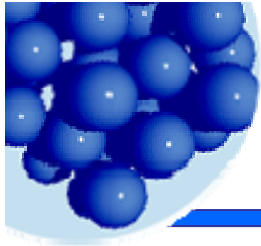


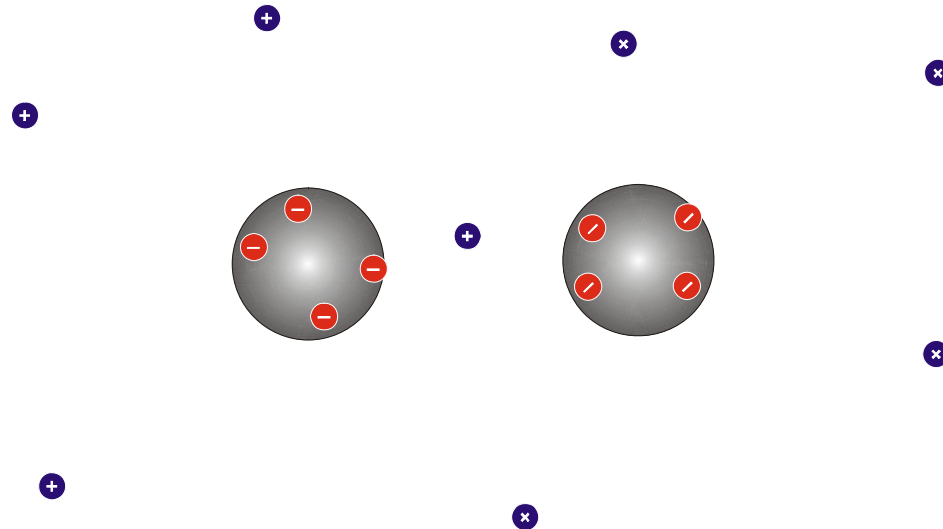
Lecture 3

Electrostatic stabilization

Dispersions in liquids: suspensions,
emulsions, and foams



Electrostatic repulsion in low salt dispersions (Generally organic solvents.)

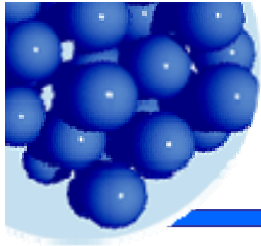


The electrostatic repulsion is determined by Coulombic forces between the charged particles:

$$\Delta G^R = \frac{\pi D \epsilon_0 d^2 \zeta^2}{d + H}$$

Generally the surface chemistry determines the zeta potential, so all the particles with the same chemistry have the same zeta potential.

Therefore the larger the particles, the more stable the dispersion.



Electrostatic stability in organic solvents

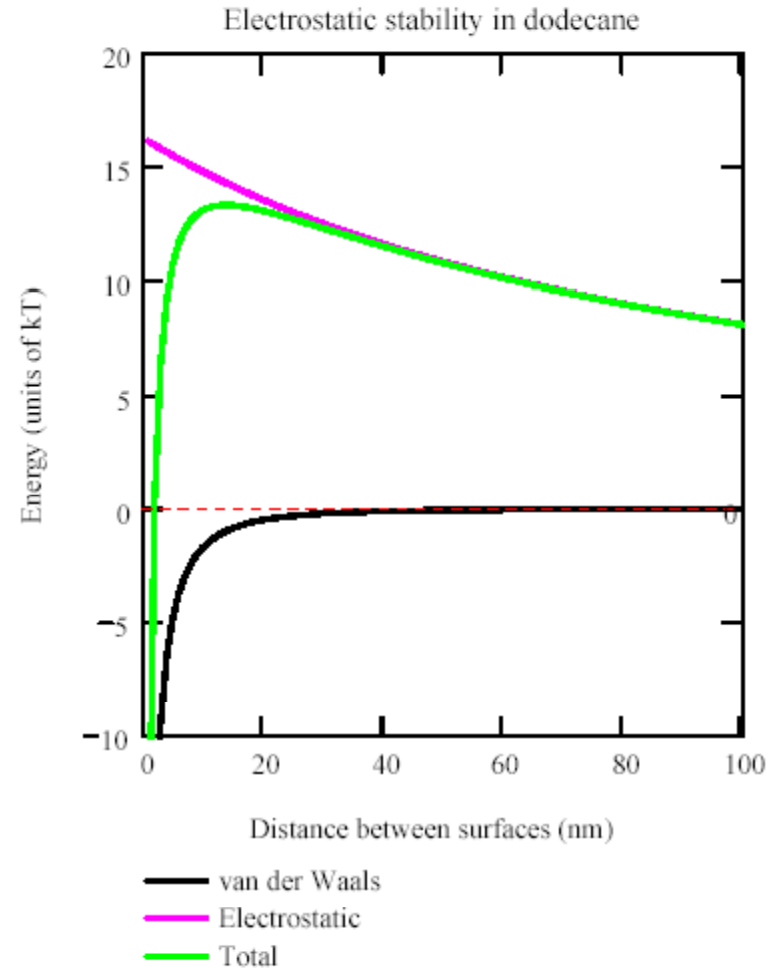
$$\Delta G^{total} = \frac{\pi D \epsilon_0 d^2 \zeta^2}{d + H} - \frac{Ad}{24H}$$

