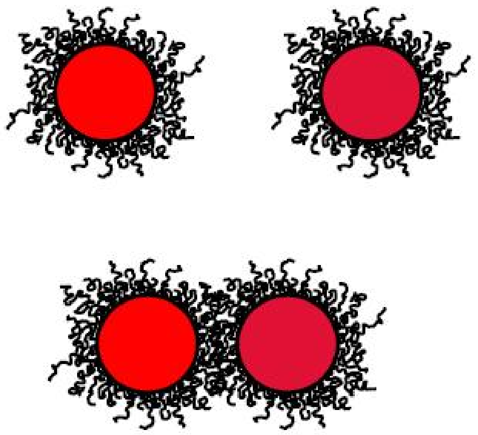
Main types of (de)stabilization of colloidal dispersions

electrostatic potential



Coulombic repulsion →
→ electrostatic stabilization

steric potential



entropy hindrance →
→ steric stabilization

DLVO Theory

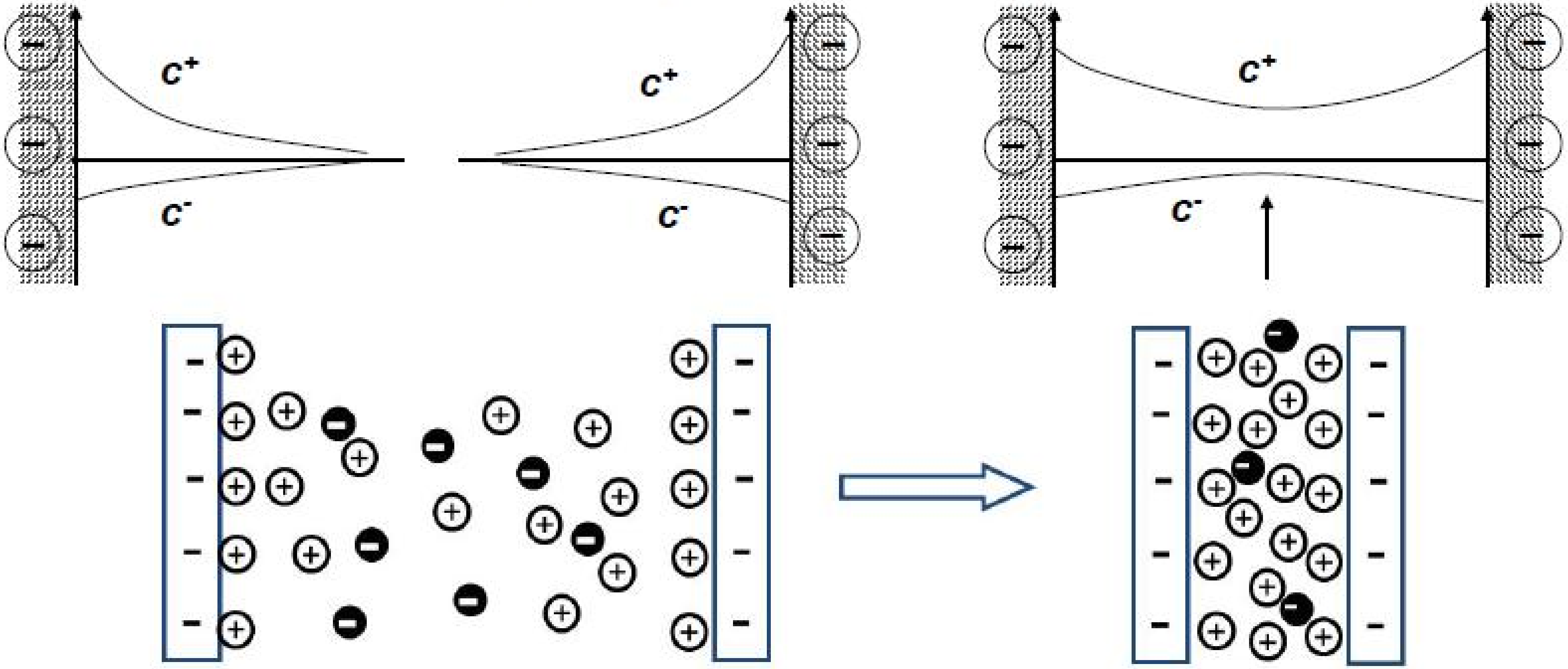
- Derjaguin and Landau (USSR, 1941)
- Verwey and Overbeek (Netherlands, 1948)

- Developed a quantitative theory in which the stability of lyophobic sols, especially in relation to added electrolyte is treated in terms of the energy changes which takes place when particles approach one another.
- The theory involves estimation of the energy due to the overlap of electric double layers (repulsion) and the van der Waals energy (attraction) in terms of inter-particle distance, and their summations to give the total interaction energy in terms of inter-particle distance.

DLVO theory

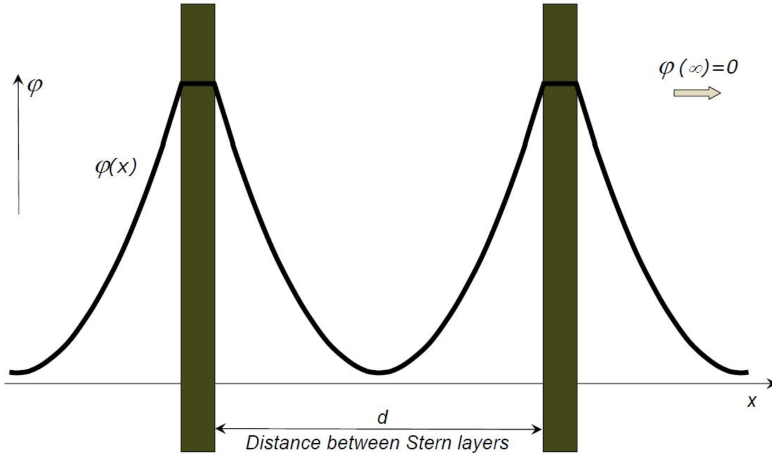
Electrical double layer interaction

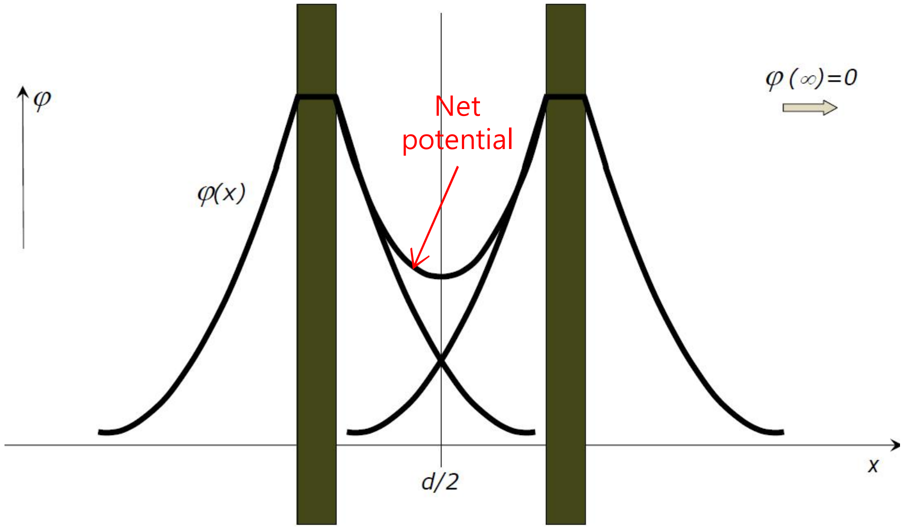
When two charged surfaces or particles approach, their corresponding electrical double layers overlap.



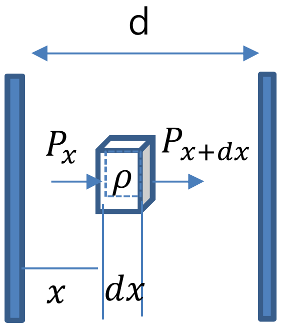
The accumulation of ions due to the overlap of the electrical double layers create an increase in osmotic pressure. Water from the bulk comes to dissolve the accumulation of ions, preventing the surfaces from approaching closer (**electrical double layer repulsion**).

Repulsion





- As the distance between the plate decreases, the potential of the inner region begins to overlap.
- Two kinds of forces operate
  - Osmotic pressure
  - Electrostatic forces



Force balance on the volume element

Osmotic Pressure: $F = PA = (P_x - P_{x+dx})dydz$

Electrostatic Force: $F = qE = (\rho \cdot dxdydz)(-\frac{d\Psi}{dx})$

ρ: *charge density*

At equilibrium

$$(P_x - P_{x+dx})dydz - (\rho \cdot dxdydz)\frac{d\Psi}{dx} = 0$$

$$\frac{(P_x - P_{x+dx})}{dx} - \rho\frac{d\Psi}{dx} = 0$$

$$-\frac{dP}{dx} - \rho\frac{d\Psi}{dx} = 0$$

$$\frac{dP}{dx} + \rho\frac{d\Psi}{dx} = 0$$

$$dP = -\rho d\Psi$$

For z:z electrolyte

$$\rho = zen_0 \exp\left(\frac{-ze\Psi}{kT}\right) - zen_0 \exp\left(\frac{ze\Psi}{kT}\right)$$

$$= -2zen_0 \sinh(\frac{ze\Psi}{kT})$$

$$dP = 2zen_0 \sinh(\frac{ze\Psi}{kT})\, d\Psi$$

Integrate from x=∞ ($P=P_0$, $\Psi=0$)
to x=d/2 (P= $P=P_{d/2}$, $\Psi= \Psi_{d/2}$)

$$P_{d/2} - P_0 = 2kTn_0\left[\cosh\left(\frac{ze\Psi_{d/2}}{kT}\right) - 1\right] = F_R$$

When d/2 is relatively large

$\Psi_{d/2}$ can be estimated as the sum of potentials from two plates

$$\Psi_{d/2} = \Psi_1 + \Psi_2 = 2\left(\frac{4kT\chi_0}{ze}\right)\exp\left(-\frac{\kappa d}{2}\right) \qquad \chi_0 = \frac{\exp\left(\frac{ze\Psi_0}{2kT}\right)-1}{\exp\left(\frac{ze\Psi_0}{2kT}\right)+1}$$

Also, in this case, $\frac{ze\Psi_{d/2}}{kT}$ is small so that $\cosh\left(\frac{ze\Psi_{d/2}}{kT}\right)$ can be expanded

The result is

$$F_R = kT\kappa n_0\left(\frac{ze\Psi_{d/2}}{kT}\right)^2 = kTn_0\left[8\Upsilon_0\exp\left(-\frac{\kappa d}{2}\right)\right]^2 = 64kTn_0\chi_0^2\exp(-\kappa d)$$

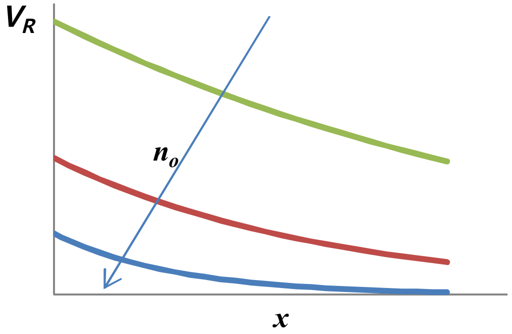
Since $\kappa \propto \sqrt{n_0}$, $\quad F_R = C_1 n_0 \exp(-C_2\sqrt{n_0})$

- Therefore, repulsion force decreases with increasing electrolyte concentration
- Addition of electrolyte into colloidal solutions induces coagulation of colloid.

