Electrostatic stabilization

Dispersions in liquids: suspensions, emulsions, and foams

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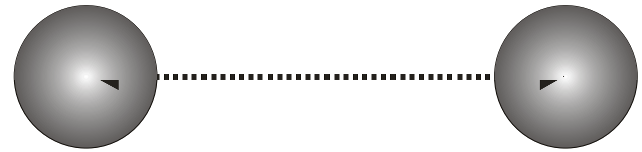
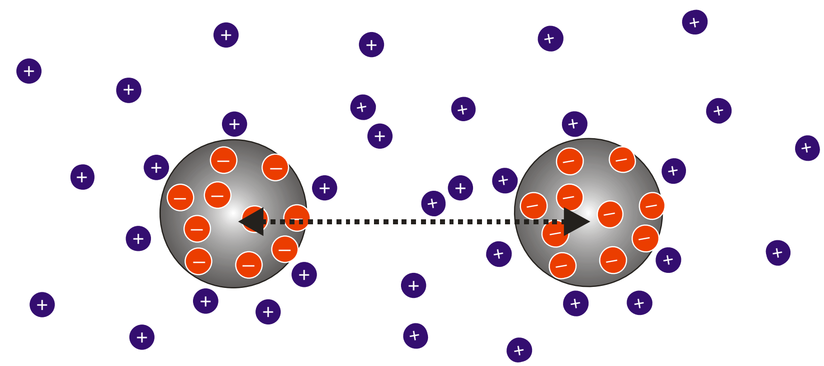
Canonical energies

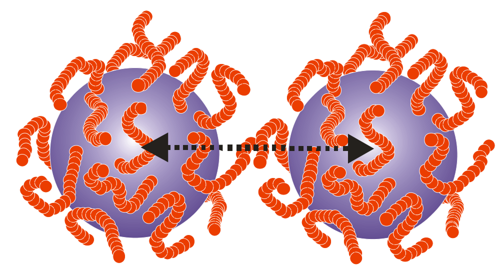
Dispersion attraction:
Long range; primarily dependent on *particle* properties



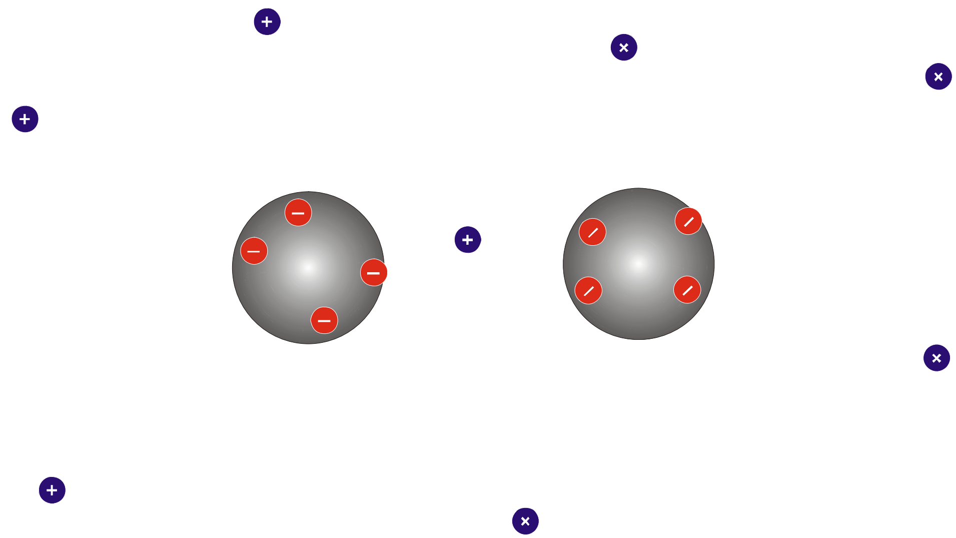
Electrostatic repulsion:
Intermediate range; heavily dependent on *solution* properties



Steric (entropic) repulsion:
Short range, primarily dependent on *solution* properties.



