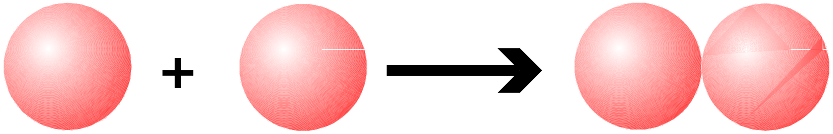
Suspension and Emulsion Stability

Lecture 3

Strength of interparticle forces – Rates of flocculation



The time for half the particles to flocculate is:

$$t_{1/2} = \frac{\eta \pi d^3 W}{8 \Phi k T}$$

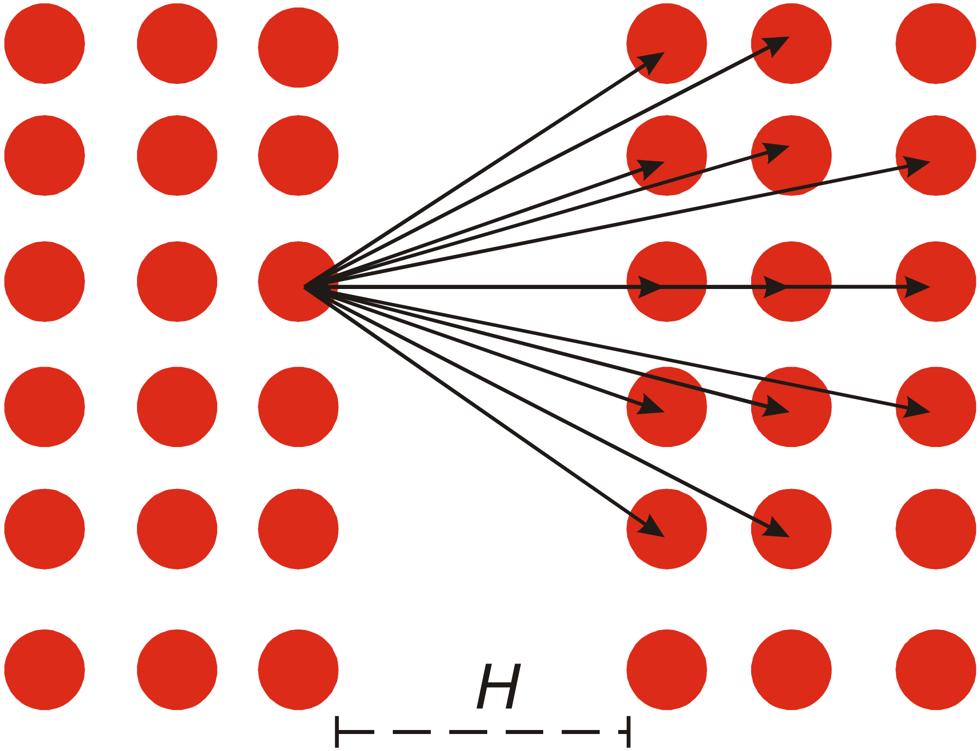
Since flocculation is a change in average particle size, the half life can be measured. And *W*, the stability ratio, determined.

The stability ratio depends on the interparticle forces:

$$W = d \int_0^\infty \exp\left(\frac{U_{11}}{kT}\right) \frac{dH}{H^2}$$

Measurements on unstable dispersions showed that particles attract each other over distances comparable to particle sizes.

Hamaker model - Calculate the attraction between particles from molecular attractions



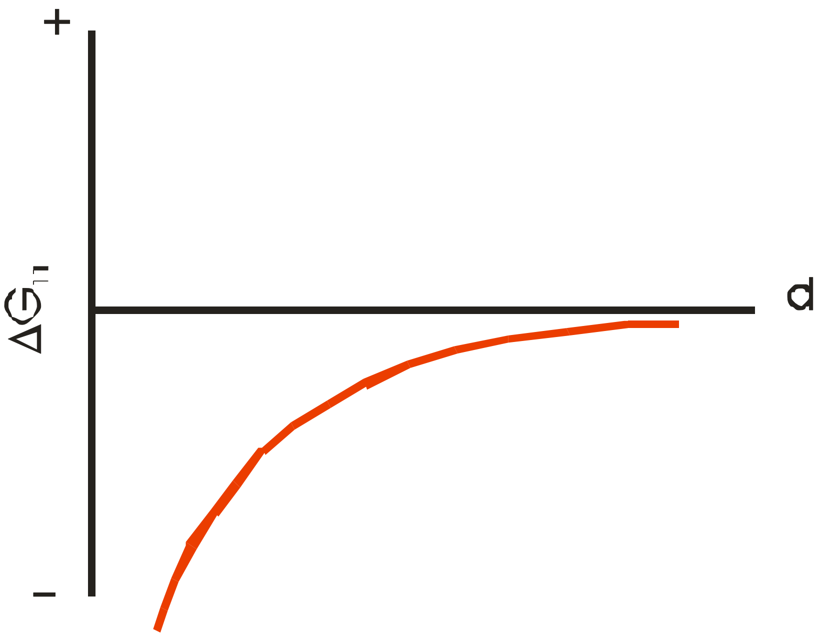
Molecules in particle 1

Molecules in particle 2

The intermolecular attraction is the London (dispersion) energy:

$$U_{11} = -\frac{3}{2}\Lambda_{11} r^{-6}$$

Hamaker equations for dispersion force attraction



For two spheres (per pair):

$$\Delta G_{11} = \frac{-A_{11}d}{24H}$$

For two flat plates (per unit area):

$$\Delta G_{11} = \frac{-A_{11}}{12\pi H^2}$$

The A_{11} are the Hamaker constants.

Hamaker constants for some materials

Substance	**A_{11} $(10^{-20}$ J)**
Graphite	47.0
Gold	45.3, 45.5, 37.6
Silicon carbide	44
Rutile (TiO_2)	43
Silver	39.8, 40.0
Germanium	29.9, 30.0
Chromiun	29.2
Copper	28.4
Diamond	28.4
Zirconia (*n*-ZrO_2)	27
Silicon	25.5, 25.6
Metals (Au, Ag, Cu)	25 – 40
Iron oxide (Fe_3O_4)	21
Selenium	16.2, 16.2
Aluminum	15.4, 14, 15.5
Cadmium sulfide	15.3
Tellurium	14.0
Polyvinyl chloride	10.82
Magnesia	10.5, 10.6
Polyisobutylene	10.10
Mica	10, 10.8
Polyethylene	10.0
Polystyrene	9.80, 6.57, 6.5, 6.4, 7.81
Polyvinyl acetate	8.91
Polyvinyl alcohol	8.84
Natural rubber	8.58
Polybutadiene	8.20
Polybutene-1	8.03
Quartz	7.93
Polyethylene oxide	7.51
Polyvinyl chloride	7.5
Hydrocarbon (crystal)	7.1
CaF_2	7
Potassium bromide	6.7
Hexadecane	6.31
Fused quartz	6.3
Polymethylmethacrylate	6.3
Polydimethylsiloxane	6.27
Potassium chloride	6.2
Chlorobenzene	5.89
Dodecane	5.84, 5.0
Decane	5.45
Toluene	5.40
1,4-Dioxane	5.26
n-Hexadecane	5.1
Octane	5.02, 4.5
Benzene	5.0
n-Tetradecane	5.0
Cyclohexane	4.82, 5.2
Carbon tetrachloride	4.78, 5.5
Methyl ethyl ketone	4.53
Water	4.35, 3.7, 4.38
Hexane	4.32
Diethyl ether	4.30
Acetone	4.20, 4.1
Ethanol	4.2
Ethyl acetate	4.17
Polypropylene oxide	3.95
Pentane	3.94, 3.8
PTFE	3.8
Liquid He	0.057

The affect of liquid between the particles

The effect of an intervening medium calculated by the principle of Archimedean buoyancy:

$$A_{121} = A_{11} + A_{22} - 2A_{12}$$

Introducing the approximation:

$$A_{12} = \left[A_{11}A_{22}\right]^{1/2}$$

Which leads to:

$$\boxed{A_{121} = \left(A_{11}^{1/2} - A_{22}^{1/2}\right)^2}$$

and

$$\boxed{A_{123} = \left(A_{11}^{1/2} - A_{22}^{1/2}\right)\left(A_{33}^{1/2} - A_{22}^{1/2}\right)}$$

Lifshitz Theory

Problem with Hamaker theory:

all molecules act independently

Lifshitz theory:

the attractions between particles are
a result of the electronic fluctuations
in the particle.