Energy of Repulsion between two plates

$$Energy, V_R = \int_{\infty}^{d} -F dx = \int_{\infty}^{d} -64kTn_0\chi_0^2 \exp(-\kappa x) dx = \frac{64kTn_0\chi_0^2}{\kappa} \exp(-\kappa x)$$

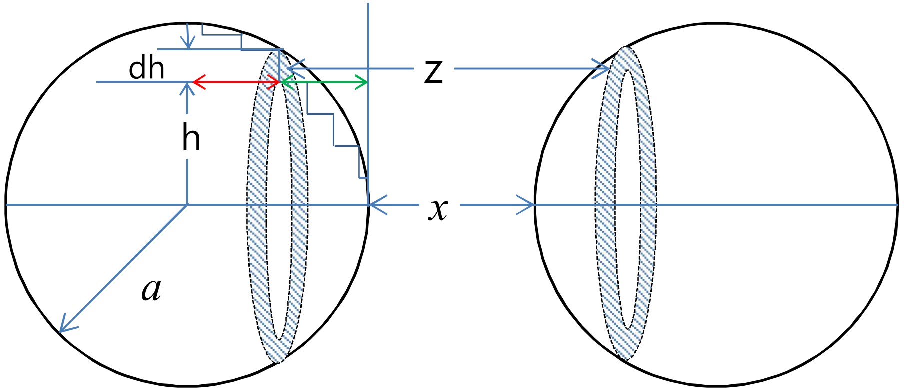
$$= C_3\sqrt{n_0}\exp(-C_2\sqrt{n_0})$$



Potential energy of repulsion decreases with increasing electrolyte concentration.

- A potential energy of repulsion may extend appreciable distances from surfaces, but its range is reduced by increasing the electrolyte content.
- The condition under which approaching particles first influence one another are at large distances of separation, for which the approximate relationship holds.
- The sensitivity of aqueous colloids to electrolyte content is due to the dependence of interparticle repulsion on this concentration.

Repulsion between spheres



Spherical particles can be approximated by a stack of circular rings with planar faces

$$dV_R = V_h dA_h \qquad dA_h = 2\pi h dh$$

$$\longleftrightarrow = \sqrt{a^2 - h^2} \qquad \longleftrightarrow = \frac{z-x}{2}$$

$$\sqrt{a^2 - h^2} + \frac{z-x}{2} = a$$

$$a\sqrt{1 - h^2/a^2}\,dz = 2hdh$$

$$dV_R = \pi a\sqrt{1 - h^2/a^2}\,V(z)dz$$

$$dV_R = \pi a\sqrt{1 - h^2/a^2}\,\frac{64kTn_0\chi_0^2}{\kappa}\exp(-\kappa z)dz$$

$$if\ h^2/a^2 \ll 1$$

$$dV_R = \frac{64\pi akTn_0\chi_0^2}{\kappa}\exp(-\kappa z)dz$$

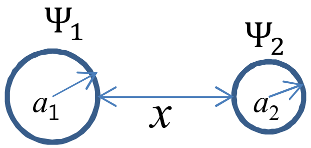
Integrate from z=x to z=x+a

But $\exp[-k(x+a)]$ *is very small*

$$V_R = \frac{64\pi akTn_0\chi_0^2}{\kappa^2}\exp(-\kappa x)$$

Other models for Spherical Particles

- Healy (1966)



$$V_R = \frac{\pi\varepsilon a_1 a_1(\Psi_1^2 + \Psi_2^2)}{(a_1 + a_2)} \left\{ \frac{2\Psi_1\Psi_2}{(\Psi_1^2 + \Psi_2^2)} ln\left(\frac{1 + \exp(-\kappa x)}{1 - \exp(-\kappa x)}\right) + \ln[1 - \exp(-2\kappa x)] \right\}$$

For equal spheres, $a_1 = a_2 = a$, $\Psi_1 = \Psi_2 = \Psi$

$$V_R = 2\pi\varepsilon a\Psi^2\, ln(1 + \exp[-\kappa x])$$

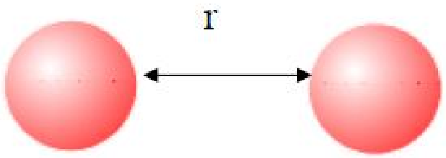
If $\exp[-\kappa x] \ll 1$

$$V_R = 2\pi\varepsilon a\Psi^2 \exp[-\kappa x] \quad \xleftrightarrow{\textbf{Same eq.}} \quad V_R = \frac{64\pi akTn_0\chi_0^2}{\kappa^2}\exp(-\kappa x)$$

Attraction between **atoms**/ molecules in vacuum

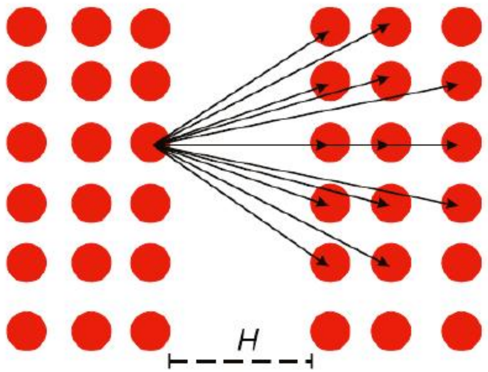
van der Waals Interaction

$$F_{vdw} \propto \frac{1}{r^7}$$



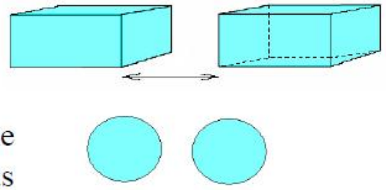
Hamaker model - Calculate the **attraction** between particles from molecular attractions

Molecules in particle 1



Molecules in particle 2

depends on geometry!



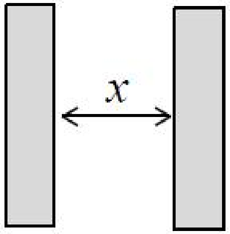
The attraction of bodies arises from London (dispersion) attraction of molecules (all molecules act independently) The effect is additive; that is, one molecule of the first colloid has a van der Waals attraction to each molecule in the second colloid. This is repeated for each molecule in the first colloid, and the total force is the sum of all of these. An attractive energy curve is used to indicate the variation in van der Waals force with distance between the particles.

Van der Waals interaction

A = Hamaker constant
x = distance between surfaces

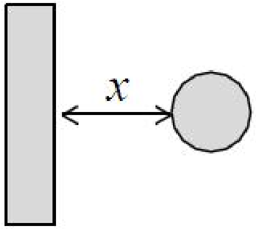
- **Between two flat surfaces:**

$$V_A = -\frac{A}{12\pi x^2} \qquad F_{vdW} = -\frac{A}{6\pi x^3} \quad \text{(per unit area)}$$



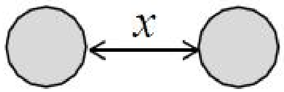
- **Between a spherical particle of radius *R* and a flat surface:**

$$V_A = -\frac{AR}{6x} \qquad F_{vdW} = -\frac{AR}{6x^2}$$



- **Between two spherical particles of radius *R* :**

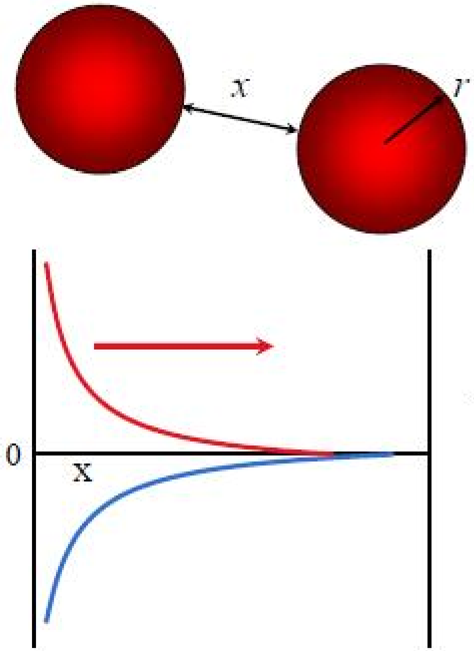
$$V_A = -\frac{AR}{12x} \qquad F_{vdW} = -\frac{AR}{12x^2}$$



The van der Waals interaction depends on the nature (Hamaker constant) and the geometry of the system. It is always attractive between particles or surfaces of the same material.

Attraction

van der Waals Interaction



attraction potential
between spherical
particles:

$$V_A(x) = -\frac{A\,r}{12\,x}$$

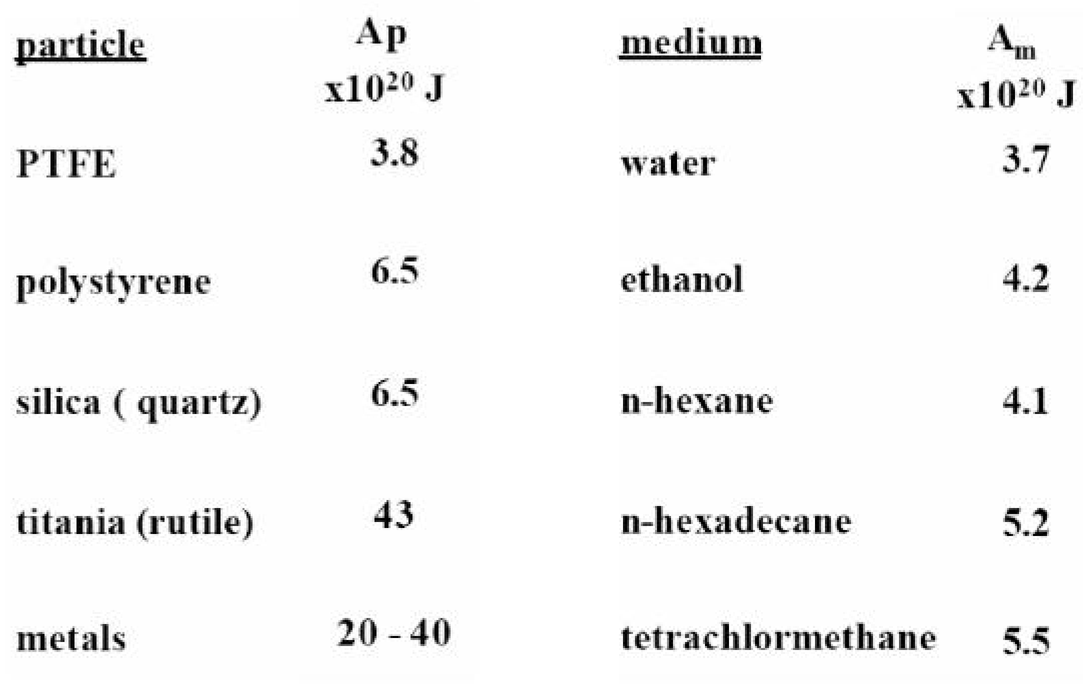
A: Hamaker constant
(attraction parameter)

attraction potential
between plate-like
particles:

$$V_A(x) = -\frac{A}{12\,\pi\,x^2} \approx 2\,\gamma_S$$

A: Hamaker constant
(attraction parameter)