Electrostatic repulsion in nonpolar liquids



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

$$\Delta G^R = \frac{\pi D \varepsilon_0 d^2 \zeta^2}{d + H}$$

Electrostatic stability in nonpolar liquids

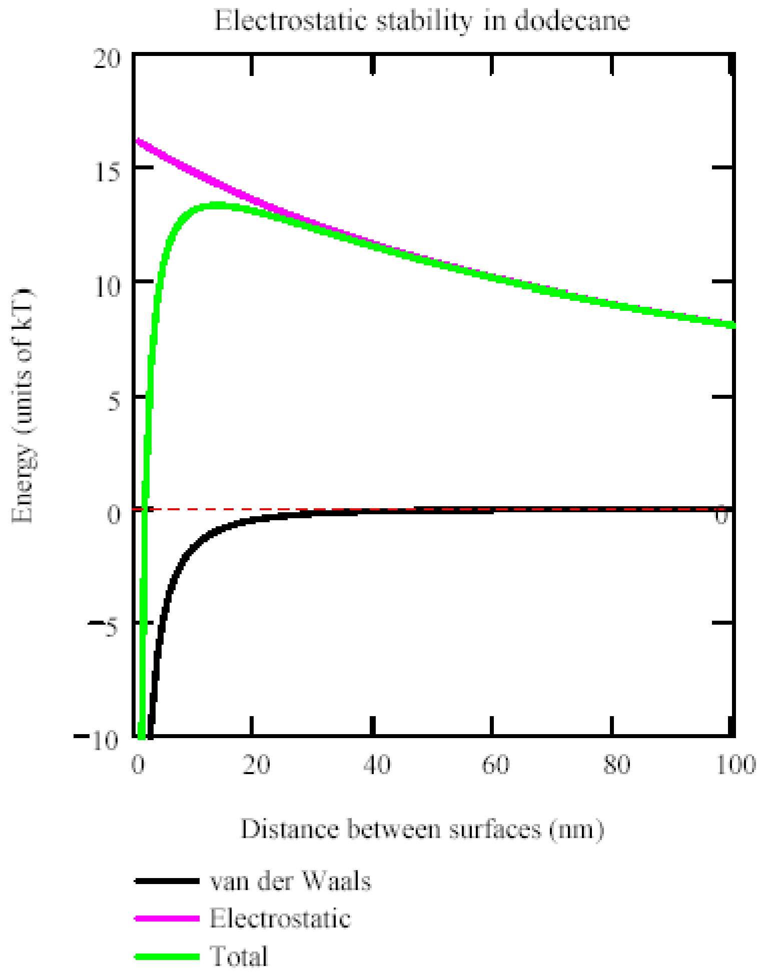
$$\Delta G^{total} = \frac{\pi D \varepsilon_0 d^2 \zeta^2}{d+H} - \frac{Ad}{24H}$$

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

$d = 100nm$

$A_{121} = 4.05x10^{-20} J$ (Titania in oil)

λ=50 pS/m

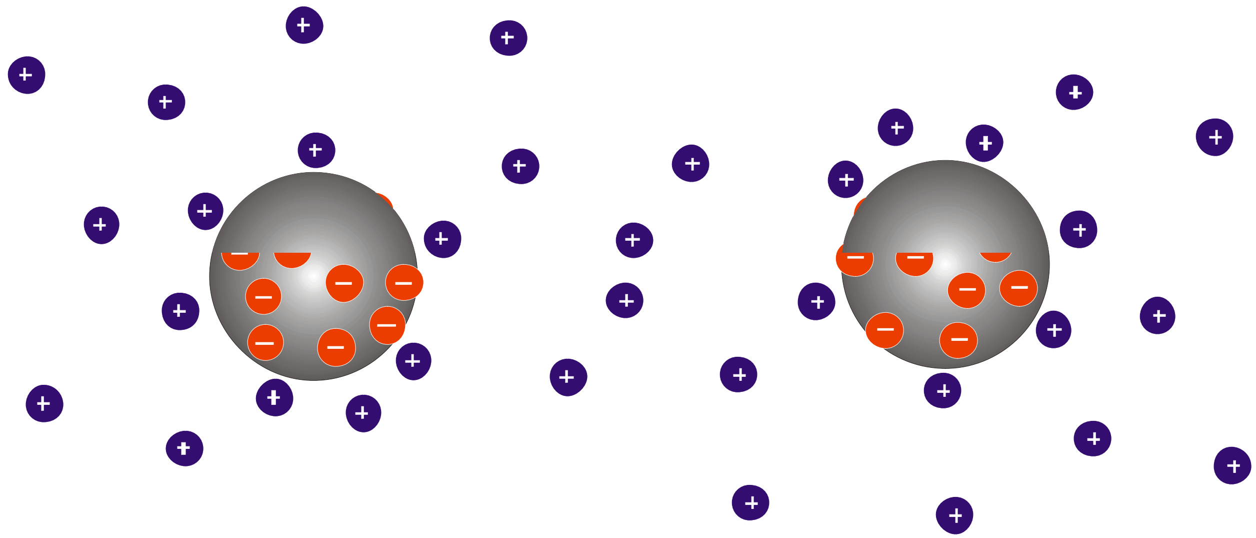


Zeta potential to stabilize dispersions in nonpolar liquids

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 (in water)