What describes the electronic fluctuations in the particle?

the absorption spectra: uv-vis-ir

Result:

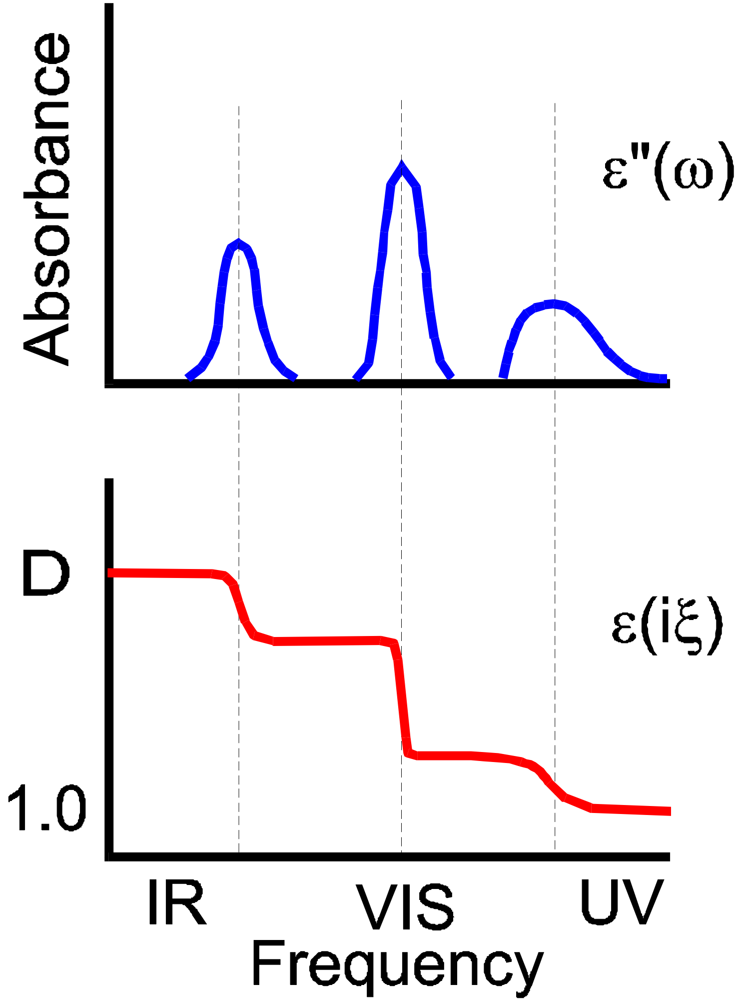
$$\Delta G_{123}^{nr} = -\frac{A_{123}^{nr}}{12\pi H^2}$$

Where the Lifshitz constant depends on the absorption spectra of the solid particles.

Lifshitz calculations

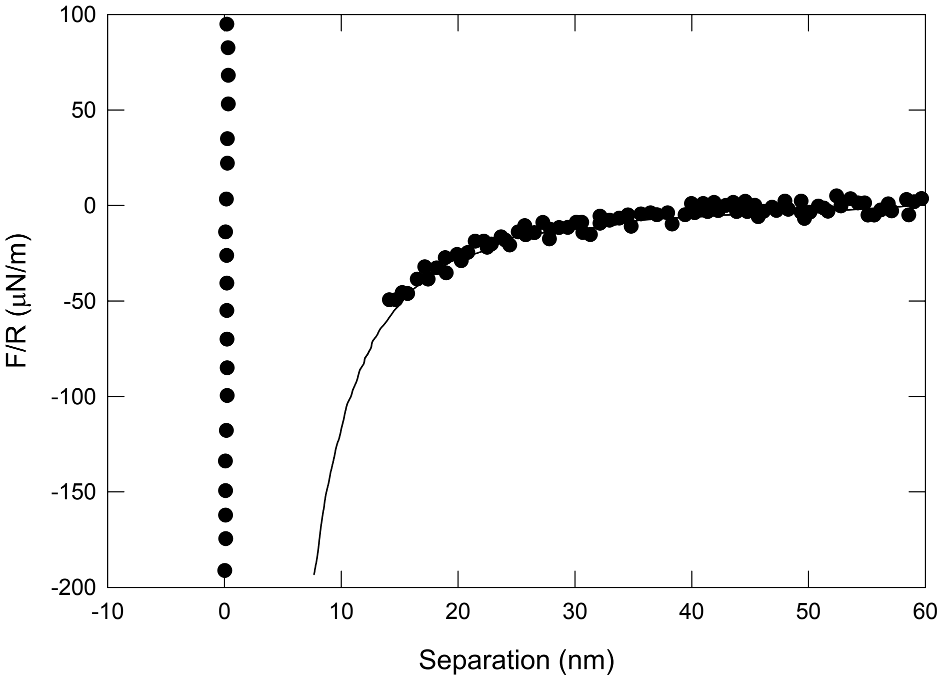
The absorption spectra is measured. Often a single peak in the UV and an average IR is sufficient. That is two amplitudes and two wavelengths.

The dielectric spectrum is calculated from the absorption spectrum. The only additional information needed is the static dielectric constant.



Lifshitz calculation vs measurement

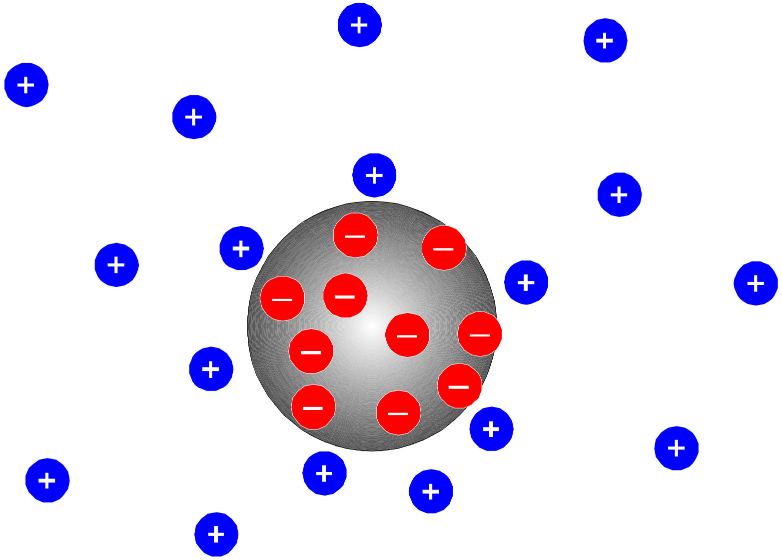
Force - separation for TiO_2 at the PZC



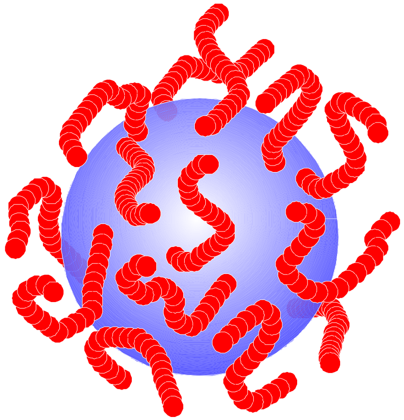
direction	$\varepsilon(0)$	ω_{IR}(rad/s)	C_{IR}	ω_{UV}(rad/s)	C_{UV}
perpendicular	86	1×10^{14}	80	7.49×10^{15}	4.77
parallel	170	1×10^{14}	163	7.24×10^{15}	6.01