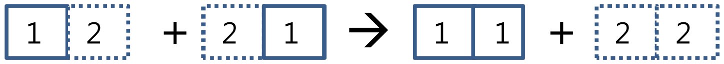
Hamaker constants of various materials



particle	Ap x10^{20} J	medium	A_m x10^{20} J
PTFE	3.8	water	3.7
polystyrene	6.5	ethanol	4.2
silica (quartz)	6.5	n-hexane	4.1
titania (rutile)	43	n-hexadecane	5.2
metals	20 - 40	tetrachlormethane	5.5

Combination of Hamaker constants

In general between phase 1 and 2

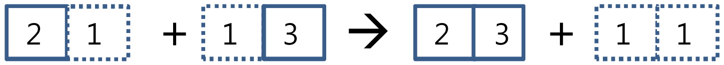


$$A_{eff} = A_{11} + A_{22} - 2A_{12} \qquad A_{12} = \sqrt{A_{11}A_{22}}$$

$$= A_{11} + A_{22} - 2\sqrt{A_{11}A_{22}}$$

$$= \left(\sqrt{A_{11}} - \sqrt{A_{22}}\right)^2 \quad \mathit{always\ positive, force\ is\ attractive}$$

For particles 2 and 3 in liquid 1

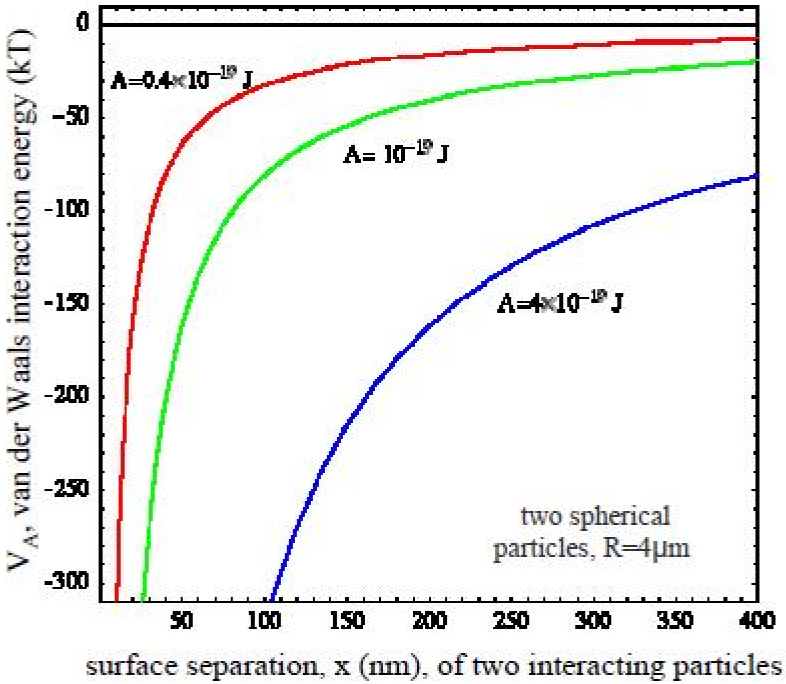


$$A_{eff} = A_{23} + A_{11} - A_{21} - A_{31}$$

$$= \sqrt{A_{22}A_{33}} + A_{11} - \sqrt{A_{11}A_{22}} - \sqrt{A_{33}A_{11}}$$

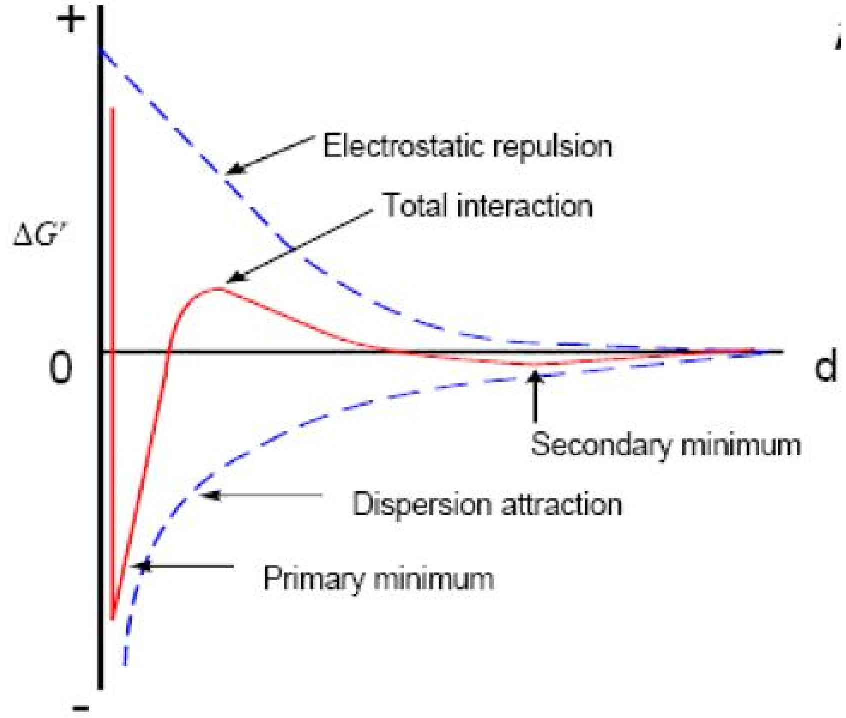
$$= \left(\sqrt{A_{33}} - \sqrt{A_{11}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{11}}\right)$$

Dependence of the van der Waals pair potential V_A between two colliding particles on the overall Hamaker constant "A" of the system



The Balance of Repulsion & Attraction

is the sum of the electrostatic repulsion and the dispersion attraction, DLVO theory:



Notice the secondary minimum.
The system flocculates, but the aggregates are weak.
This may imply *reversible* flocculation.

$$V_\mathrm{T} = V_\mathrm{A} + V_\mathrm{R}$$

$$V_A(H) \approx -\frac{Aa}{12H}$$

$$V_R(H) \approx a(kT)^2 \gamma^2 z^{-2} \exp(-\kappa H)$$

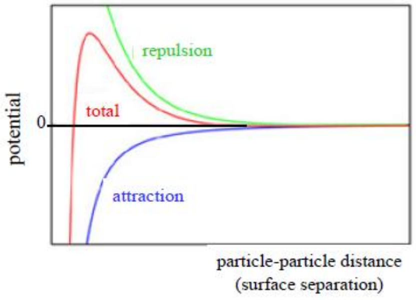
$$\gamma = \frac{\exp\left[\frac{ze\psi_{St}}{2kT}\right] - 1}{\exp\left[\frac{ze\psi_{St}}{2kT}\right] + 1}$$

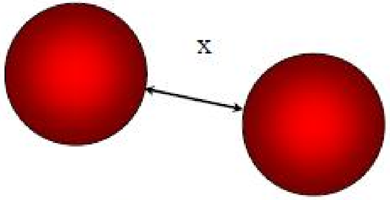
The point of maximum repulsive energy is called the energy barrier. Energy is required to overcome this repulsion . The height of the barrier indicates how stable the system is .The electrostatic stabilization is highly sensitive with respect to surface charge (ζ~ψ~pH) and salt concentration (κ, z).

DLVO theory: the resultant (total) potential is:

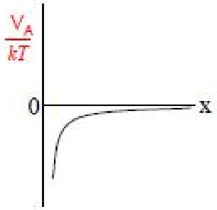
$$V_T = V_A + V_R$$

$$= \frac{64\pi a k T n_0 \chi_0^2}{\kappa^2}\exp(-\kappa x) - \frac{Aa}{12x}$$





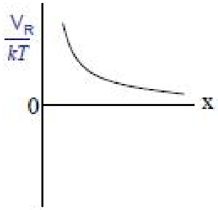
attraction potential
(van der Waals forces)

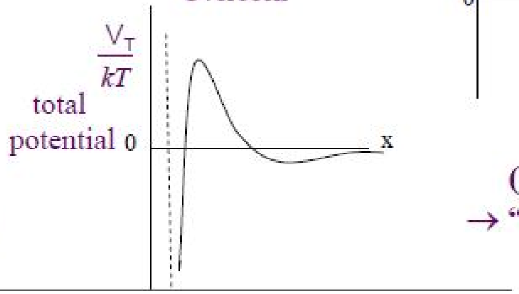


DLVO theory

Derjagin
Landau
Verwey
Overbeek

repulsion potential
(Coulombic repulsion;
aqueous medium, large ε)

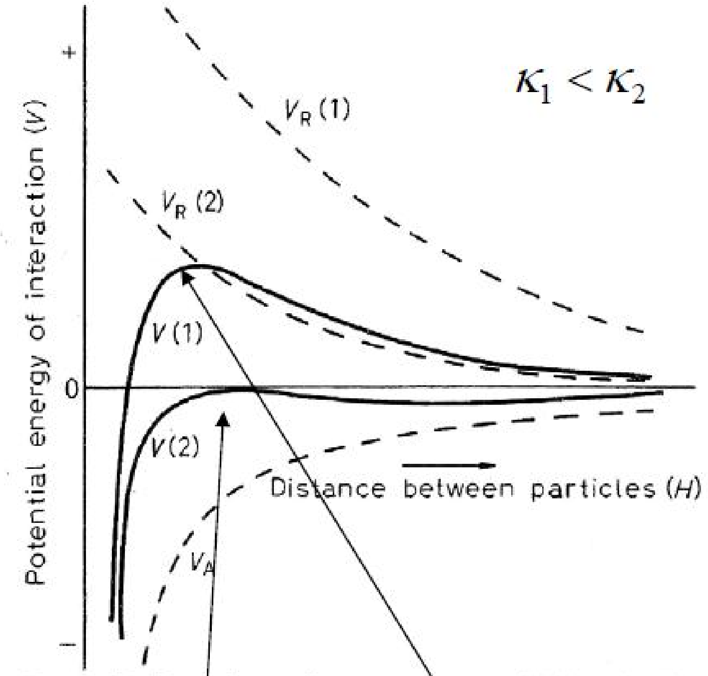




$V_T = V_A + V_R$

$(V_T/kT) \geq 10$:
→ "colloid stabiliy"

Electrostatic stability of dispersions



$\kappa_1 < \kappa_2$

Figure 8.1. Total interaction energy curves (V(1) and V(2), obtained by the summation of an attraction curve, V_A, with different repulsion curves, $V_R(1)$ and $V_R(2)$

An increase in electrolyte concentration leads to a compression of the double layer (kappa increase) and so the energy barrier to coagulation decreases or disappears. If the barrier is cleared, then the net interaction is all attractive, and as a result the particles coagulate.