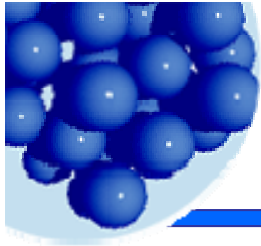
$\zeta = -105 \text{ mV}$ (8 charges/particle)

$d = 100 \text{ nm}$

$A_{121} = 4.05 \times 10^{-20} \text{ J}$ (Titania in oil)

$\lambda = 50 \text{ pS/m}$

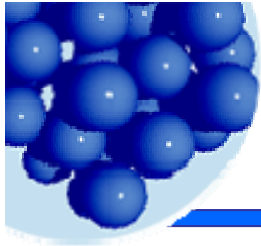




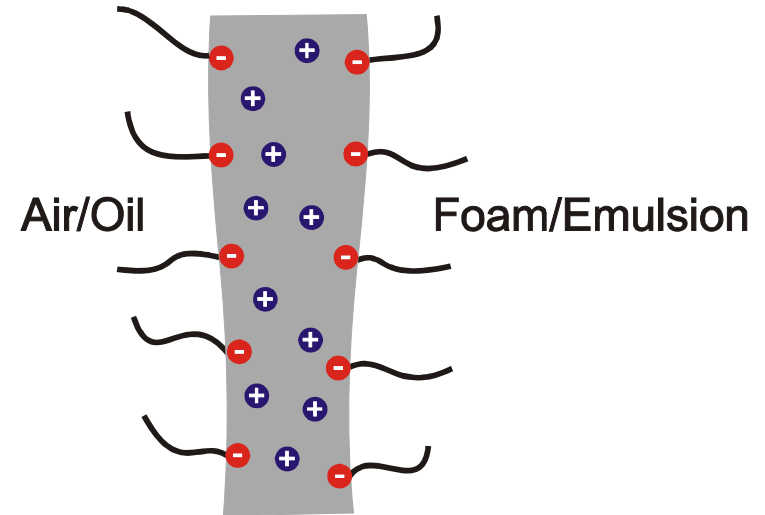
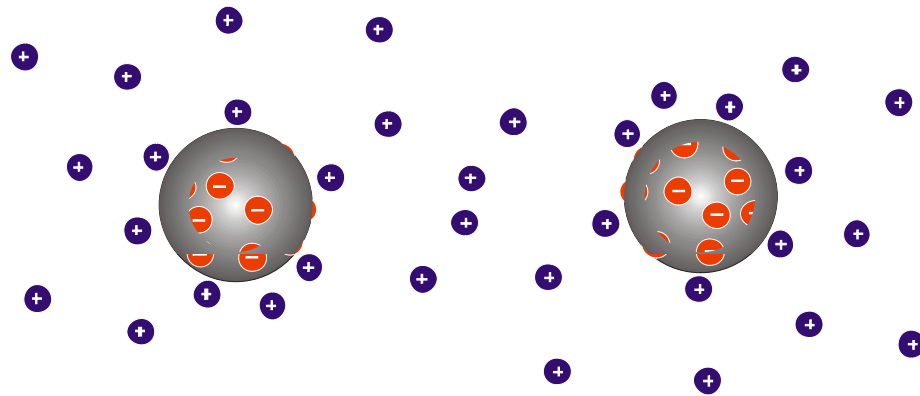
Zeta potential to stabilize dispersions in nonpolar liquids

Diameter (μm)	Zeta Potential (mV)
0.02	224
0.10	100
0.2	71
0.6	41
1.0	32
1.5	26
2.0	22
10.0	10

About the same potential and particle size effect as in water.

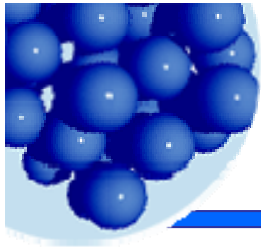


Electrostatic repulsion



Loosely held countercharges form “electric double layers” next to each surface. The concentration of ions is determined by a balance between the attraction to the surface and kinetic energy.

Electrostatic repulsion results from the interactions of ions around each surface.