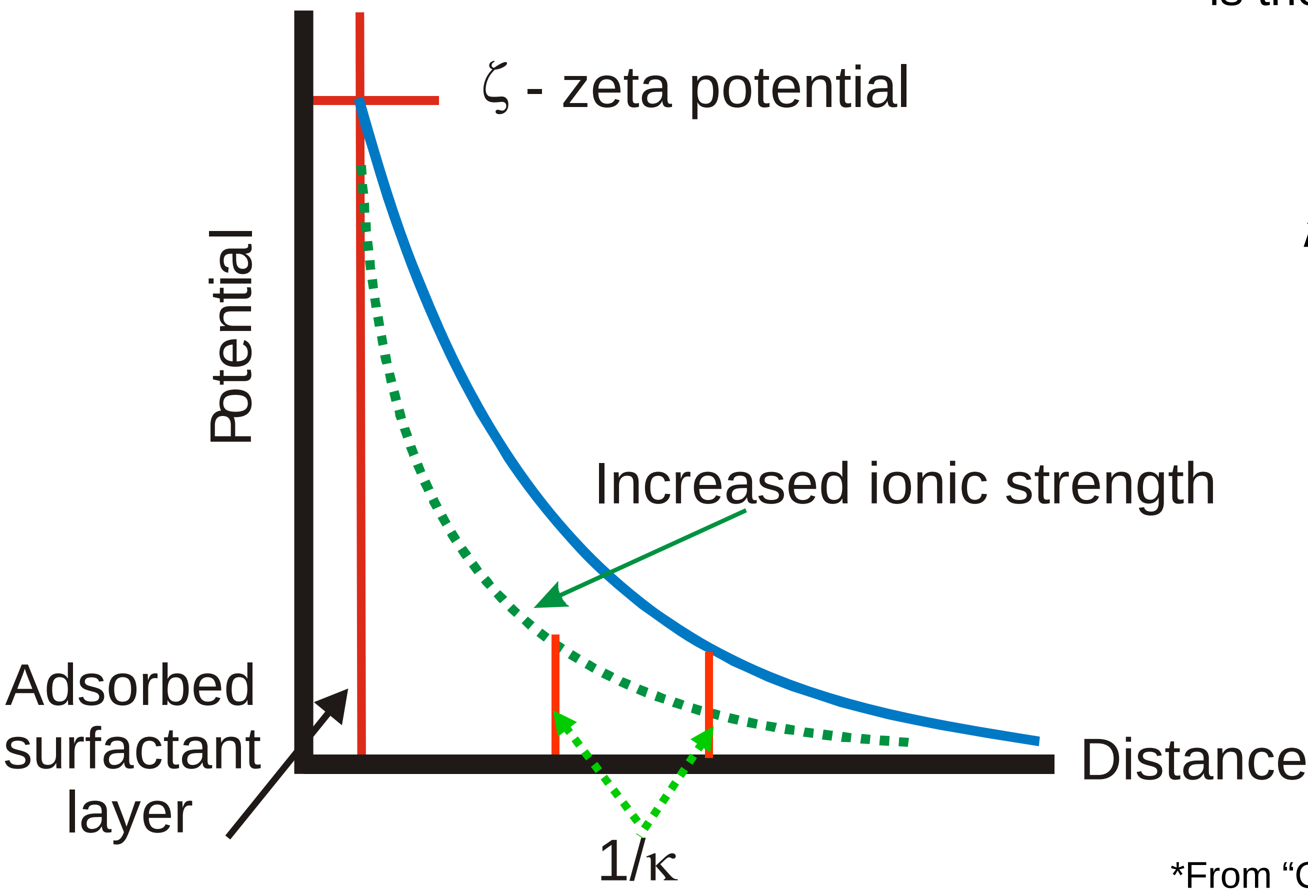
The loosely held countercharges form “electric double layers.”

The electrostatic repulsion results from the interpenetration of the double layer around each charged particle.

Stern's model for a charged surface*

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

(The surface potential is the zeta potential.)

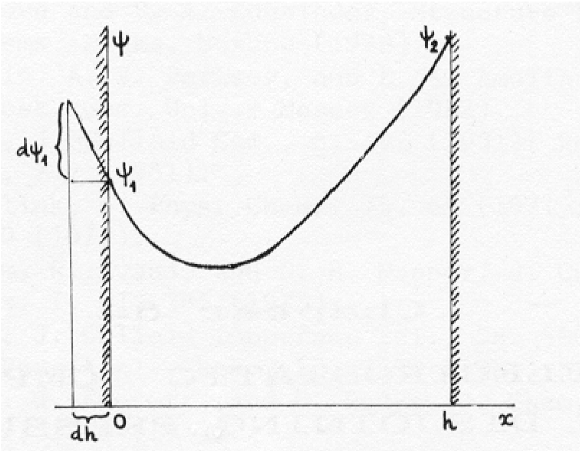


$$\kappa = \sqrt{\frac{e^2 \sum_i c_i z_i^2}{D\varepsilon_0 kT}}$$

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

*From "Charged surfaces" lecture.

Electrostatic component of disjoining pressure* (1)



Internal field gradients between two flat plates. External are assumed to have same potential. Derjaguin, **1987**, Fig. 6.1.

$$\Pi(h) = \frac{\varepsilon}{2}\left(E_h^2 - E_o^2\right)$$

But the field gradients are not known!

(1) The disjoining pressure is the excess Maxwell stresses between the inside (*E_h*) field gradients and the outside field gradients (*E_0*).

(2) A thermodynamic argument gives:

$$\left.\frac{\partial \Pi}{\partial \psi_1}\right|_{h,\psi_2} = \left.\frac{\partial \sigma_1}{\partial h}\right|_{\psi_1,\psi_2}$$

(3) And the *P-B* equation must apply:

$$\frac{d^2\psi}{dh^2} = -\frac{1}{\varepsilon}\sum_i z_i e n_{i0} \exp\left(-\frac{z_i e\psi}{kT}\right)$$

*Following Derjaguin, **1989**, pp 98 – 107.

*See lecture on "Surface forces" for a discussion on disjoining pressure; a slide is attached at the end of this presentation.

*In the wiki, eventually.