This inner region is after referred to as an energy trap since the colloids can be considered to be trapped together by van der Waals forces.

What concentration of salt (n_0) just eliminates the repulsive barrier?

Curve 1: Low ionic strength: primary minimum and high maximum → stable colloidal dispersion.

Curve 2: High ionic strength: only primary minimum → unstable colloidal dispersion.

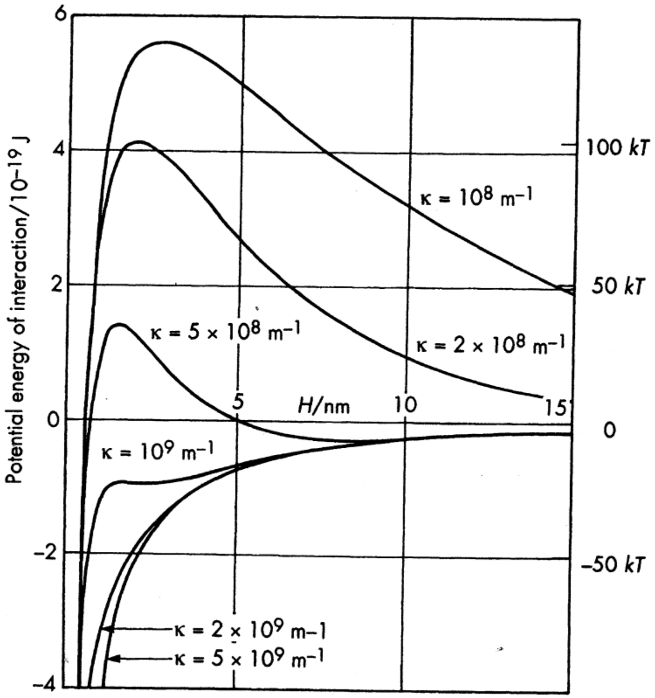


Figure 8.3 The influence of electrolyte concentration, κ, on the total potential energy of interaction of two spherical particles: $a = 10^{-7}$ m; $T = 298$ K; $z = 1$; $A_{11} = 2 \times 10^{-19}$ J; $A_{33} = 0.4 \times 10^{-19}$ J; $\epsilon/\epsilon_0 = 78.5$; $\psi_d = 50$ mV $\approx 2kT/e$. V_R and V_A calculated using equations (8.7), (8.9) and (8.13)

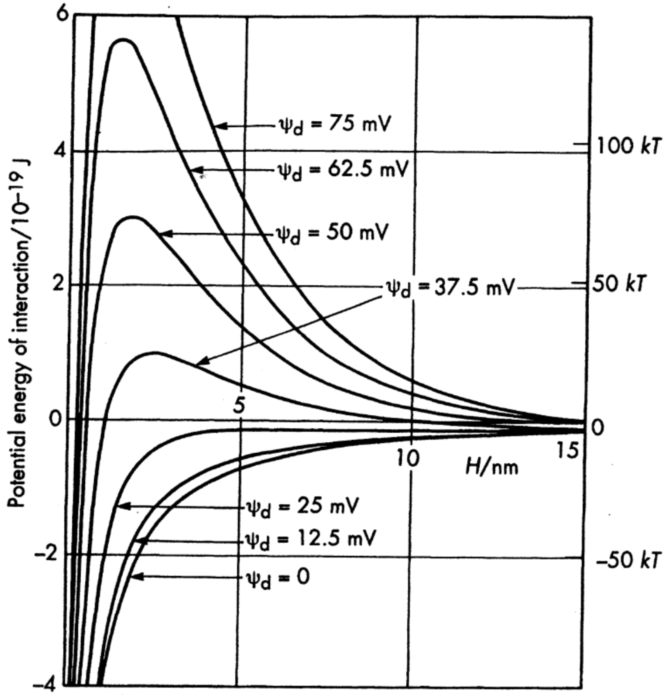


Figure 8.4 The influence of Stern potential, ψ_d, on the total potential energy of interaction of two spherical particles: $a = 10^{-7}$ m; $T = 298$ K; $z = 1$; $A_{11} = 2 \times 10^{-19}$ J; $A_{33} = 0.4 \times 10^{-19}$ J; $\epsilon/\epsilon_0 = 78.5$; $\kappa = 3 \times 10^8$ m^{-1}. V_R and V_A calculated using equations (8.7), (8.9) and (8.13)

DLVO theory

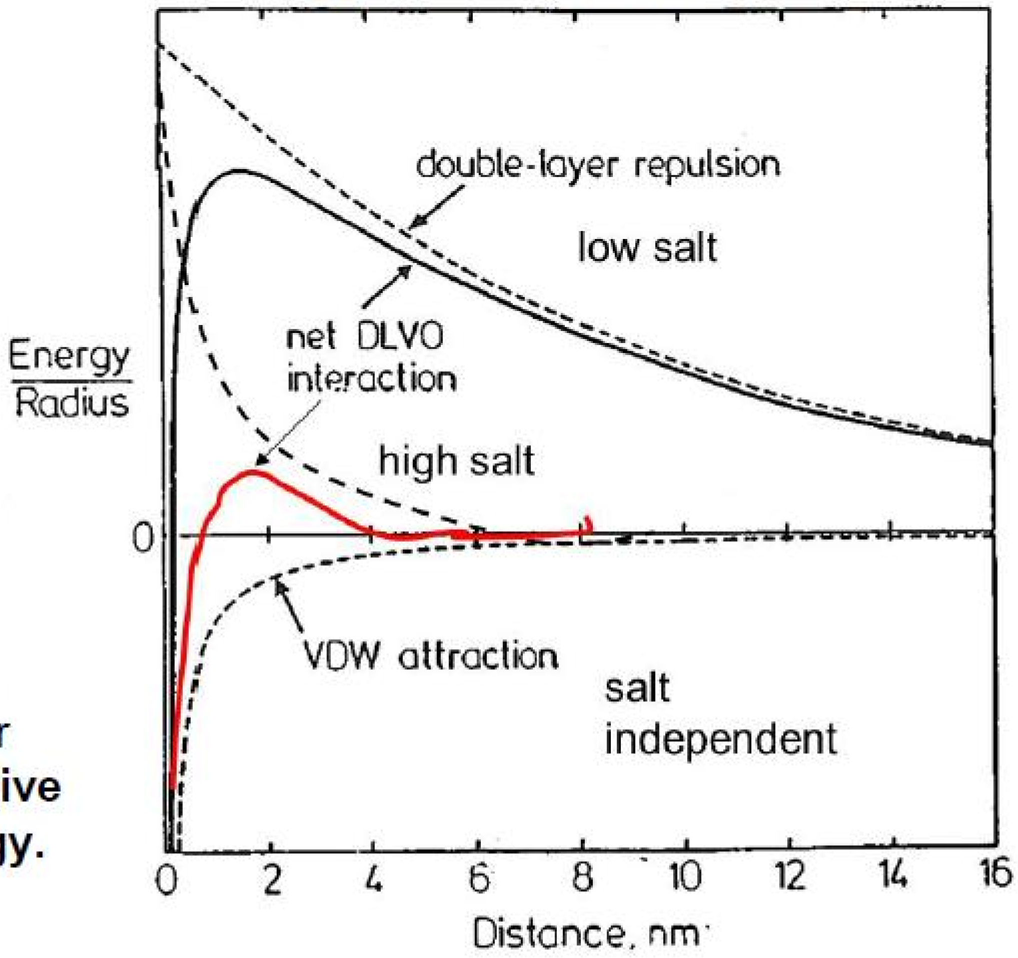
$$V_T = V_R + V_A$$

V_A is not affected by the presence of salt.

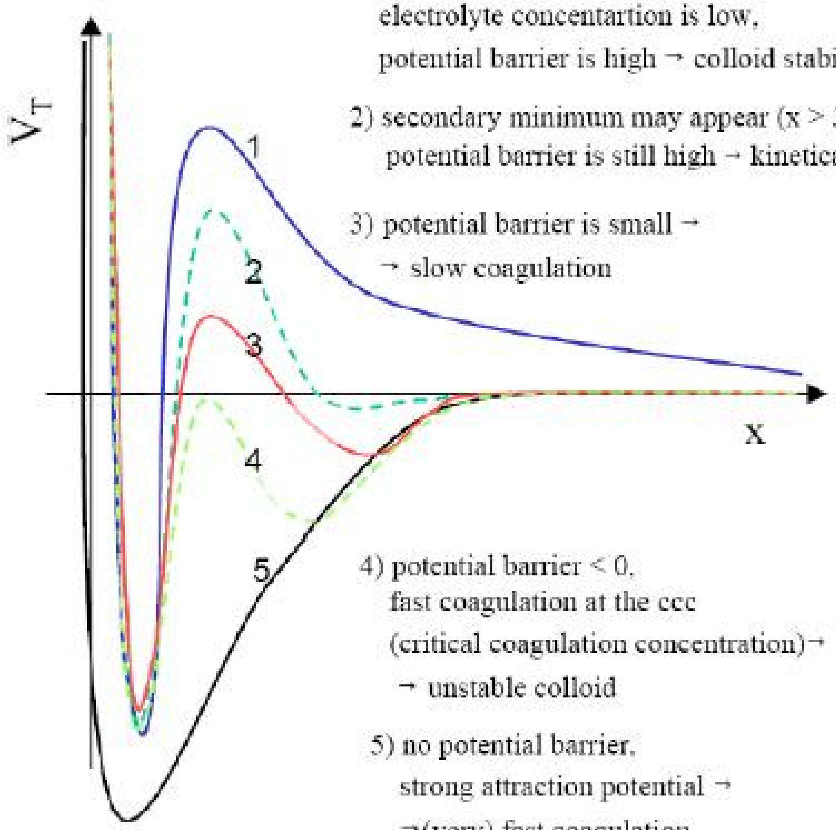
V_R depends on the salt concentration.