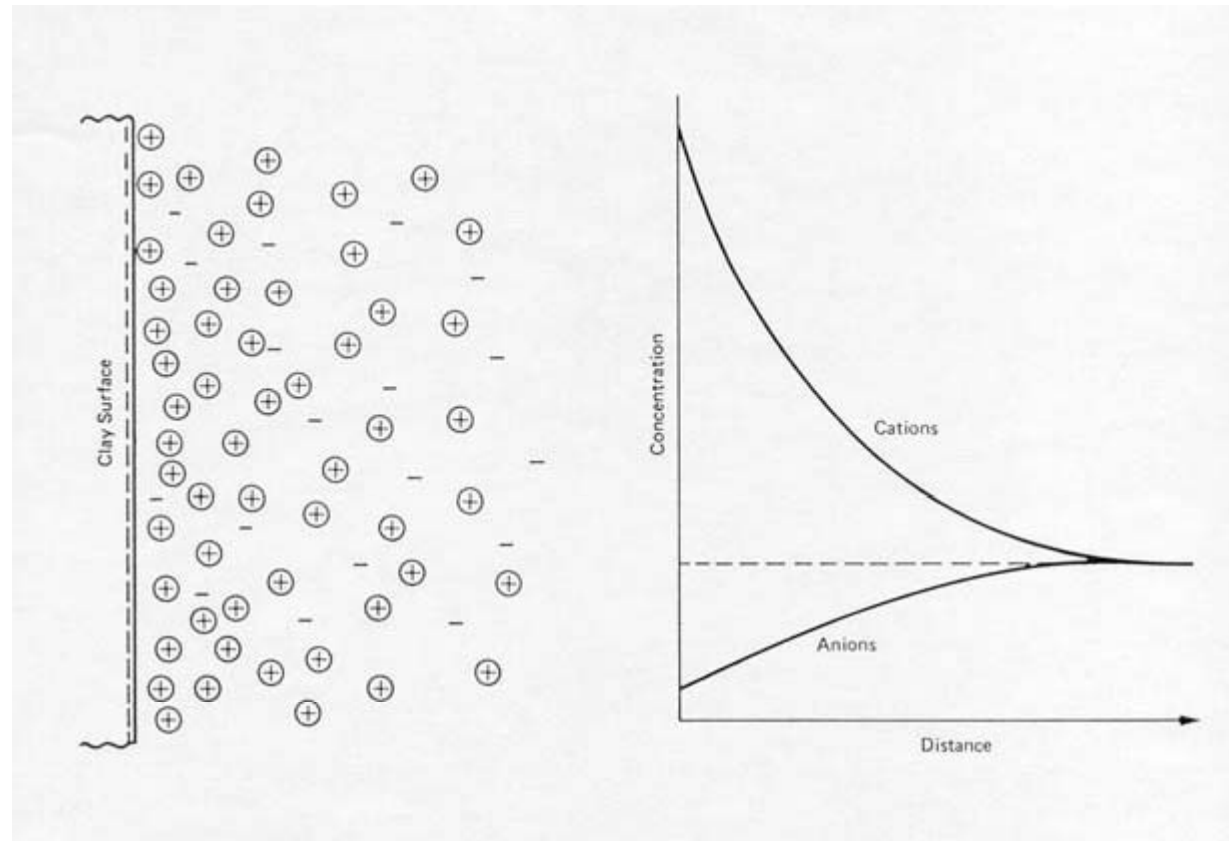


Charged surfaces in high salt dispersions. (Generally, water.)

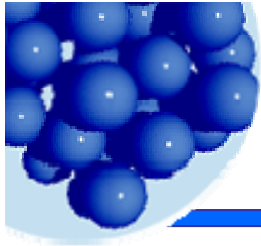
The clay surface has a net negative charge, a negative electric potential. But we cannot measure it directly because the clay is an insulator and it is isolated.

The surface potential is measured electrokinetically.

Properties of the diffuse cloud of ions are calculated.



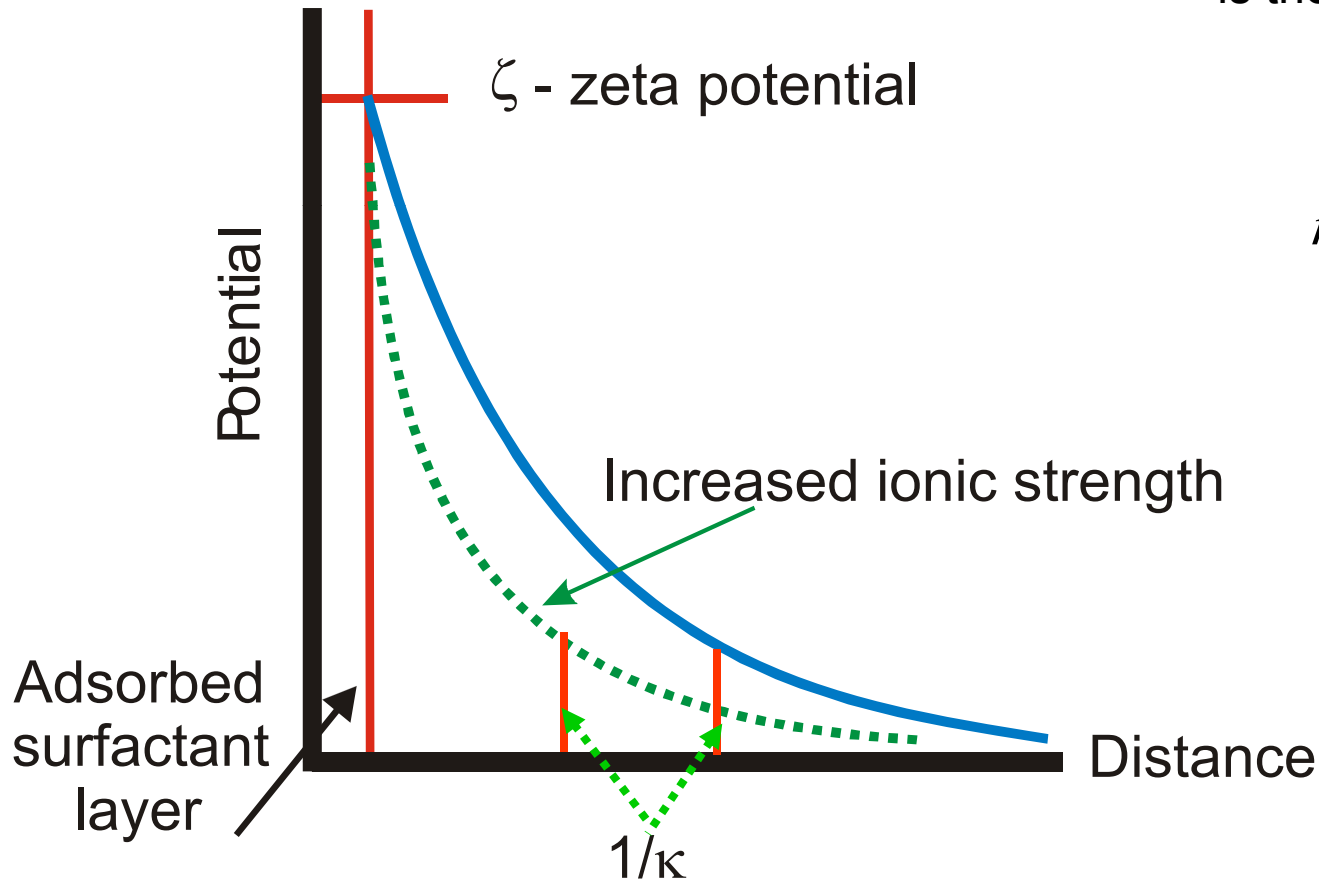
http://appliedgeophysics.berkeley.edu:7057/dc/figures/fig43_11.jpg