Larson, I.; et al
JACS, **1993**, *115*,11885-11890.

Colloidal stability requires a repulsion force:



Electrostatically stabilized



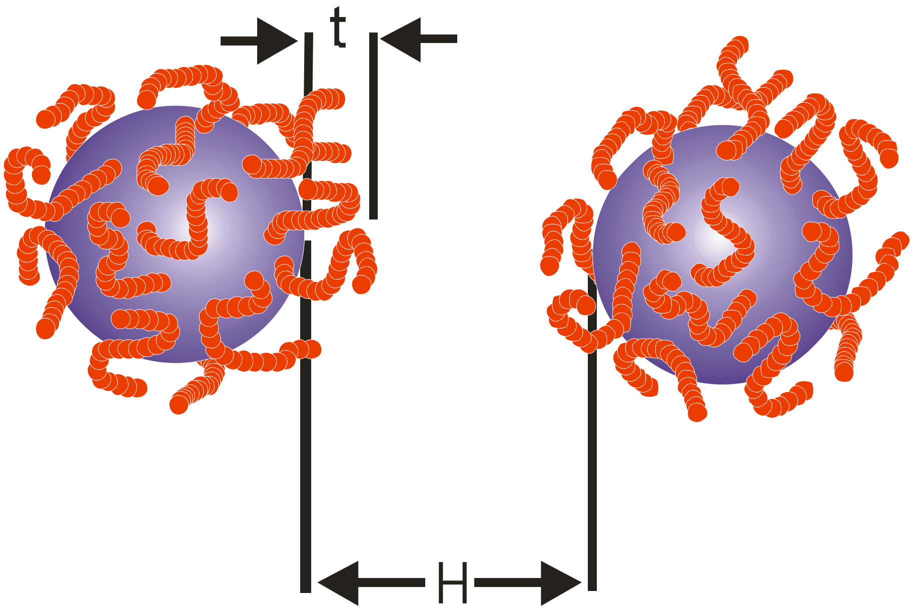
Sterically stabilized

All particles naturally attract each other.

Electrical charges or attached polymer layers screen the attraction.

Steric stabilization

Criterion for Steric Stabilization

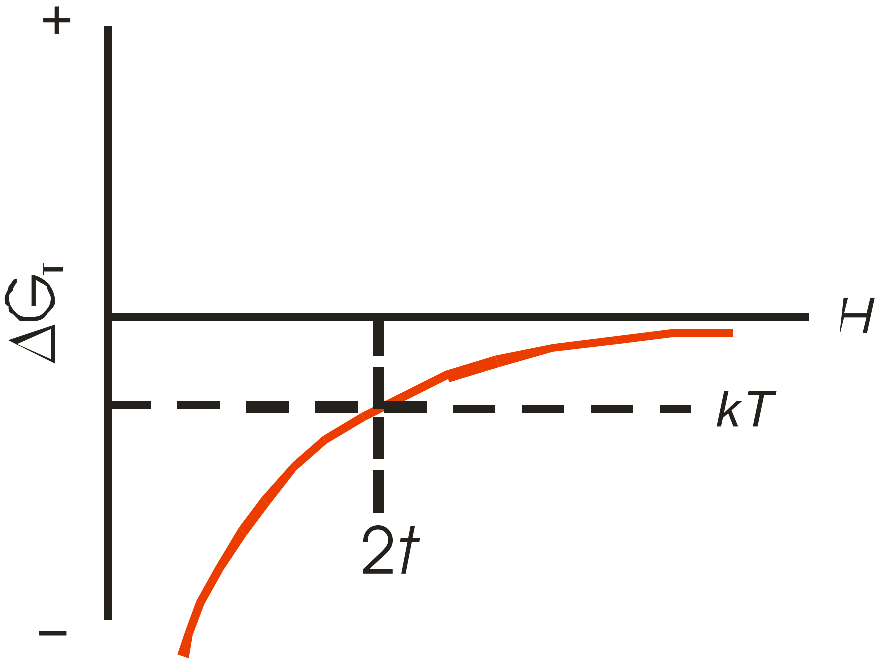


Work is required to push the particles closer together than their polymer layers keep them apart.

In thermodynamic terms, this is: $\Delta G \gg 0$ when $H < 2t$

Dispersion attraction between spheres

For two spheres: $\Delta G_{121} = \frac{-A_{121} d}{24H}$



Criterion for Steric Stabilization (1st order)

Dispersion stability is obtained when kinetic energy is always greater than the energy of attraction between particles during a collision. This criterion can only be obtained when the particles are held far enough apart that the energy of attraction is small. The energy balance is:

$$kT > \frac{A_{121} d}{48t}$$

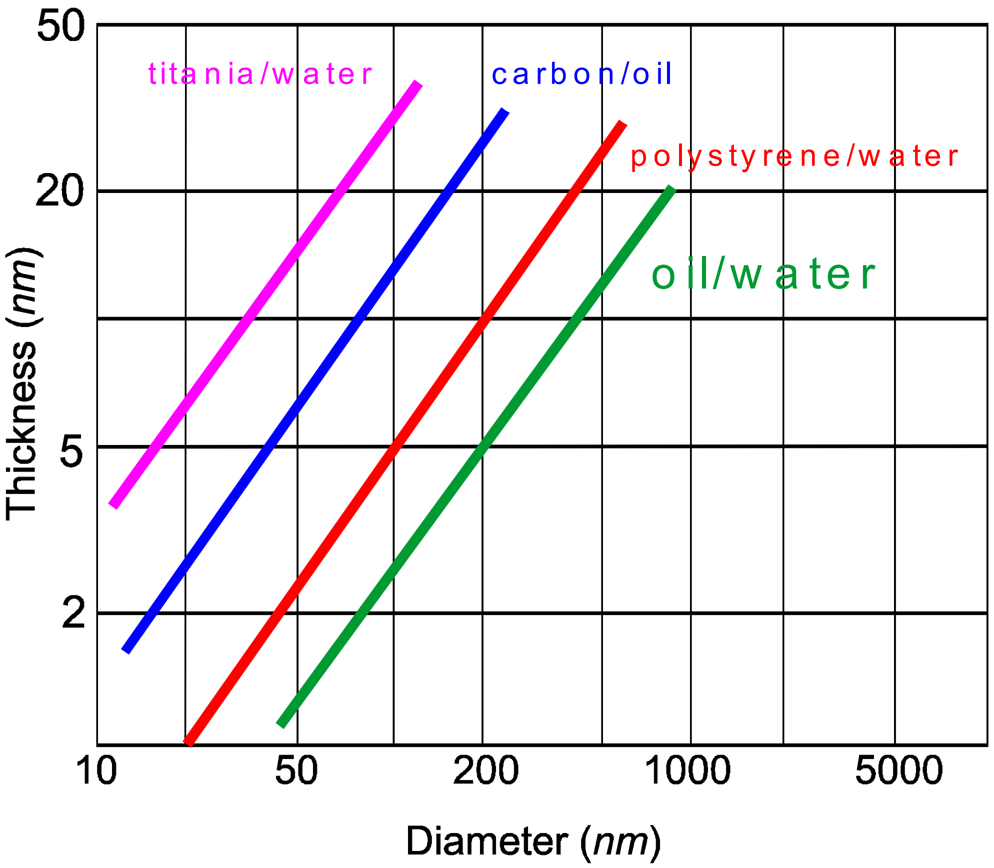
Therefore the polymer layer thickness around each particle, *t*, as a function of diameter must be greater than:

$$t > \left(\frac{A_{121}}{48kT} \right) d$$

For example:

	A_{121} (x 10^{20}) J	$A_{121}/48kT$
Oil-water	0.5	0.025
Polystyrene-water	1.05	0.05
Carbon-oil	2.8	0.14
TiO_2 – water	7.0	0.35

Polymer thickness sufficient for steric stabilization



A simple theory for the polymer “thickness”

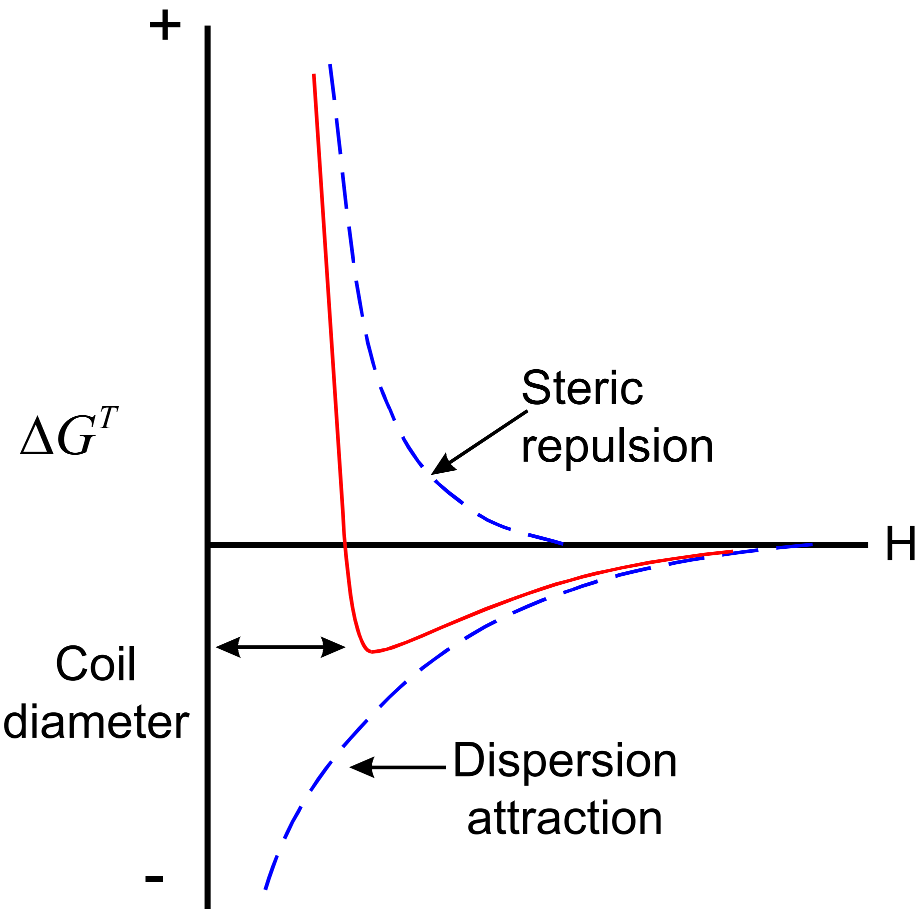
Average end-to-end distance for linear polymers:

$$\left\langle r^2 \right\rangle^{1/2} \sim 0.06\, MW^{1/2}$$

Molecular weight	"Length" (nm) $\left\langle r^2 \right\rangle^{1/2}$
1,000	2
10,000	6
100,000	20
1,000,000	60

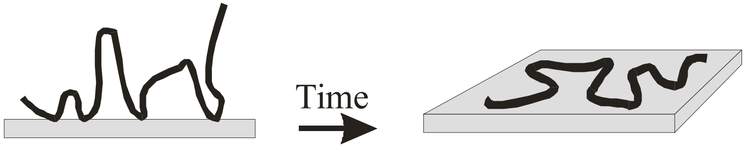
A reasonable assumption is that the surface coating has a thickness equal to the half the end-to-end distance.

Steric stabilization for spheres

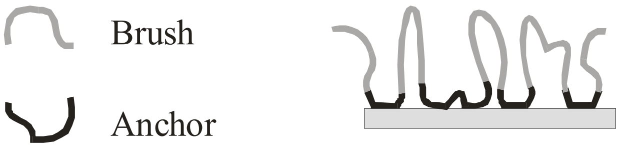


Configurations of adsorbed polymers

Homopolymers

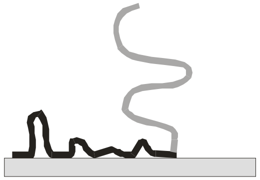


Random copolymers



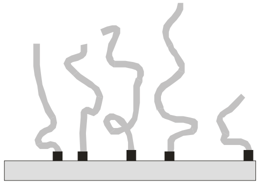
Block copolymers

Two or three segments
are common.

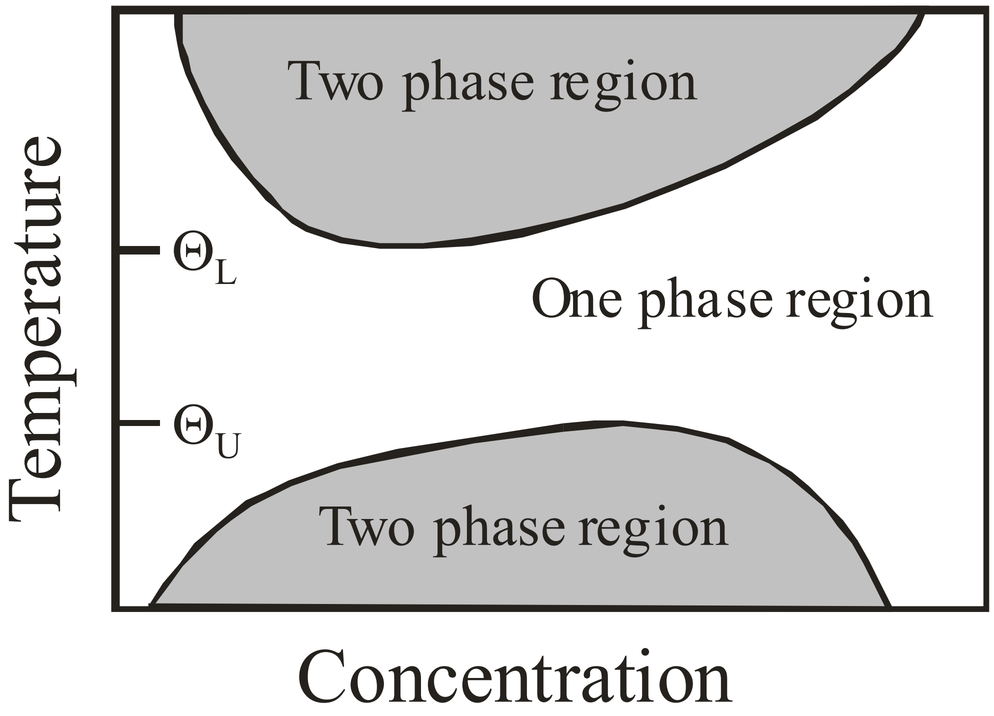


Grafted polymers

Polymers may be
attached to or grown
from the surface.