Electrostatic component of disjoining pressure (2)

Solving the differential equations (2) and (3) from the previous slides using the boundary values, some partial differential identities, with the restriction of just two types of ions, gives:*

$$\Pi(h) = kT\left[n_1\left(\exp\left(\frac{z_1 e\psi(h)}{kT}\right)-1\right)+n_2\left(\exp\left(-\frac{z_2 e\psi(h)}{kT}\right)-1\right)\right]-\frac{\varepsilon}{2}\left(\frac{d\psi(h)}{dx}\right)^2$$

This gets tricky! First try: same potential on each plate; binary electrolytes.

$$\Pi(h) = 2kTn\left(\cosh\left[\phi_m(h)\right]-1\right) \quad \text{where } \phi_m = \frac{ze}{kT}\psi_m \quad \text{(at the midplane)}$$

For those who know, this can be transformed to an elliptic integral of the first kind.*

$$\Pi = 4kTn\left(\frac{1}{k^2}-1\right) \qquad \frac{\kappa h}{2} = k\int_0^{\omega_1}\frac{d\omega}{\sqrt{1-k^2\sin^2\omega}}$$

$$k = \frac{1}{\cosh\left(\frac{\phi_m}{2}\right)};\ \cos\omega = \frac{\sinh\left(\frac{\phi_m}{2}\right)}{\sinh\left(\frac{\phi}{2}\right)};\ \cos\omega_1 = \sinh\left(\frac{\phi_m}{2}\right)\Big/\sinh\left(\frac{\phi_0}{2}\right)$$

Solution: For a Φ_0 and *h*, The integral equation can be solved for *k*. From *k*, Π can be calculated. Repeat for all necessary values of *h*.

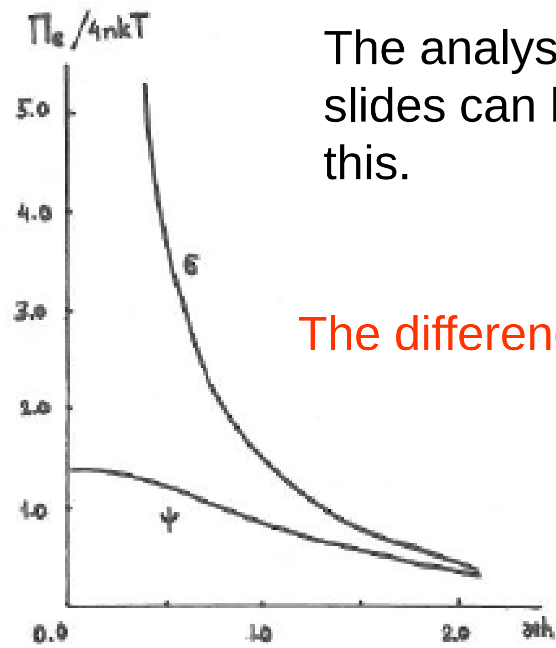
Electrostatic component of disjoining pressure* (3)

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!

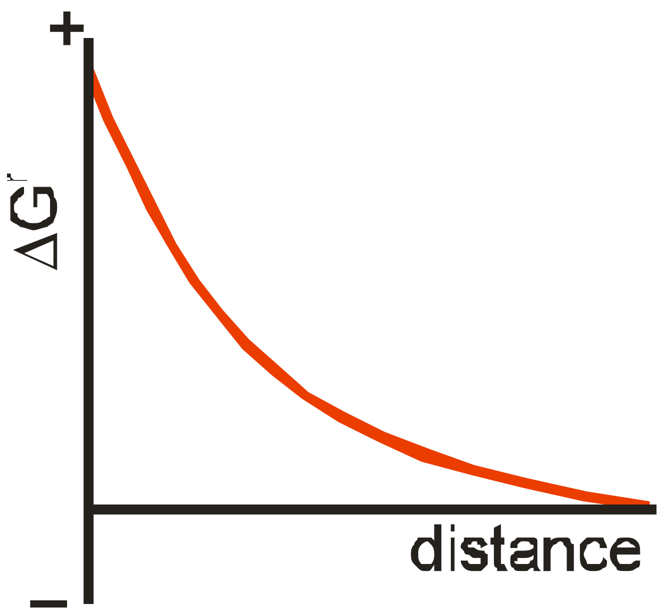
*Following Derjaguin, **1987**, pp. 181 – 183.

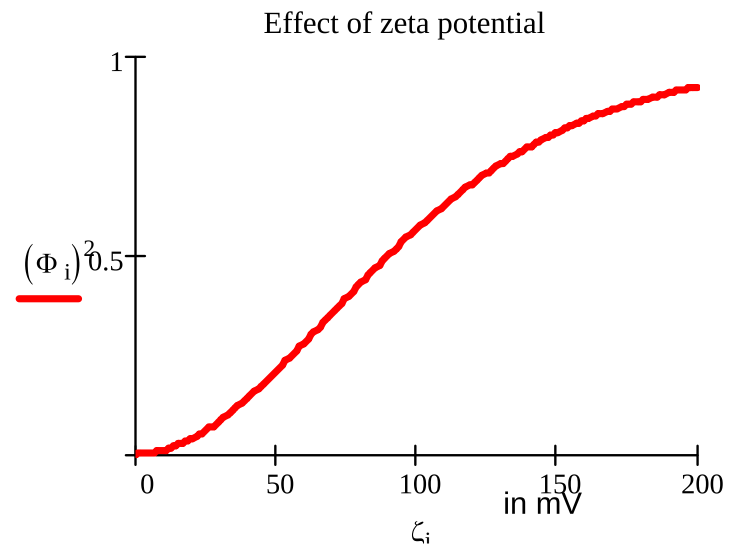
The repulsion between spheres – linear model

$$\Delta G^r = \frac{32 n_0 k T \pi d \Phi^2}{\kappa^2} \exp(-\kappa H)$$

(After a little math found in any textbook)