Stern's model for a charged surface

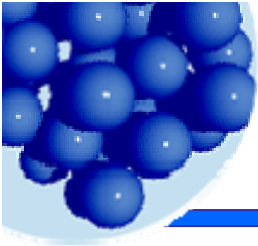
$$\text{Potential} = \zeta \exp(-\kappa x)$$

(The surface potential is the zeta potential.)



$$\kappa = \sqrt{\frac{e^2 \sum_i c_i z_i^2}{D \epsilon_0 k T}}$$

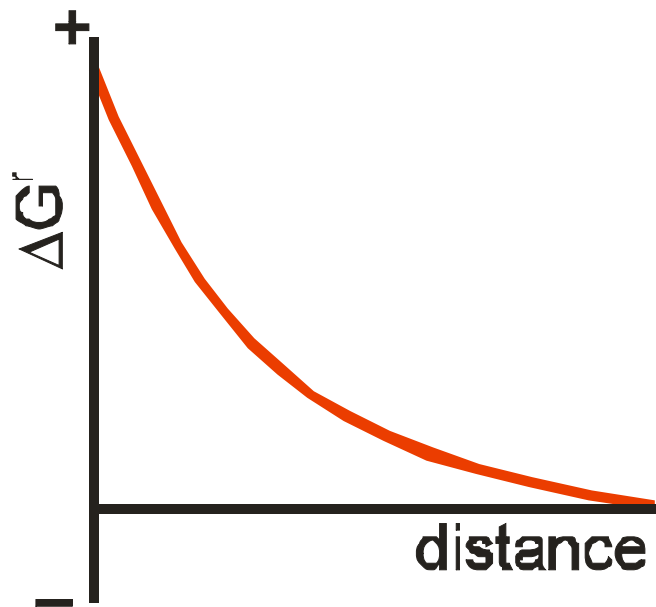
$$I = \frac{1}{2} \sum_i c_i z_i^2$$



The repulsion between spheres – linear model

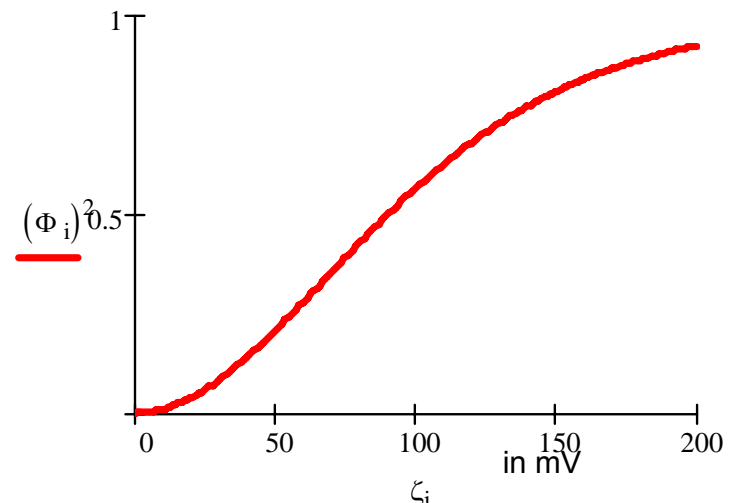
$$\Delta G^r = \frac{32n_0kT\pi d\Phi^2}{\kappa^2} \exp(-\kappa H)$$