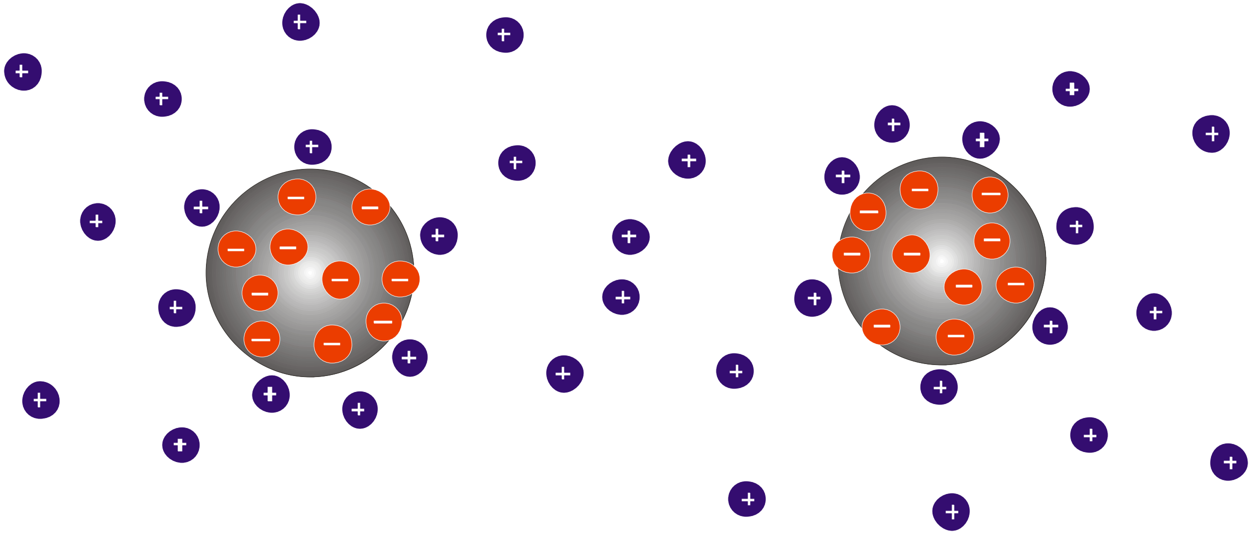


Polymer Solution Phase Diagram



Sterically stabilized dispersions are stable when the polymer is soluble – the one phase regions.

Electrostatic repulsion in aqueous dispersions

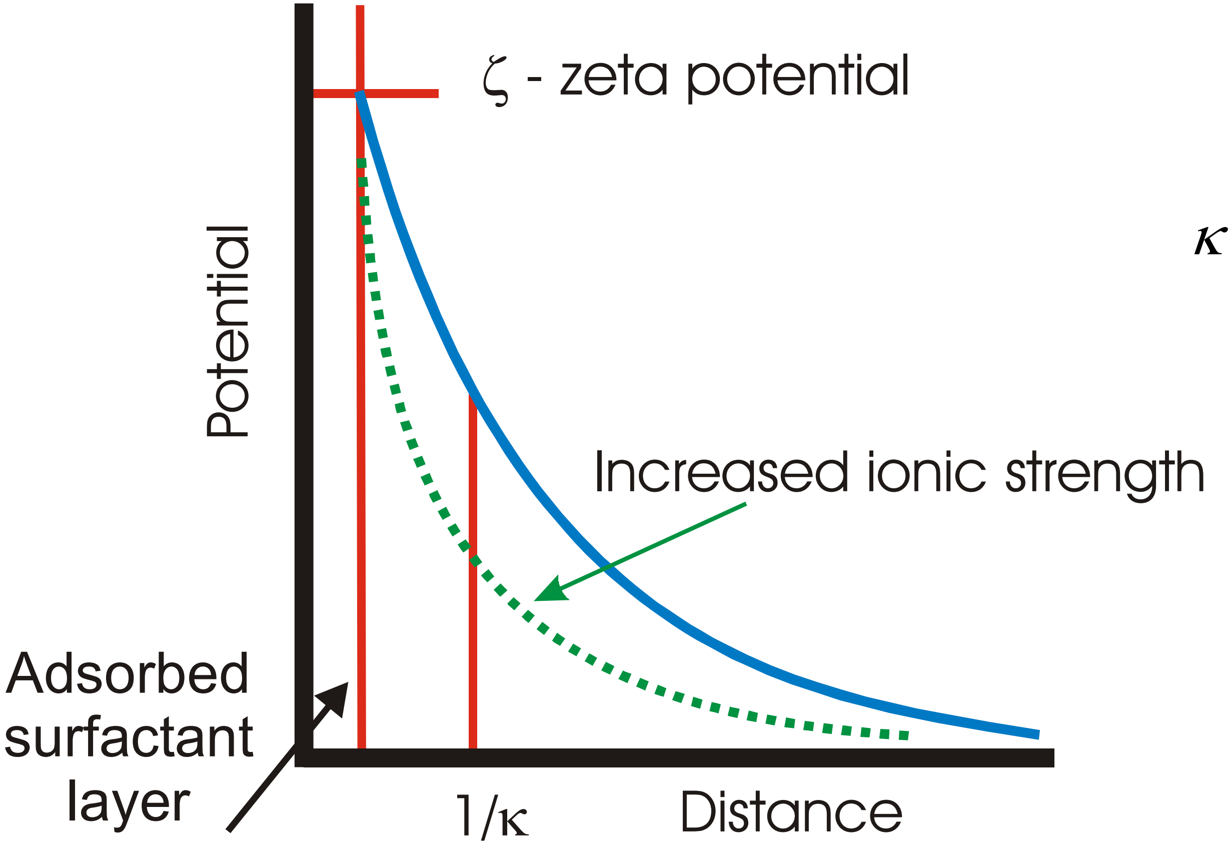


The loosely held countercharges form “electric double layers.”