The higher the salt concentration, the lower V_R and the more attractive the total interaction energy.

Typical interaction curves



DLVO theory: conditions for colloid stability



1) surface charge density is high,
electrolyte concentartion is low,
potential barrier is high → colloid stability

2) secondary minimum may appear (x > 3 nm),
potential barrier is still high → kinetically stable colloid

3) potential barrier is small →
→ slow coagulation

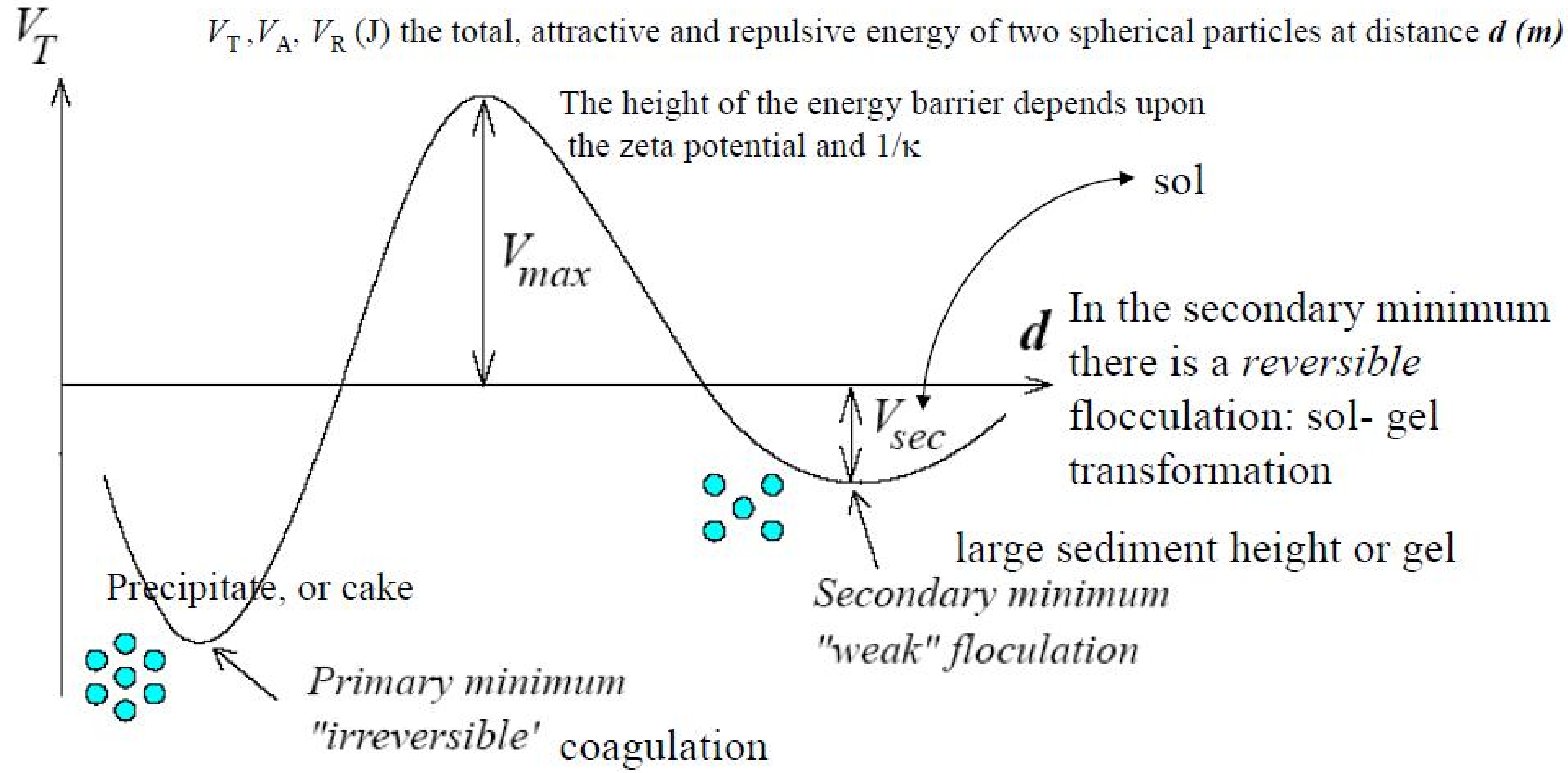
4) potential barrier < 0,
fast coagulation at the ccc
(critical coagulation concentration)→
→ unstable colloid

5) no potential barrier,
strong attraction potential →
→(very) fast coagulation

1-5:
electrolyte concentration increases, diffuse electric double layer is narrow !

Total Interaction= sum of the attractive and repulsive interactions

$V_T = V_A + V_R$



V_T, V_A, V_R (J) the total, attractive and repulsive energy of two spherical particles at distance ***d (m)***

The height of the energy barrier depends upon the zeta potential and $1/\kappa$

In the secondary minimum there is a *reversible* flocculation: sol- gel transformation

large sediment height or gel

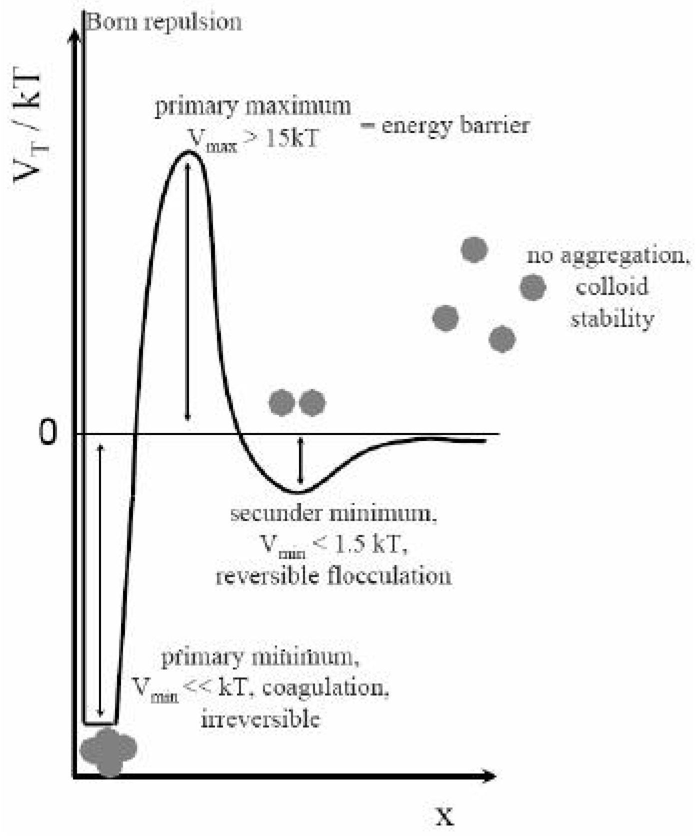
Secondary minimum
"weak" floculation

Precipitate, or cake

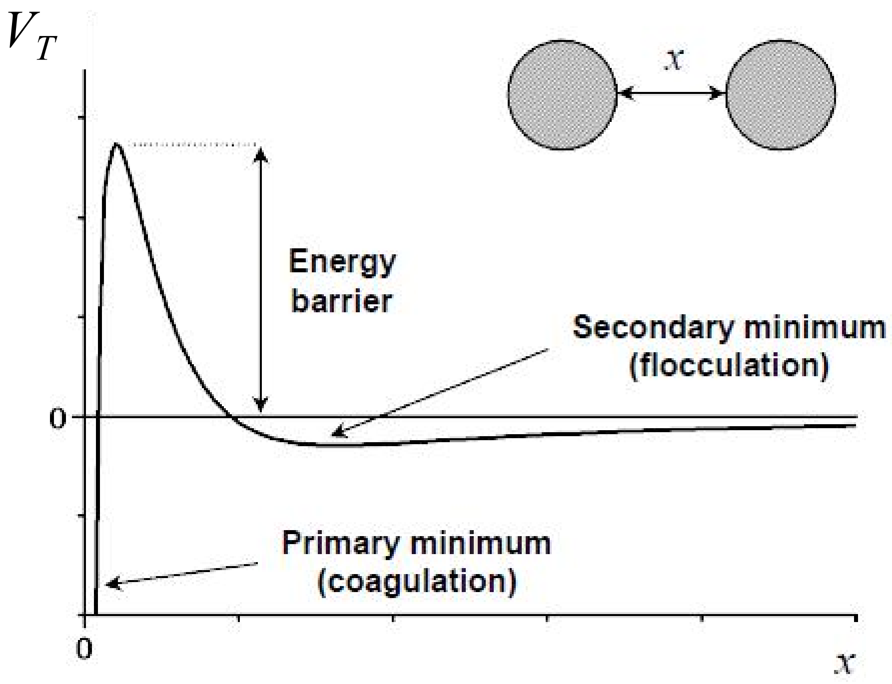
Primary minimum
"irreversible' coagulation

van der Waals attraction will predominate at small and at large interparticle distances. At intermediate distances double layer repulsion may predominate, depending on the actual values of the forces. In order to agglomerate, two particles on a collision course must have sufficient kinetic energy due to their velocity and mass, to “jump over” this barrier.