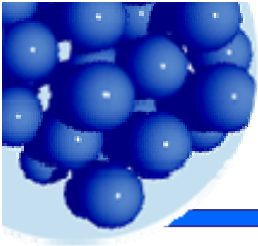
(After a little math found in any textbook)



$$\Phi = \tanh \frac{ze\zeta}{4kT}$$

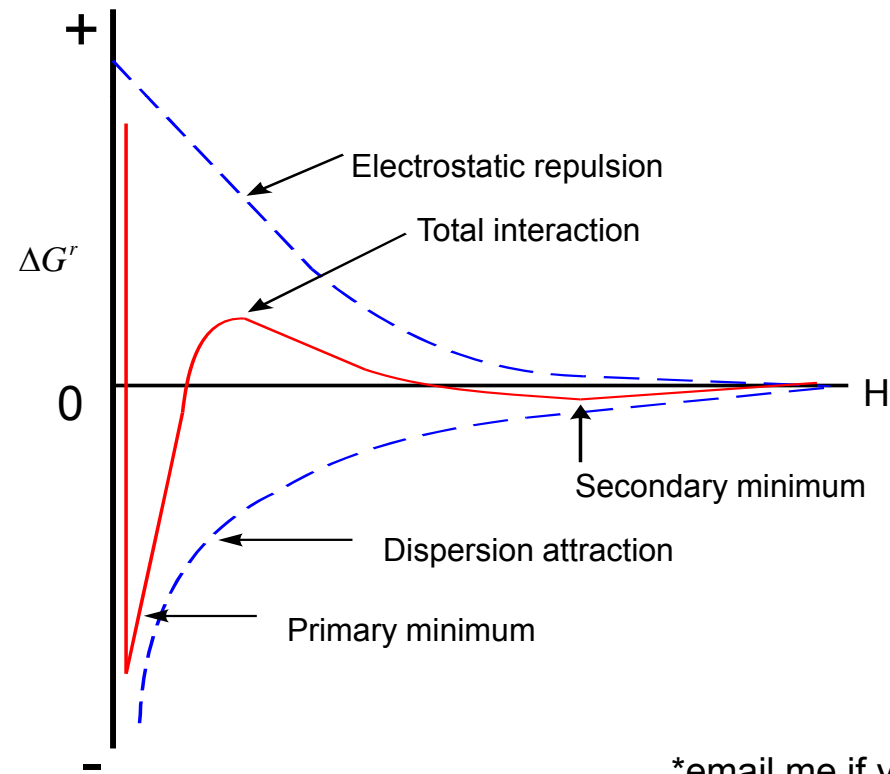
Effect of zeta potential



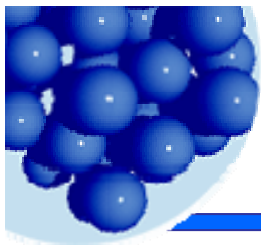


Electrostatic stability of dispersions*

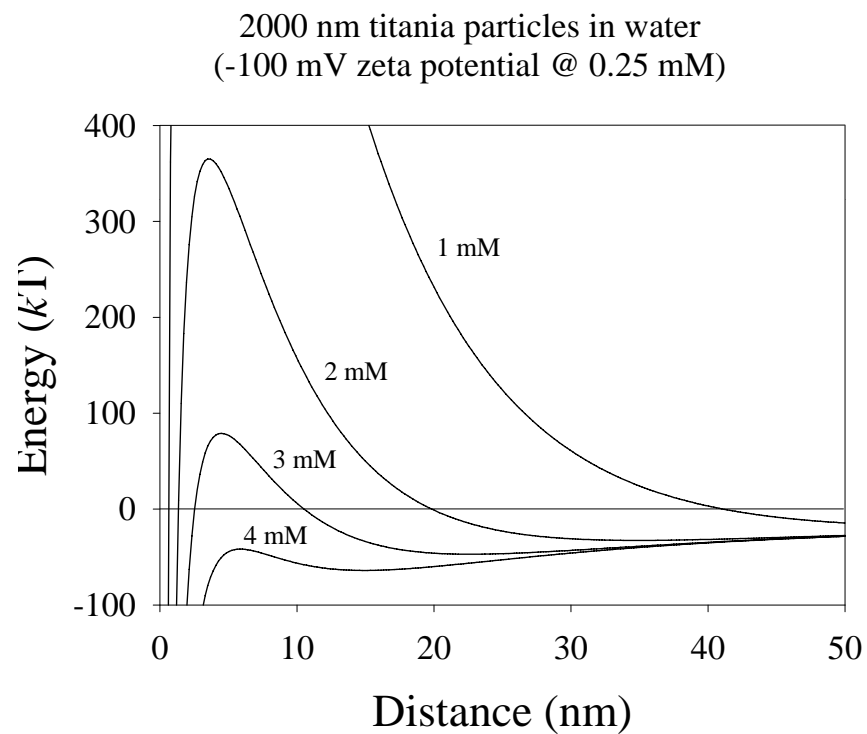
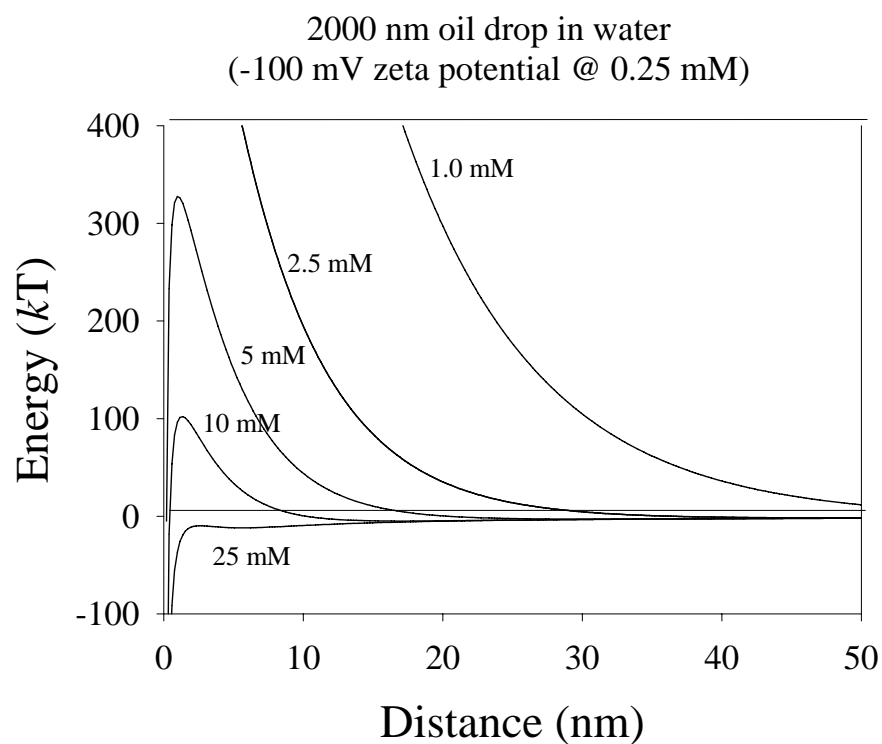
$$\Delta G^T = \frac{32n_0kT\pi d\Phi^2}{\kappa^2} \exp(-\kappa H) - \frac{A_{121}d}{24H}$$