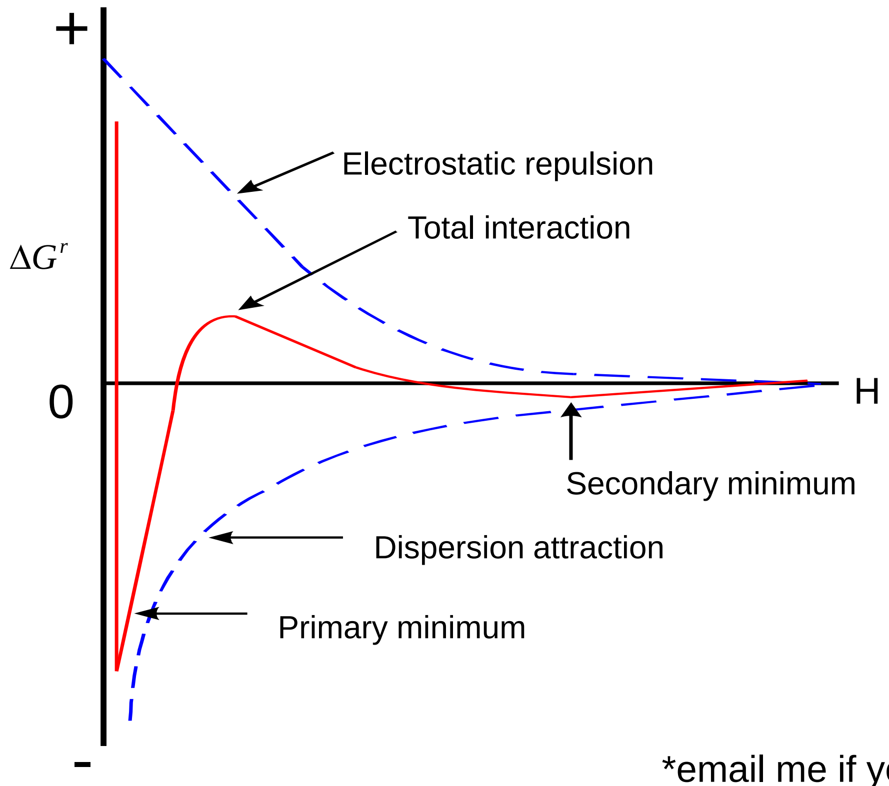
$$\Phi = \tanh \frac{ze\varsigma}{4kT}$$