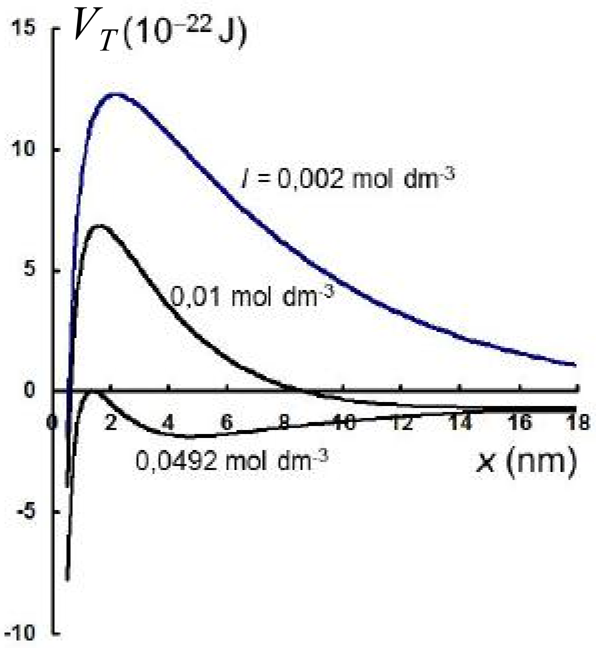
DLVO theory: conditions for colloid stability



DLVO theory

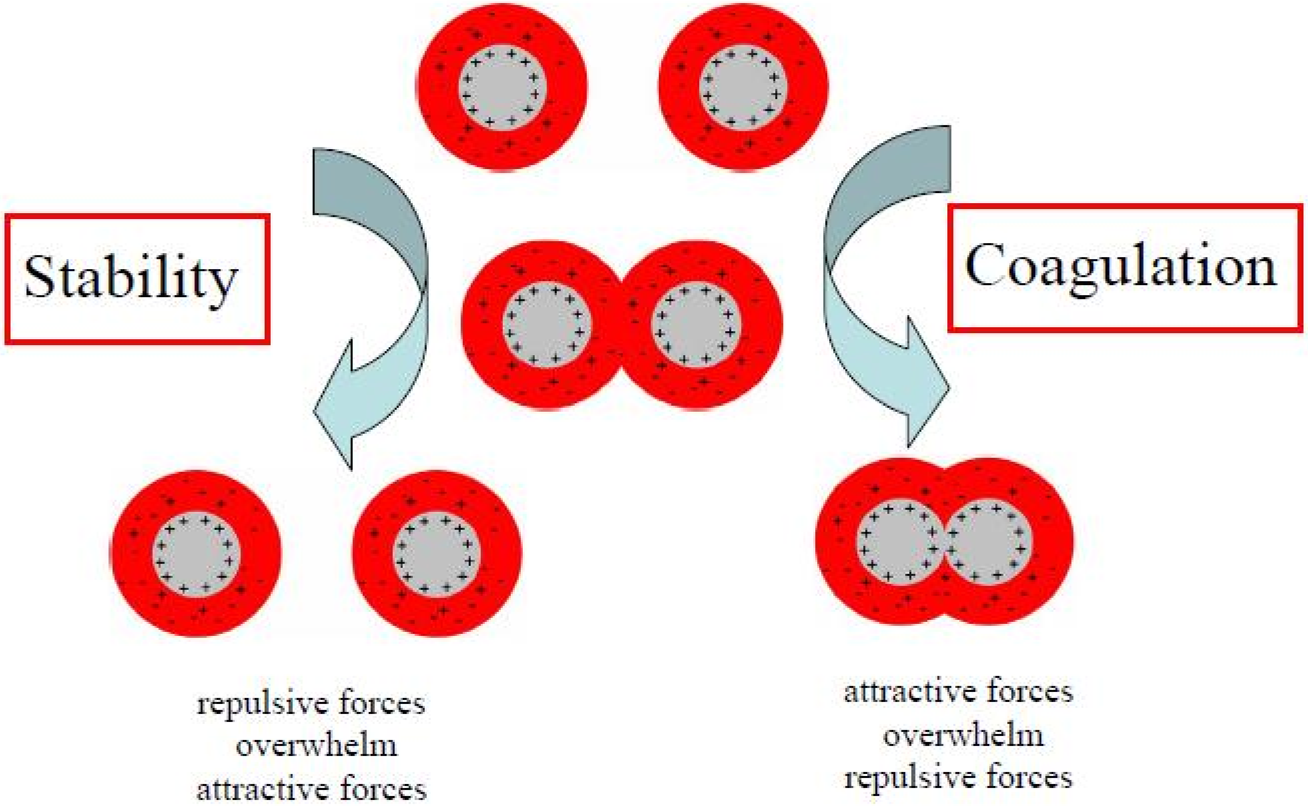


$$V_T = V_R + V_A$$



An increase of the salt concentration provokes a reduction of the energy barrier, which decreases the stability of the system.

The **critical coagulation concentration (ccc)** is the salt concentration at which the energy barrier disappears. The system is unstable, and any approximation between particles results in aggregation.



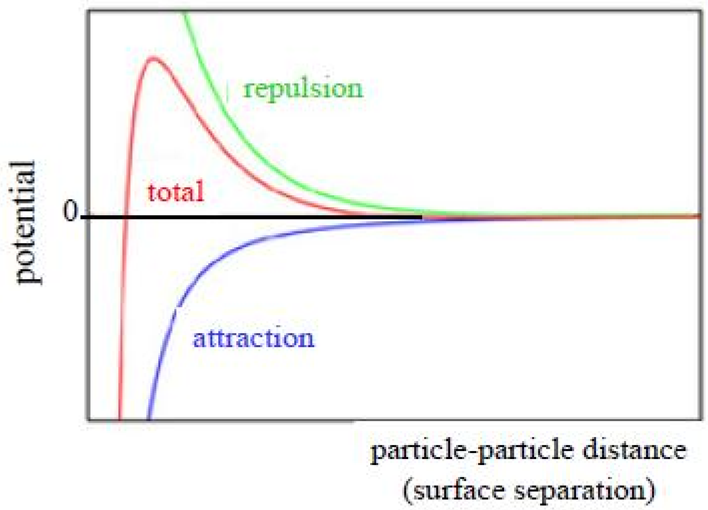
Stability

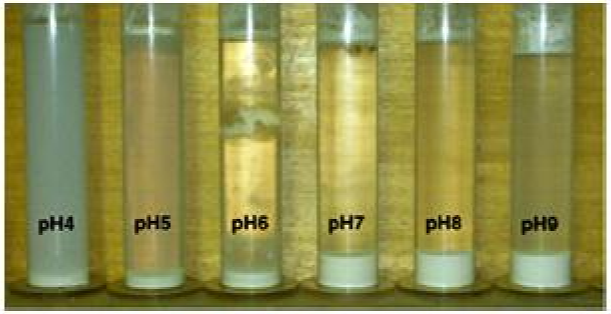
Coagulation

repulsive forces
overwhelm
attractive forces

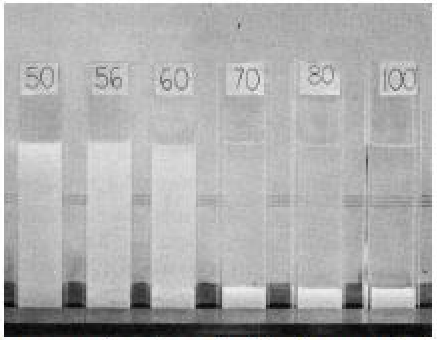
attractive forces
overwhelm
repulsive forces

Colloid stability/flocculation/coagulation/ are controlled by the relative magnitudes of the van der Waals and the Coulombic forces



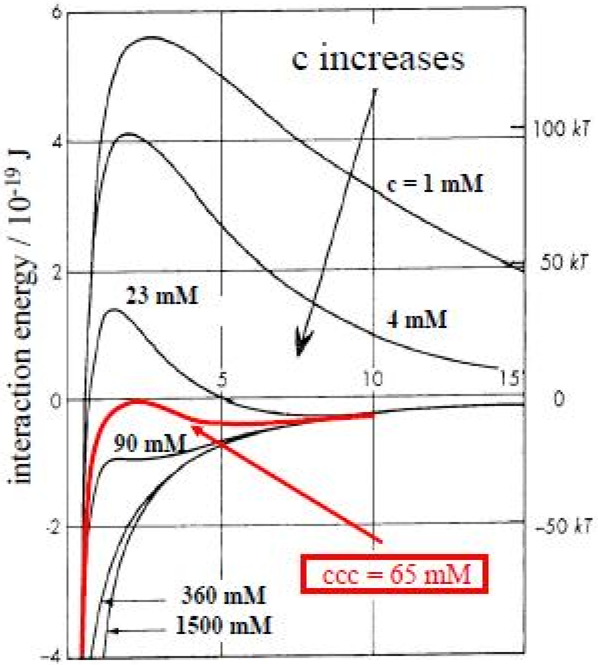


aqueous Al_2O_3 suspension
at different pHs

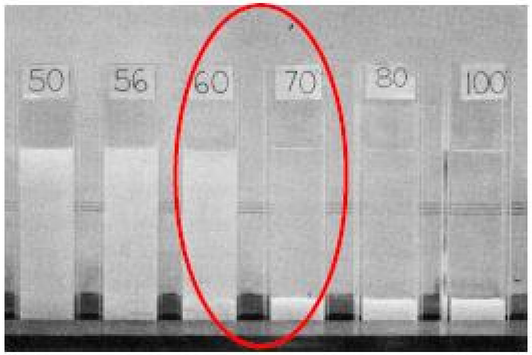


aqueous As_2S_3 sol with increasing
background electrolyte concentraion
(1:1 electrolyte, mM)

Schulze-Hardy Rule: Stability depends on the sixth power of the charge on the ions



$r = 0.1\mu m$; $T = 298K$; $A_{212} = 10^{-19} J$; $\psi_{St} = 50 mV$; $z = 1$; $\varepsilon = 78.5$



As_2S_3 sol in 1:1 electrolyte

$$V_T = V_R + V_A = \frac{64\pi akTn_0\chi_0^2}{\kappa^2}\exp(-\kappa x) - \frac{Aa}{12x} = 0$$

$$\frac{dV_T}{dx} = -\kappa V_R + \frac{V_a}{x} = 0$$

$$\rightarrow \kappa x = 1$$

$$\frac{64\pi akTn_0\chi_0^2}{\kappa^2}\exp(-1) - \frac{Aa\kappa}{12} = 0$$

giving $$\kappa^3 = \frac{(887.2)kTn_0\chi_0^2}{A}$$

$since \quad \kappa = \sqrt{\frac{2z^2e^2n_0}{\varepsilon kT}}$ $\qquad n_0 = \frac{(98380)\varepsilon^3k^5T^5\chi^4}{z^6e^6A^2}$

$$Therefore, \qquad ccc \propto \frac{1}{z^6}$$

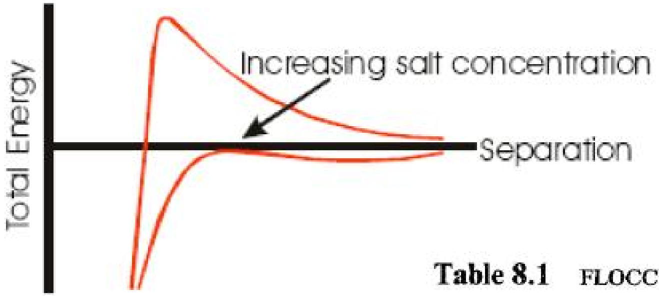
For $V_T = 0$, $V_R = -V_A$. In this case, the DLVO theory predicts the ccc ratio for 1:2:3 valence of charge of ions to be 1000:16:1.3.

Schulze-Hardy rule: $$\text{ccc} \propto \frac{1}{z^6} \qquad \left(\frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6} \right)$$

electrolyte	ccc (M) (As_2S_3 dispersion)	Schulze-Hardy-rule
NaCl	**5,1 10^{-2}**	$5.00\text{x}10^{-2}$
KCl	**5,0 10^{-2}**	
$MgCl_2$	**7,2 10^{-4}**	$7.81\text{x}10^{-4}$
$CaCl_2$	**6,5 10^{-4}**	
$AlCl_3$	**9,3 10^{-5}**	$6.86\text{x}10^{-5}$

Critical coagulation concentration

What concentration of salt (n_0) eliminates the repulsive barrier?