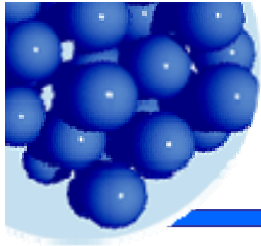
*email me if you have trouble with units.



Effect of electrolyte

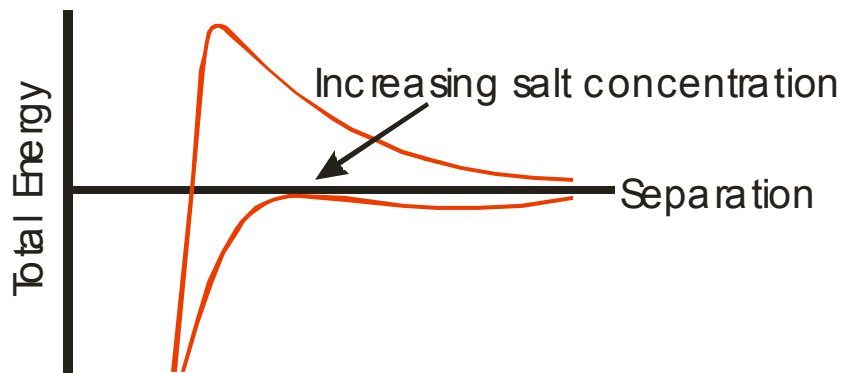


(Corrected from textbook.)



Critical coagulation concentration

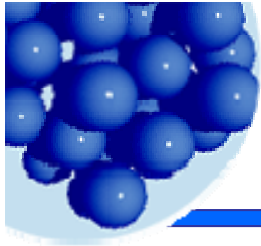
Or, what concentration of salt (n_0) eliminates the repulsive barrier?



$$\Delta G^t \Big|_{H=H_0} = 0 \quad \text{and} \quad \frac{d\Delta G^t}{dH} \Big|_{H=H_0} = 0$$