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

Stern’s model for a charged particle

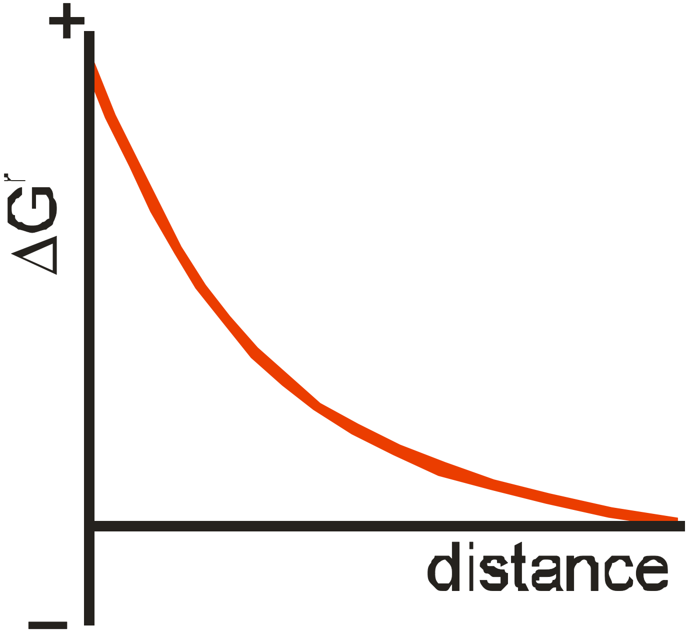
$$\text{Potential} = \zeta \exp(-\kappa H)$$

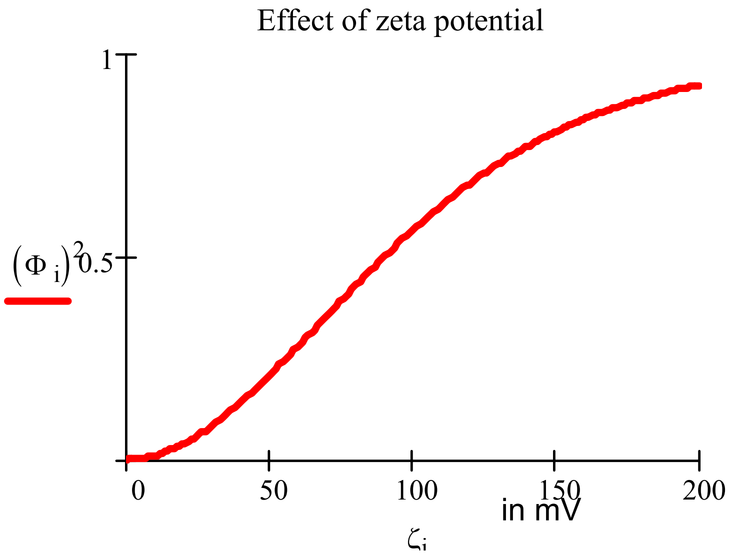


$$\kappa = \sqrt{\frac{e^2 \sum_i c_i z_i^2}{D\varepsilon_0 kT}}$$

The electrostatic repulsion between spheres

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

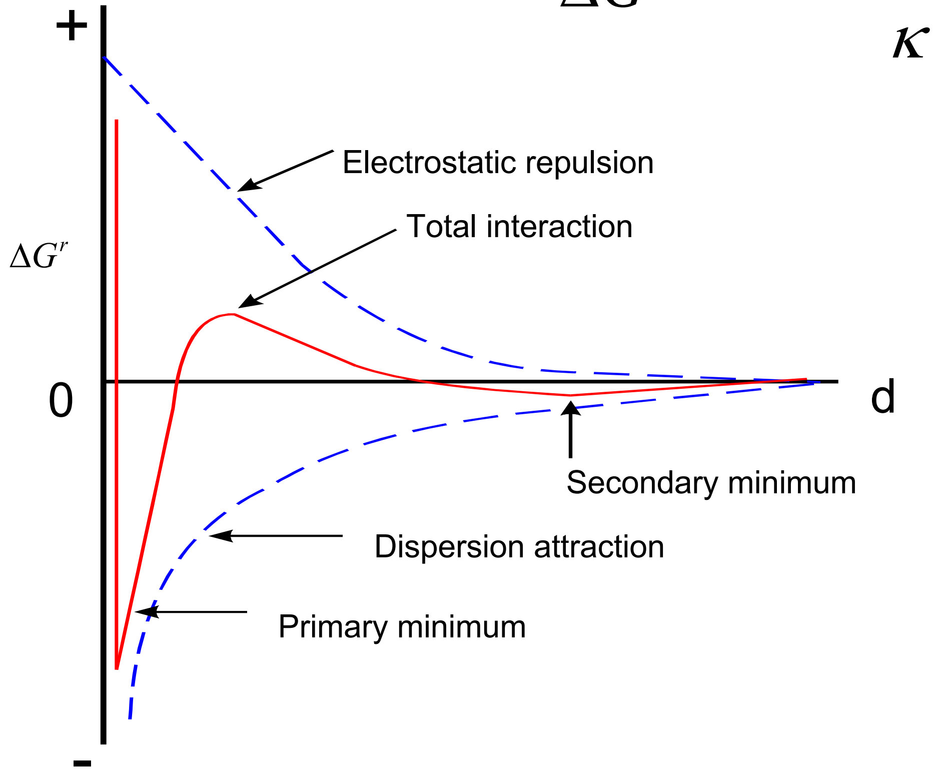




Electrostatic stability of dispersions*

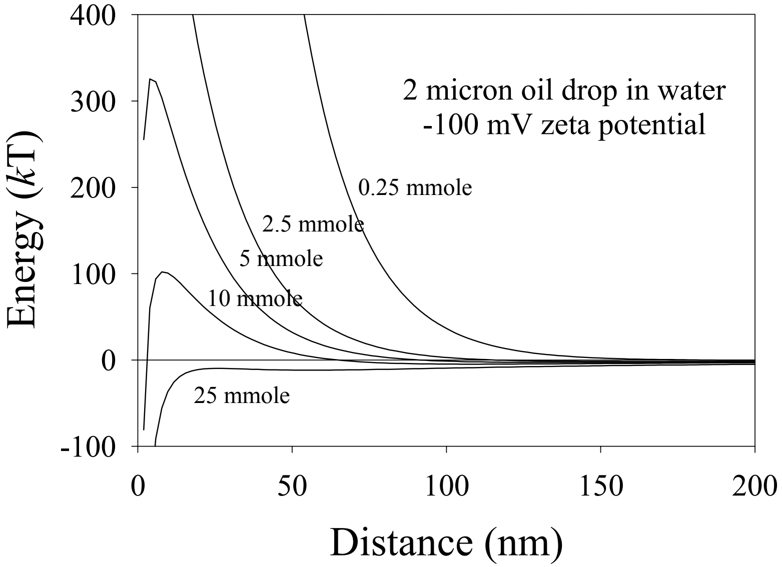
The total interaction between two spheres is the sum of the electrostatic repulsion and the dispersion attraction:

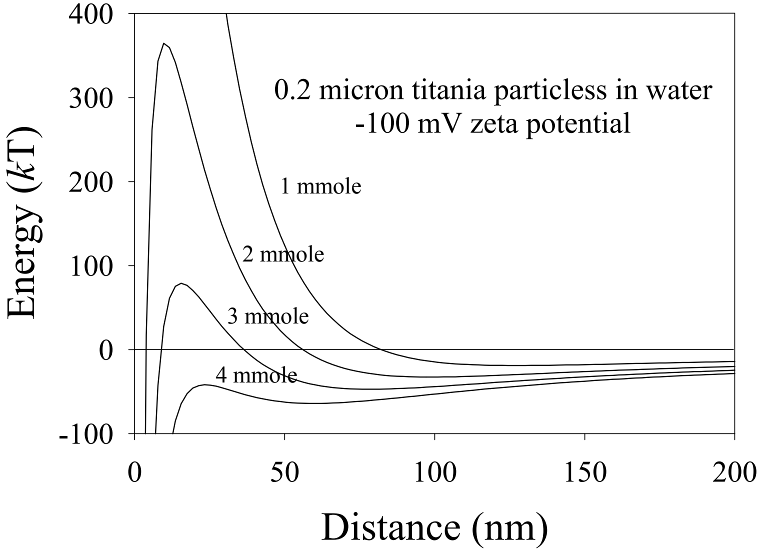
$$\Delta G^T = \frac{32 n_0 k T \pi d \Phi^2}{\kappa^2} \exp(-\kappa H) - \frac{A_{121} d}{24 H}$$