If the potential energy maximum is large compared with the thermal energy, kT of the particles, the system should be stable; otherwise, the system should coagulate.

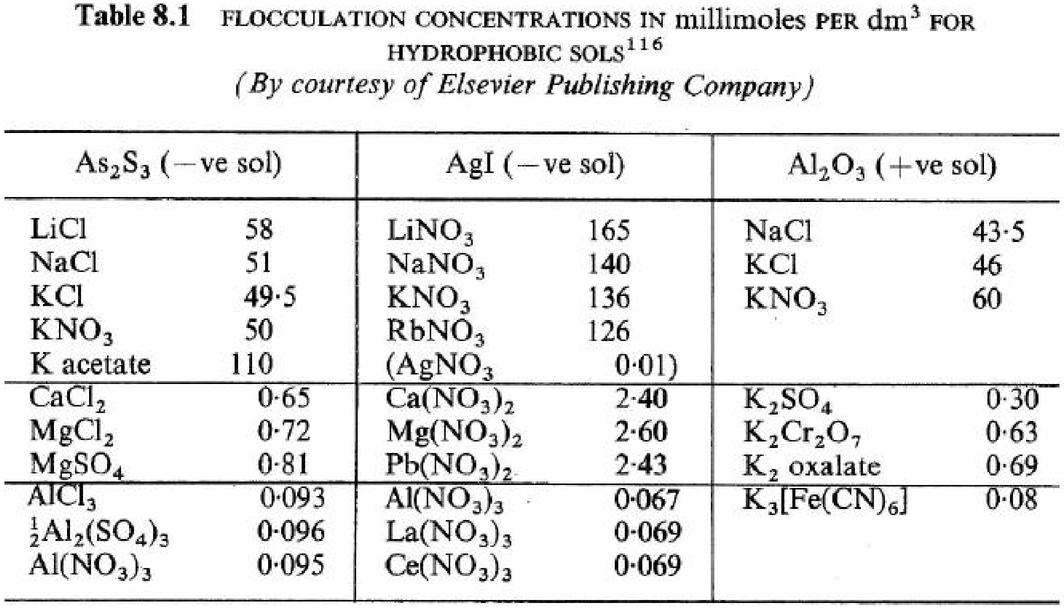


Table 8.1 FLOCCULATION CONCENTRATIONS IN millimoles PER dm^3 FOR HYDROPHOBIC SOLS[116]

(By courtesy of Elsevier Publishing Company)

As_2S_3 (−ve sol)		AgI (−ve sol)		Al_2O_3 (+ve sol)	
LiCl	58	$LiNO_3$	165	NaCl	43·5
NaCl	51	$NaNO_3$	140	KCl	46
KCl	49·5	KNO_3	136	KNO_3	60
KNO_3	50	$RbNO_3$	126		
K acetate	110	($AgNO_3$	0·01)		
$CaCl_2$	0·65	$Ca(NO_3)_2$	2·40	K_2SO_4	0·30
$MgCl_2$	0·72	$Mg(NO_3)_2$	2·60	$K_2Cr_2O_7$	0·63
$MgSO_4$	0·81	$Pb(NO_3)_2$	2·43	K_2 oxalate	0·69
$AlCl_3$	0·093	$Al(NO_3)_3$	0·067	$K_3[Fe(CN)_6]$	0·08
$\frac{1}{2}Al_2(SO_4)_3$	0·096	$La(NO_3)_3$	0·069		
$Al(NO_3)_3$	0·095	$Ce(NO_3)_3$	0·069		

Counter -ion valency
c.c.c (in mol/L) ~z^{-6}

c.c.c. is the concentration of salt just eliminates the repulsive barrier.

ccc

stable $Fe(OH)_3$ sol

The sol undergoes coagulation upon the addition of $Al_2(SO_4)_3$ solution

Non-DLVO forces

Forces not taken into account in the DLVO theory:

- Hydration forces
- Hydrophobic forces
- Steric repulsion
- Bridging attraction
- Depletion forces
- Hydrodynamic forces
- Structural undulation forces

Non-DLVO forces

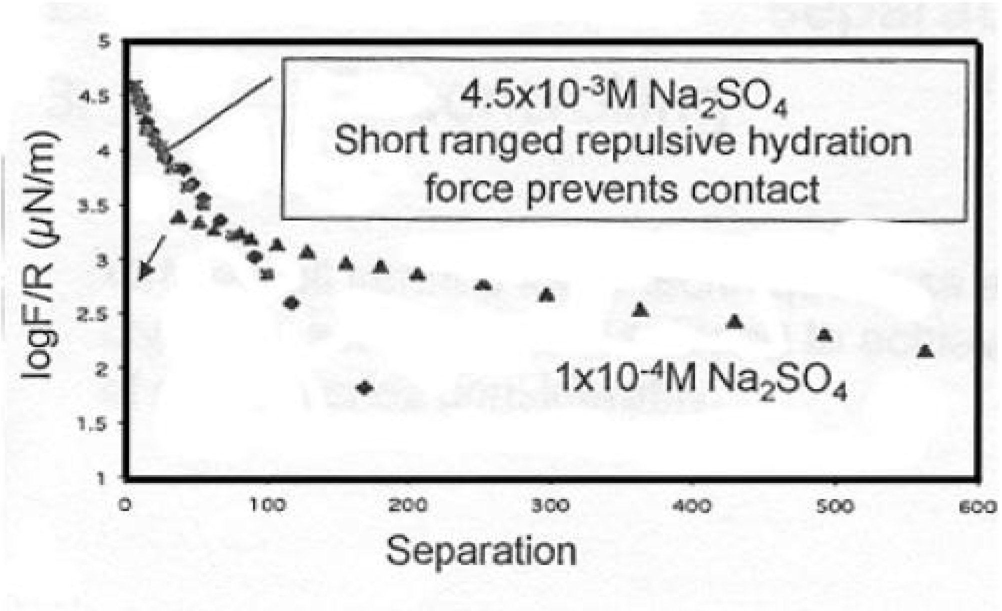
Interaction	Origin	Typical range
Electrostatic (electro-osmotic)	Dissociating ions	1-50 nm
van der Waals	Electromagnetic interactions	5-10 nm
Steric	Adsorbed polymers or surfactants	1-5 nm
Bridging	Adsorbed polymers or particles	5-50 nm
Structural Undulation	Molecular packing	0.5-2 nm
Hydration	Hydration layer	1 nm
Hydrophobic	Hydrophobic surfaces	10-30 nm

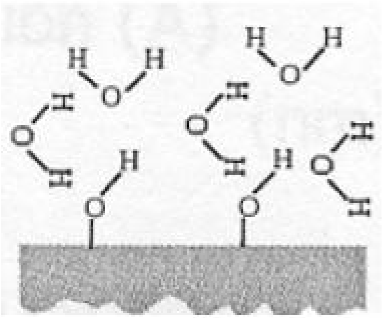
Non-DLVO forces

Hydration forces

Short-ranged repulsive forces. They occur when surface groups (or adsorbed ions) are very hydrated.

Work is required to remove hydration layer. The overlap of hydration layers leads to a repulsive force. This repulsion can completely screen the van der Waals attraction.

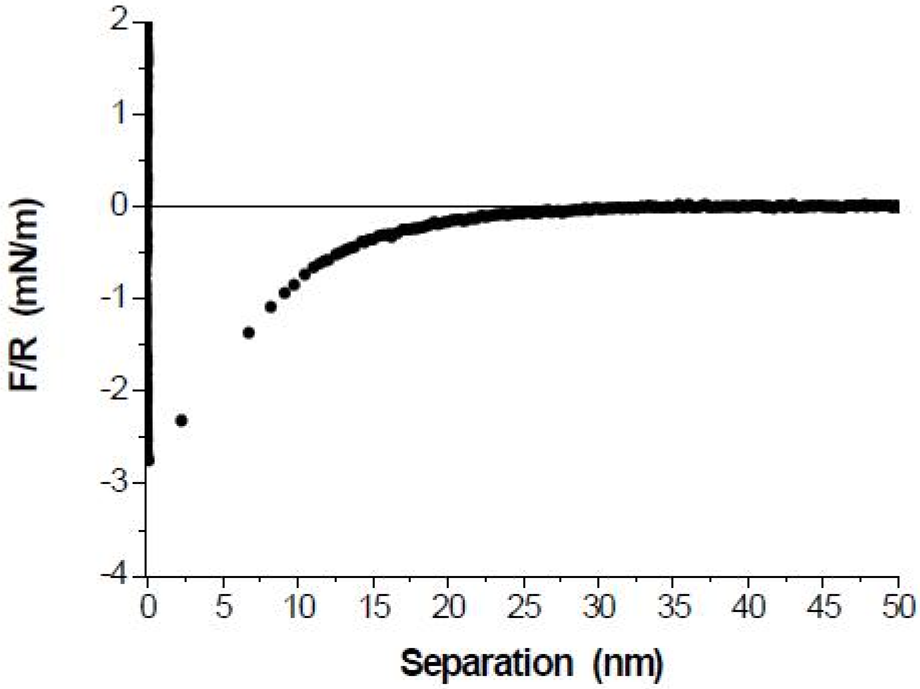




Non-DLVO forces

Hydrophobic forces

Attraction of longer range than van der Waals forces
due to the hydrophobic nature of the surfaces
interacting in an aqueous medium.