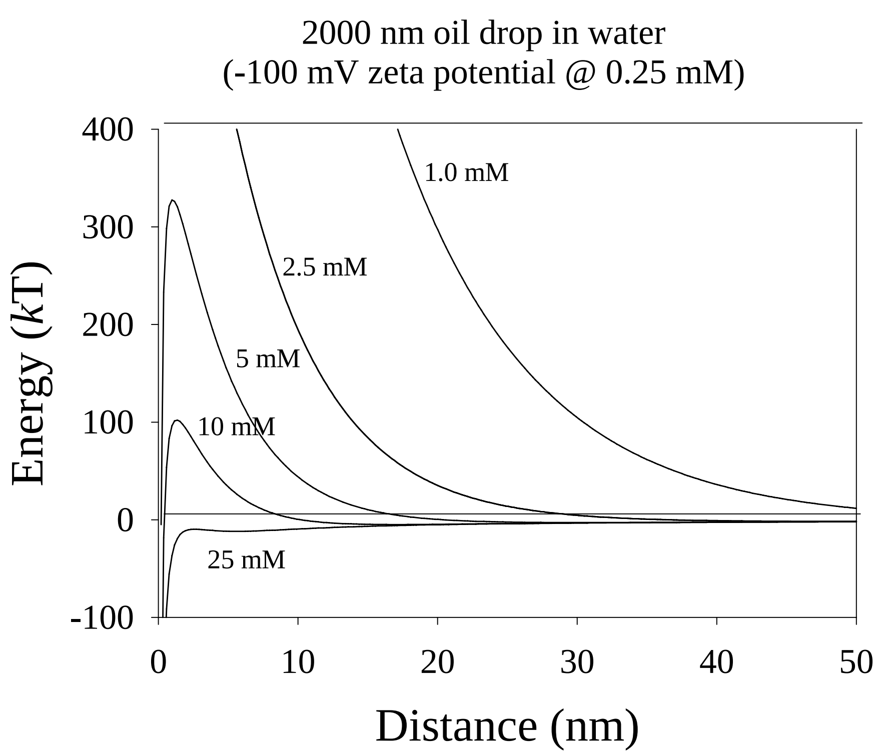
Electrostatic stability of dispersions*

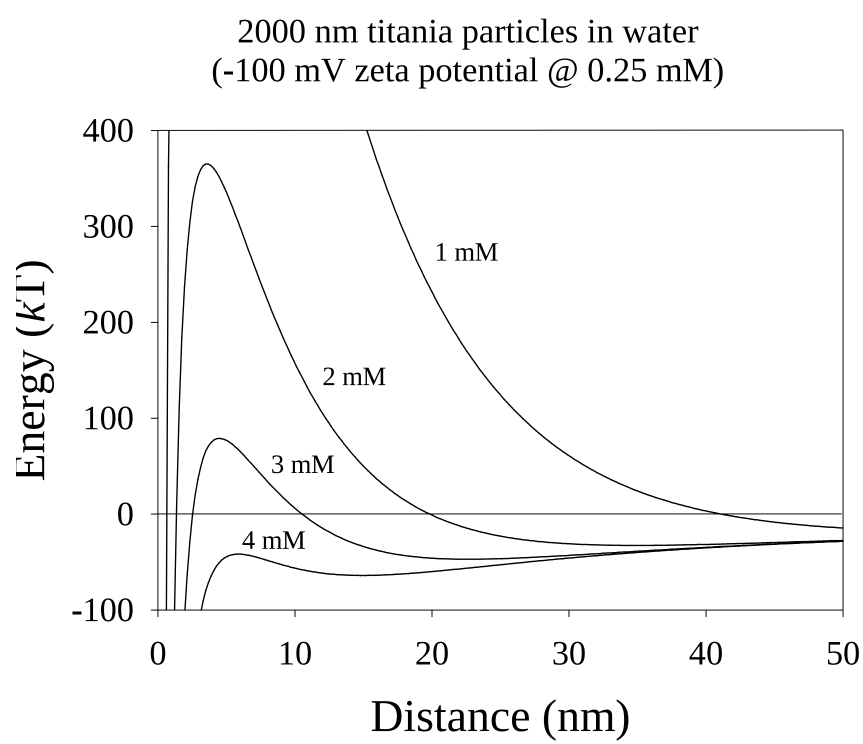
$$\Delta G^T = \frac{32 n_0 kT\pi d\Phi^2}{\kappa^2}\exp(-\kappa H) - \frac{A_{121} d}{24H}$$



*email me if you have trouble with units.

Effect of electrolyte

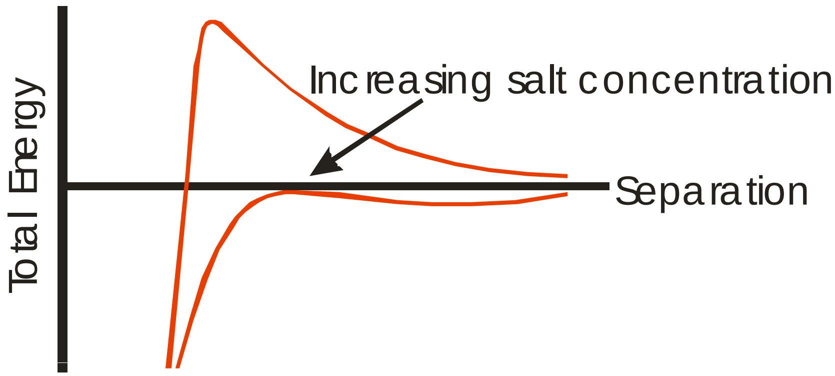




(Corrected from textbook.)

Critical coagulation concentration

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



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

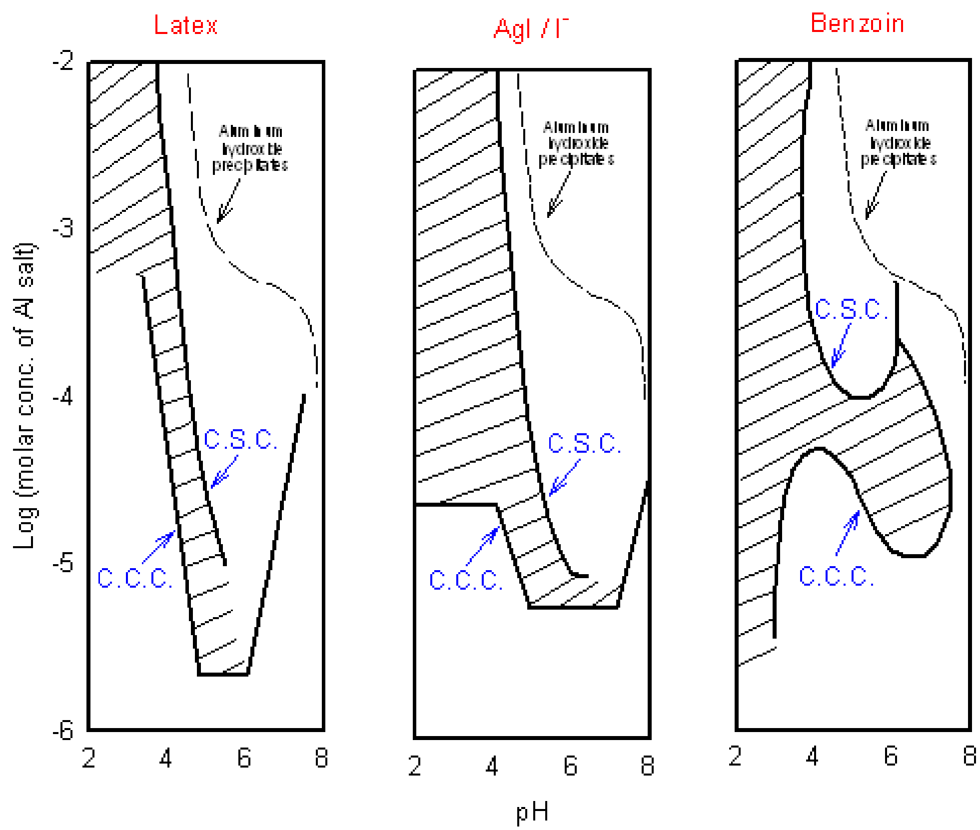
$$n_0(\text{molecules/cm}^3) = \frac{\left(4\pi\varepsilon_0 DkT\right)^3 2^{11} 3^2 \Phi^4}{\pi \exp\left(4\right) e^6 A_{121}^2 z^6} \propto \frac{1}{z^6}$$