*DLVO theory

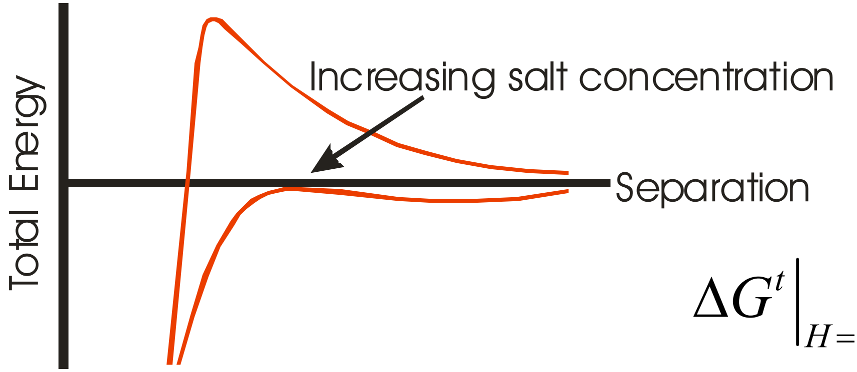
Stability of dispersions as a function of electrolyte concentration





Critical coagulation concentration

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



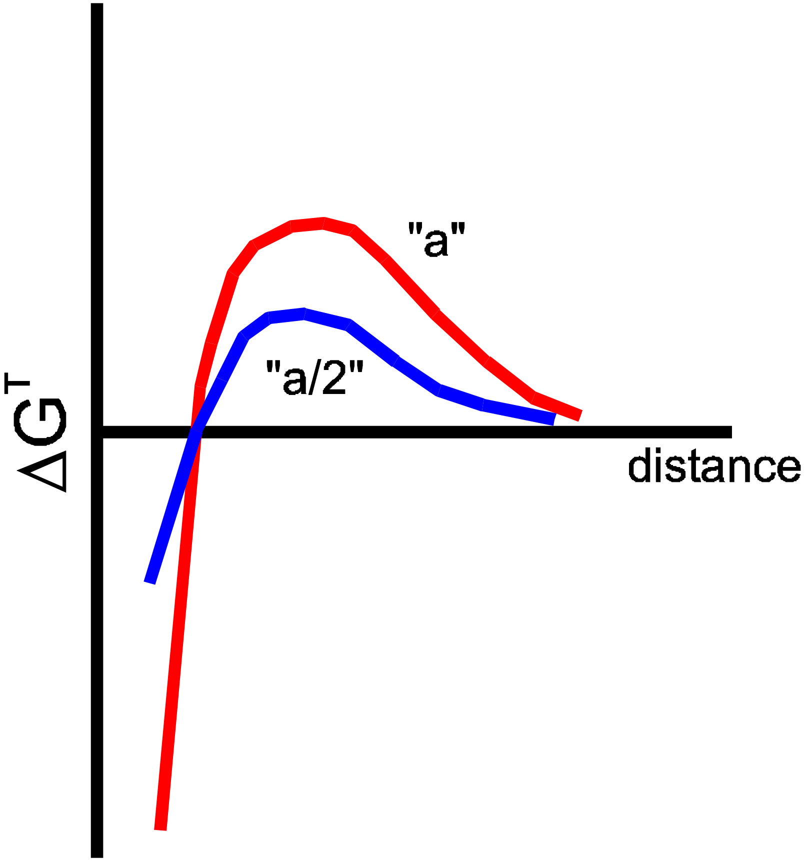
$$\Delta G^t\Big|_{H=H_0} = 0 \quad \text{and} \quad \frac{d\Delta G^t}{dH}\Big|_{H=H_0} = 0$$

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

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

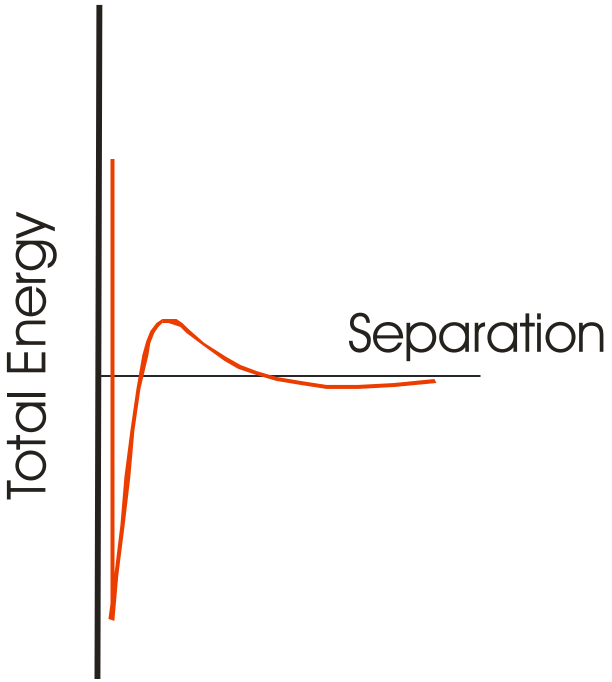
Particle size effect in electrostatic stabilization

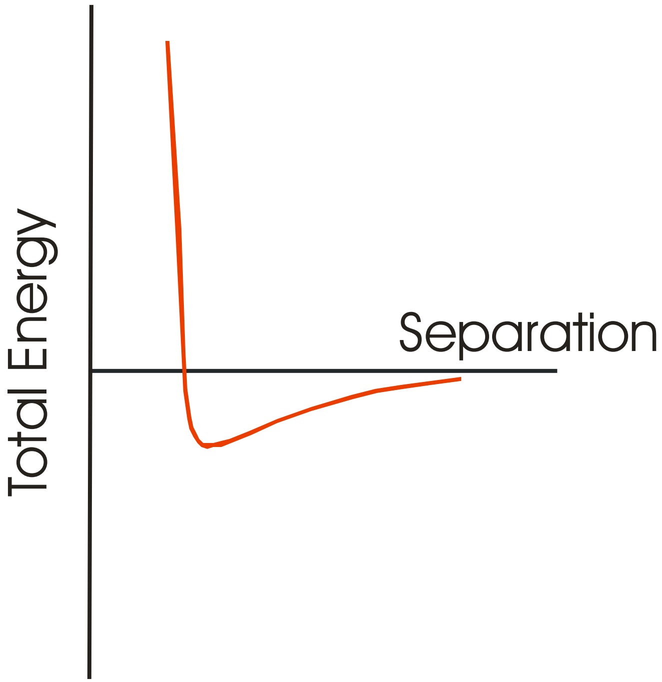
$$\Delta G^{T} = \frac{32 n_0 k T \pi d \Phi^2}{\kappa^2} \exp(-\kappa H) - \frac{A_{121} d}{24H}$$