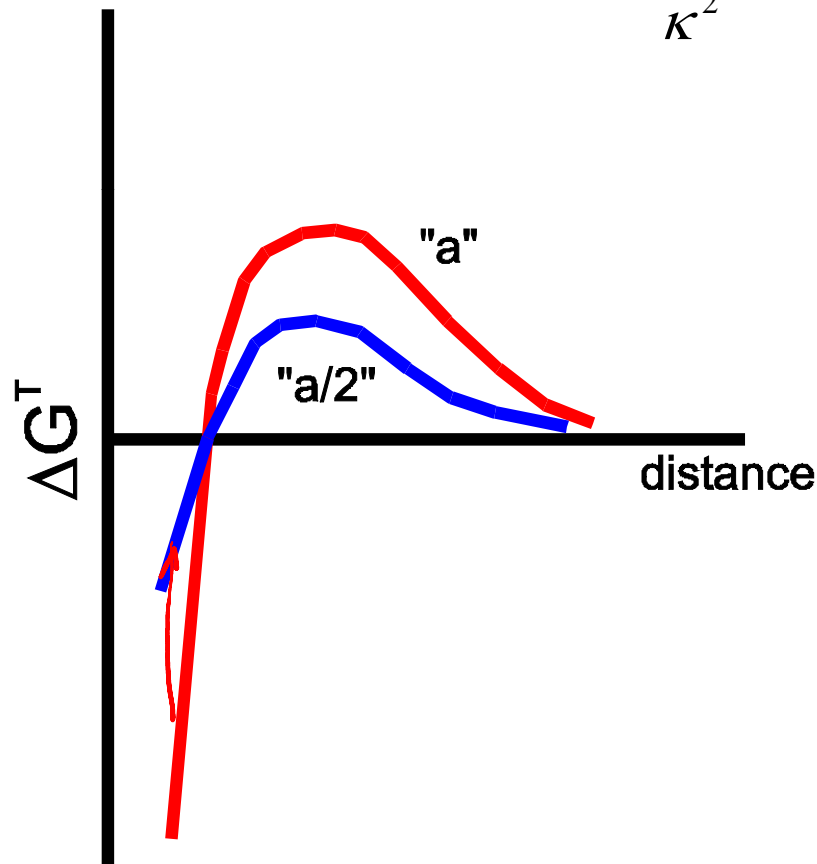
$$n_0 \text{ (molecules/cm}^3\text{)} = \frac{(4\pi\epsilon_0 DkT)^3 2^{11} 3^2 \Phi^4}{\pi \exp(4) e^6 A_{121}^2 z^6} \propto \frac{1}{z^6}$$

The Schulze – Hardy Rule: the stability depends on the sixth power of the charge on the ions!

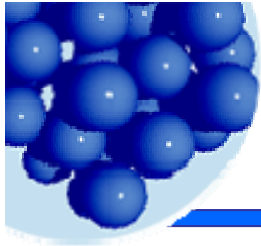


Particle size effect

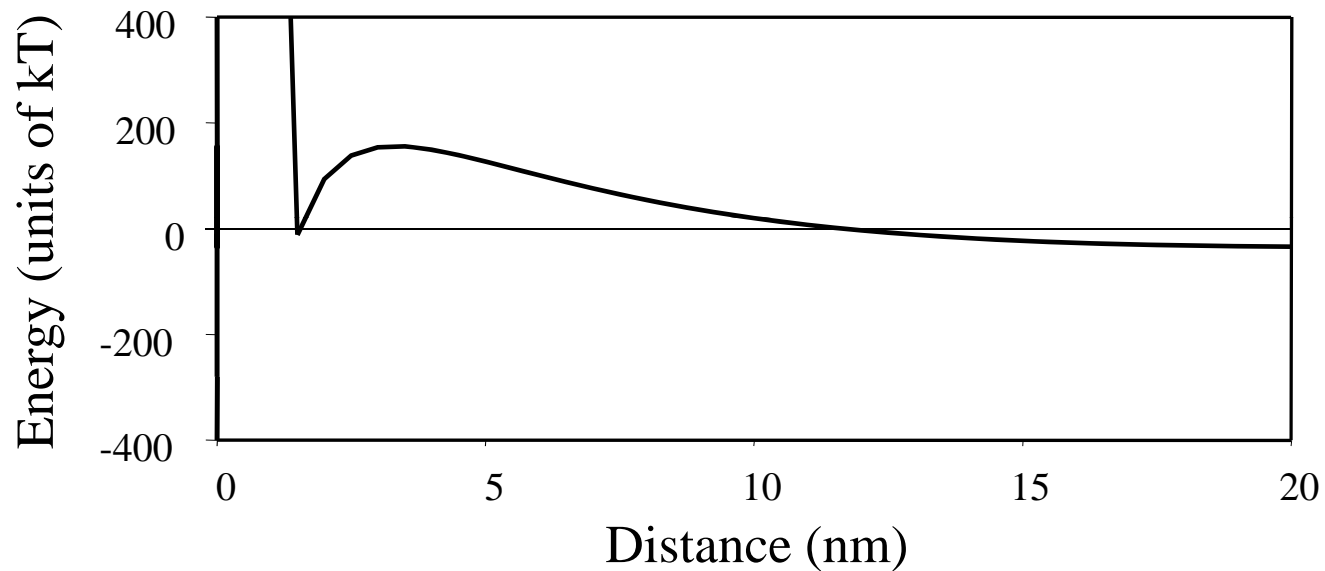
$$\Delta G^T = \frac{32n_0kT\pi d\Phi^2}{\kappa^2} \exp(-\kappa H) - \frac{A_{121}d}{24H}$$



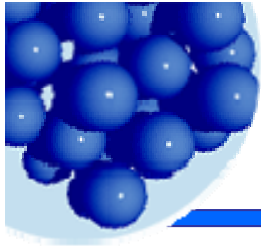
The larger the particles,
the more stable the
dispersion!