The Schulze – Hardy Rule: the stability depends on

the sixth power of the charge on the ions!

Stability as a phase diagram

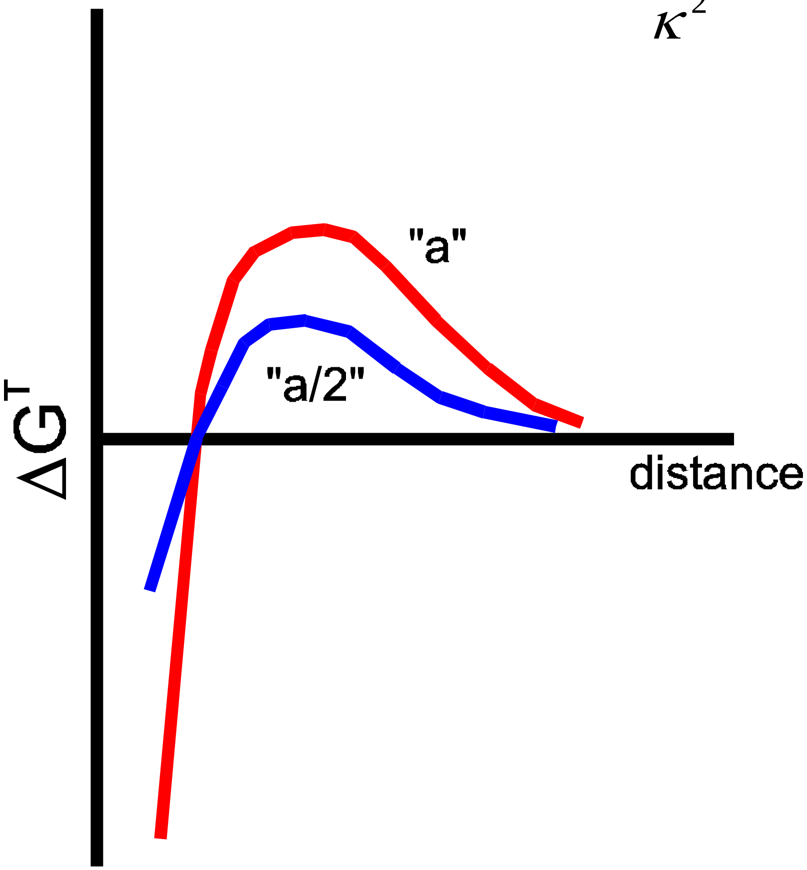
Phase diagrams of three hydrophobic sols, showing stability domains as a function of $Al(NO_3)_3$ or $AlCl_3$ concentration and pH; styrene-butadiene rubber (SBR) latex (left); silver iodide sol (middle); and benzoin sols prepared from powdered Sumatra gum (right).