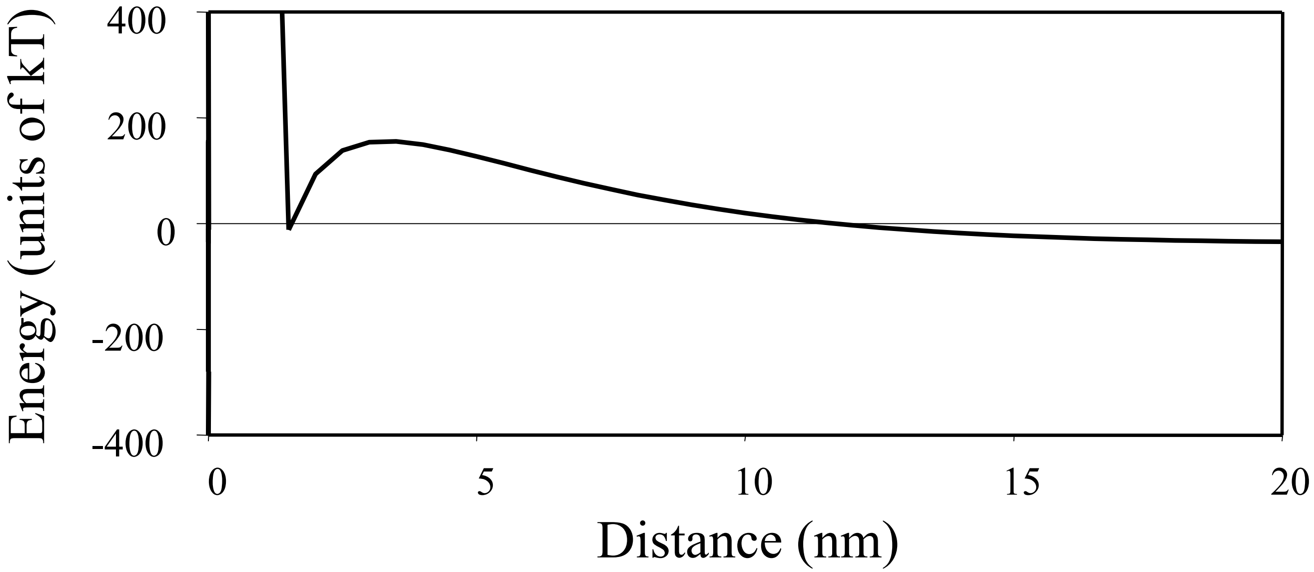
The larger the particles, the more stable the dispersion!

Electrostatic versus steric stabilization



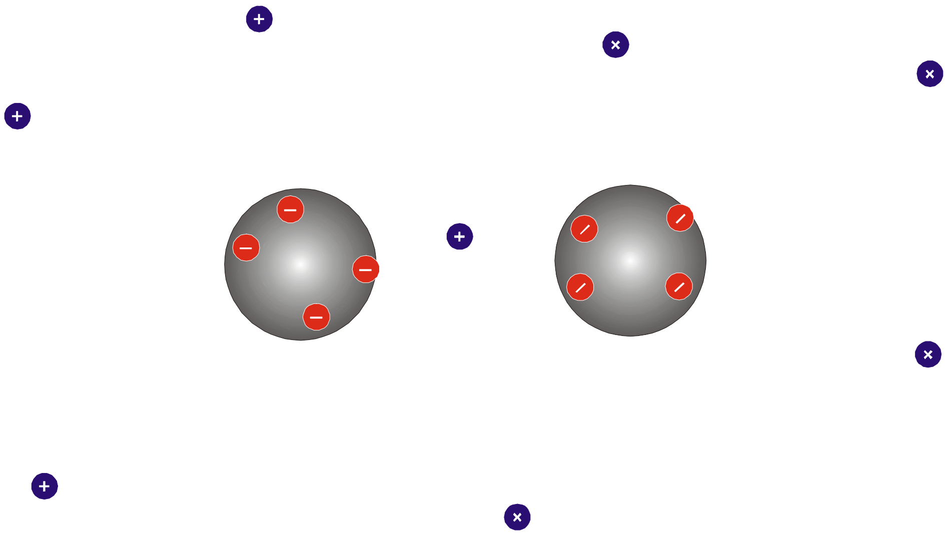


Electrosteric stabilization



200 nm particles, A_{121} = 7x10^{-20} J, -100 mV zeta potential, 4 mM ionic strength, 1 nm polymer layer.

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

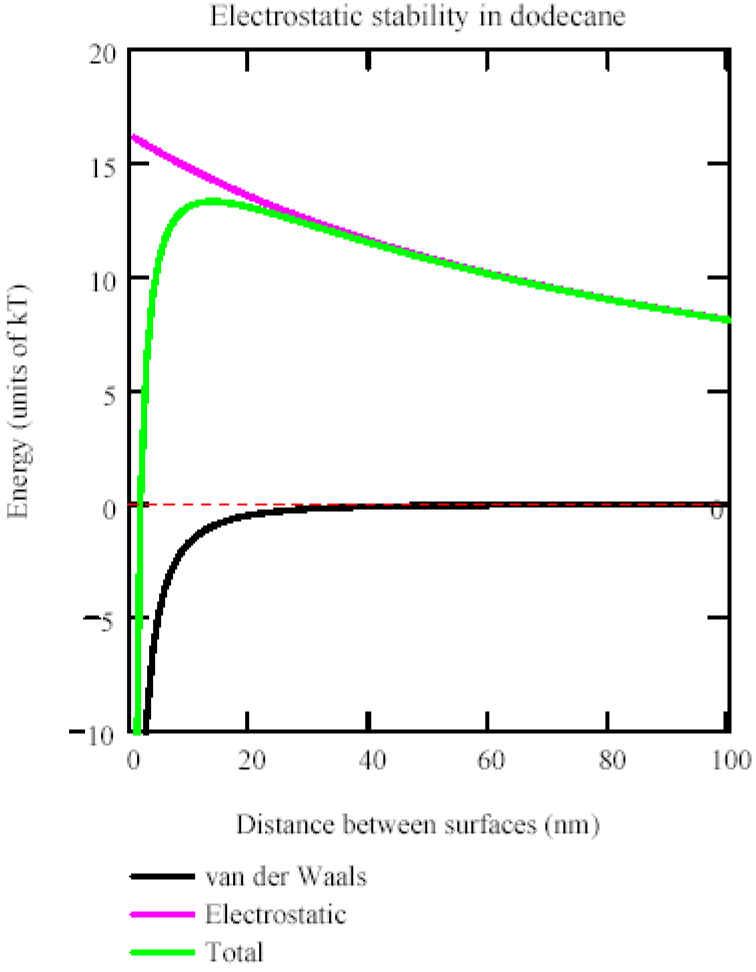
$$\Delta G^{total} = \frac{\pi D \varepsilon_0 d^2 \zeta^2}{d+H} - \frac{Ad}{24H}$$

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

$d = 100 nm$

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

λ=50 pS/m



Electrostatic stability in nonpolar liquids

$$\text{Stability ratio} = W = d\int_0^\infty \exp\left(\frac{\Delta G^{total}}{kT}\right)\frac{dH}{H^2}$$

The integral can be calculated approximately:

$$W \cong \left(\frac{Ak^2T^2}{384D^3\varepsilon_0^3 d^3\zeta^6}\right)^{1/4}\exp\left(\frac{\pi D\varepsilon_0 d\zeta^2}{kT}\right)$$

A reasonable criterion for stable dispersions is:

$$\zeta^2 \geq \frac{2x10^3}{Dd} \text{ with } \zeta \text{ in } mV \text{ and } d \text{ in } \mu m$$

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