Electrosteric stabilization

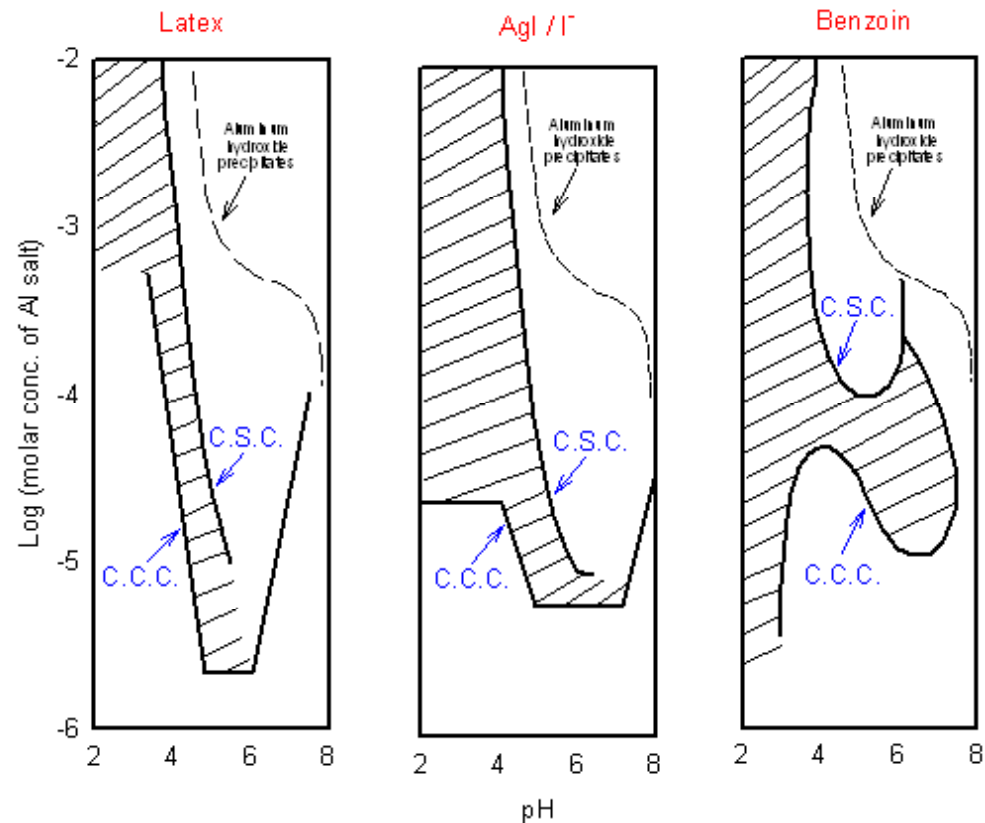


200 nm particles, $A_{121} = 7 \times 10^{-20}$ J, -100 mV zeta potential, 4 mM ionic strength, 1 nm polymer layer.

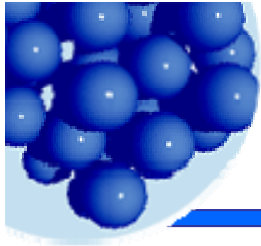


Stability as a phase diagram

Phase diagrams of three hydrophobic sols, showing stability domains as a function of $\text{Al}(\text{NO}_3)_3$ or AlCl_3 concentration and pH; styrene-butadiene rubber (SBR) latex (left); silver iodide sol (middle); and benzoin sols prepared from powdered Sumatra gum (right).



Matijevic', *JCIS*, 43, 217, 1973.



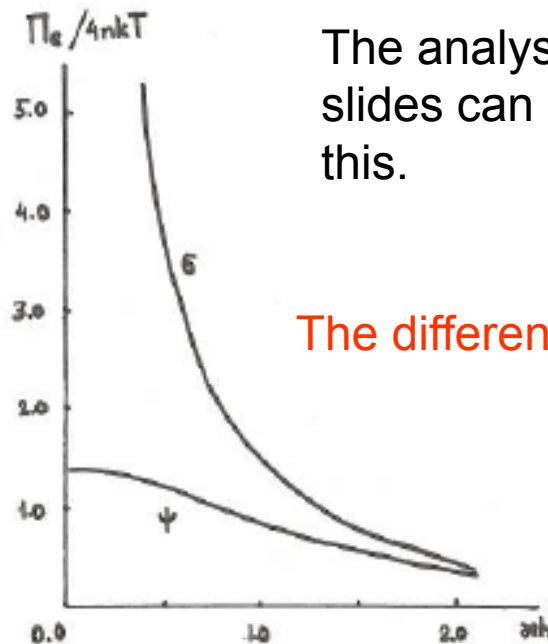
Electrostatic component of disjoining pressure*

Constant surface potential or constant surface charge?

If two surfaces approach each other and surface potential remain constant, the charge per unit area must decrease. Ions must either adsorb or desorb!

If two surfaces approach each other and the surface charge remain constant (no ion adsorption or desorption), the electric potential must increase!

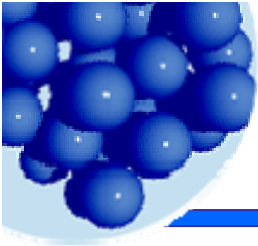
Disjoining pressure as a function of κh in a symmetrical electrolyte at constant potential (lower curve) and constant surface charge (upper curve).



The analysis of the last few slides can be used to study this.

The difference in behavior is huge!

*Following Derjaguin, 1987, pp. 181 – 183.



Electrostatic versus steric stabilization