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

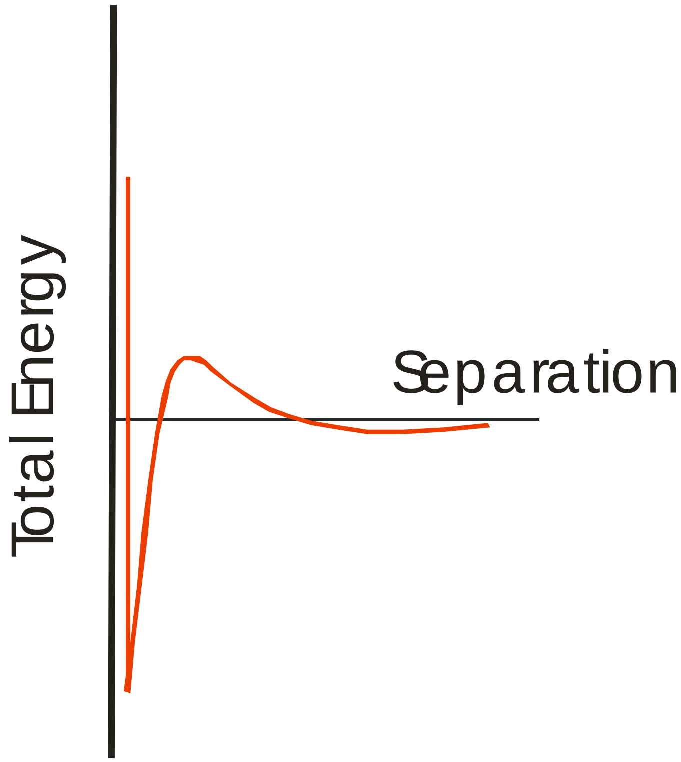
Particle size effect

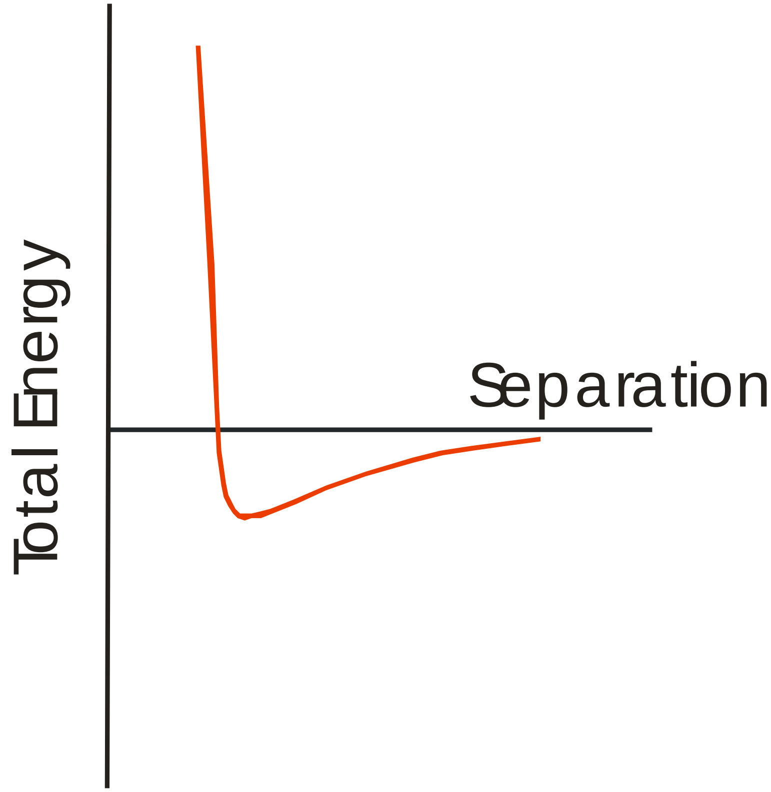
$$\Delta G^T = \frac{32 n_0 k T \pi d \Phi^2}{\kappa^2} \exp(-\kappa H) - \frac{A_{121} d}{24 H}$$



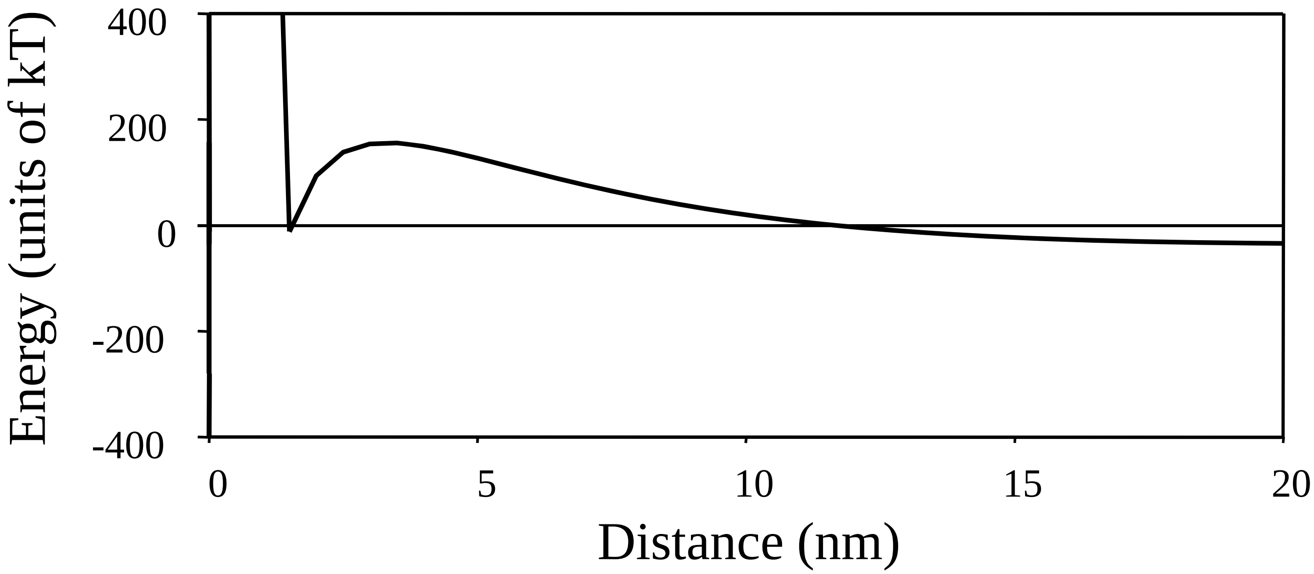
The larger the particles, the more stable the dispersion!

Electrostatic versus steric stabilization





Electrosteric stabilization



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