Non-DLVO forces

Steric forces

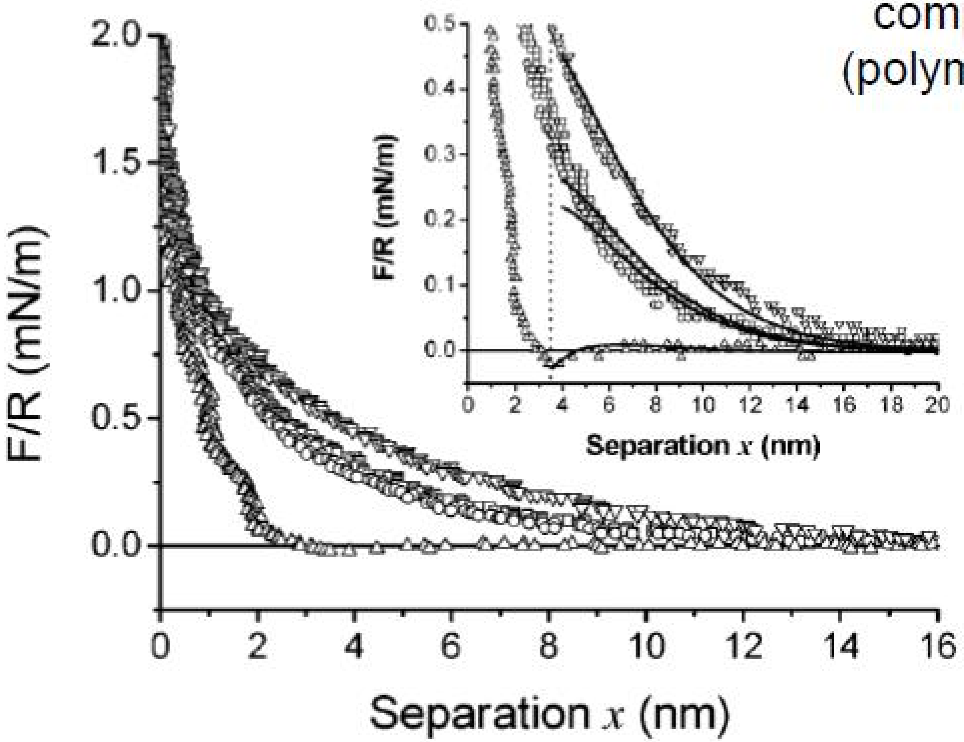
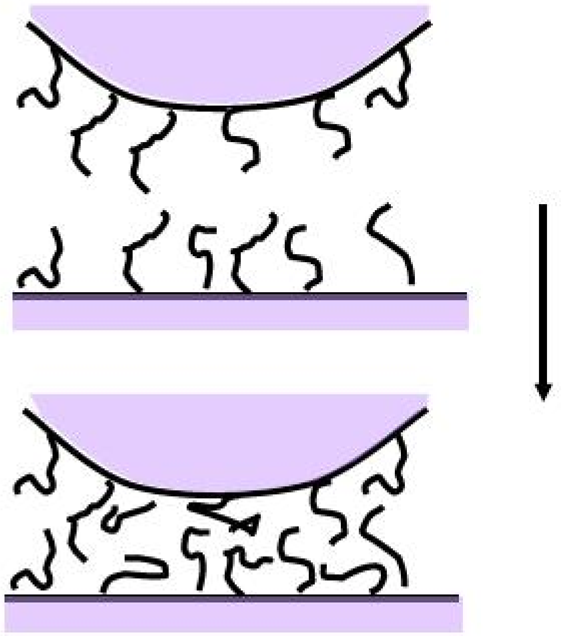


Figure 1. Normalized force vs separation distance *x* for BSA−BSA interaction in 0.01 M NaCl at different pHs: (□) pH 9; (○) pH 7; (△) pH 5; (▽) pH 3. The inset is a zoom of the graph. The lines are the DLVO theory predictions

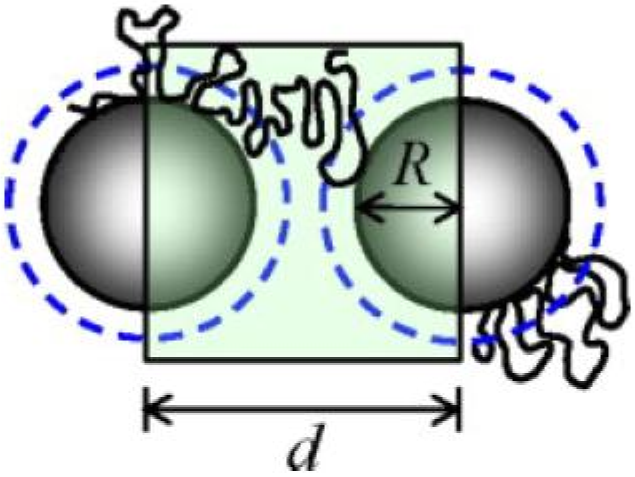
Repulsive forces due to the compression of adsorbed layers (polymers, surfactants, proteins…).

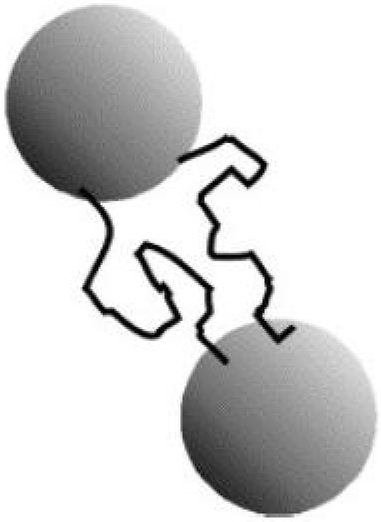


Non-DLVO forces

Bridging attraction

Attraction due to the adsorption of some polymers on two different particles.

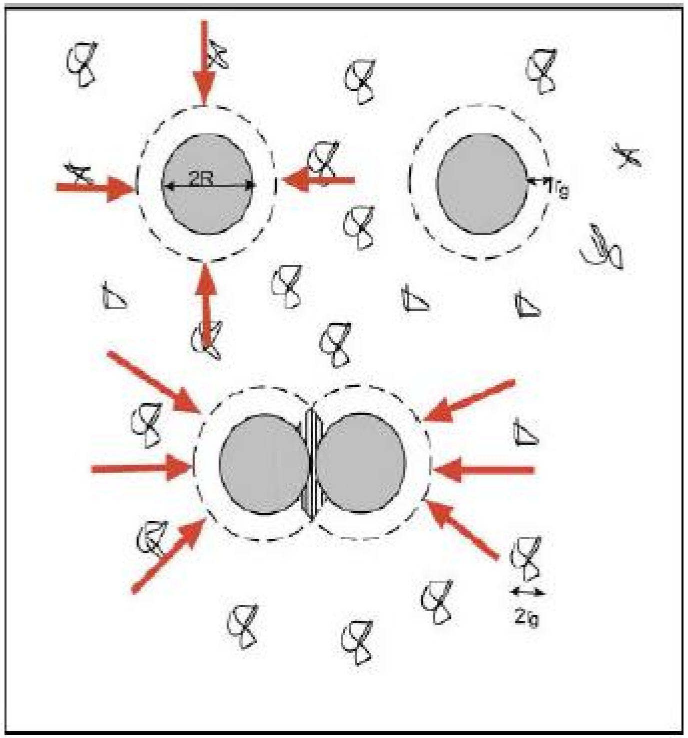




Non-DLVO forces

Depletion forces

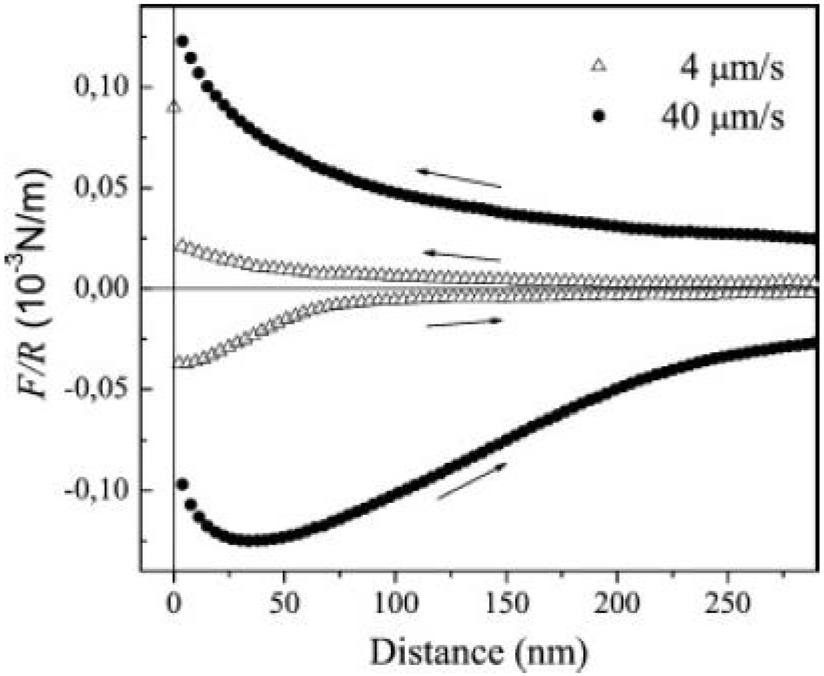
Attraction between particles due to the “pressure” exerted by non-adsorbing polymers in solution.



Non-DLVO forces

Hydrodynamic forces

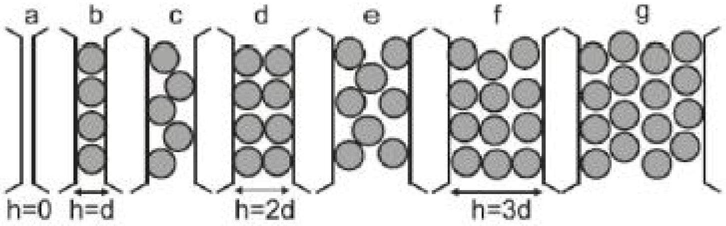
The medium has a resistance against the movement of colloidal particles or surfaces. That resistance is more important at high approaching speeds.

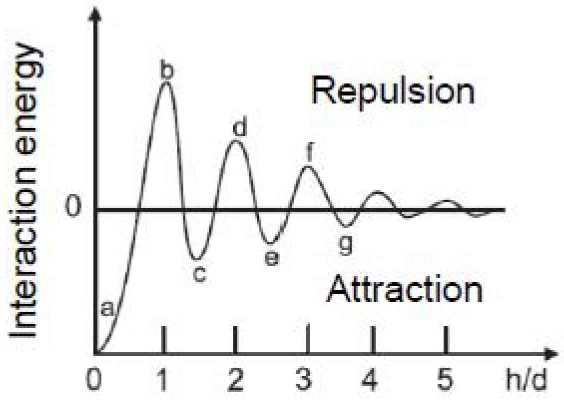


Non-DLVO forces

Structural undulation forces

Oscillatory forces due to the arrangement of solvent molecules at very short separation distances between the surfaces. Observed only between very smooth surfaces.





Summary

- ✦ Ions in solution arrange around a charged surface forming an **electrical double layer**. **Gouy-Chapman** and **Stern** models describe the structure of electrical double layers.

- ✦ The **Debye length** is an estimate of the thickness of the electrical double layer. It decreases as the salt concentration in solution increases.

- ✦ The **point of zero charge** of a particle is the pH at which its surface charge is zero. The **isoelectric point** of a particle is the pH at which its electrophoretic mobility is zero.

- ✦ The **DLVO theory** is an old and popular theory to explain the stability of colloidal solutions. It takes into account two types of interaction: **van der Waals attraction** and **electrical double layer repulsion**.

- ✦ An increase of the salt concentration provokes a reduction of the electrical double layer repulsion, which is completely suppressed at the **critical coagulation concentration (ccc)**.

- ✦ Several types of interaction forces are not considered in the DLVO theory. Some examples of **non-DLVO forces** are: hydration forces, hydrophobic forces, steric repulsion, bridging attraction, depletion forces, hydrodynamic forces, structural undulation forces.