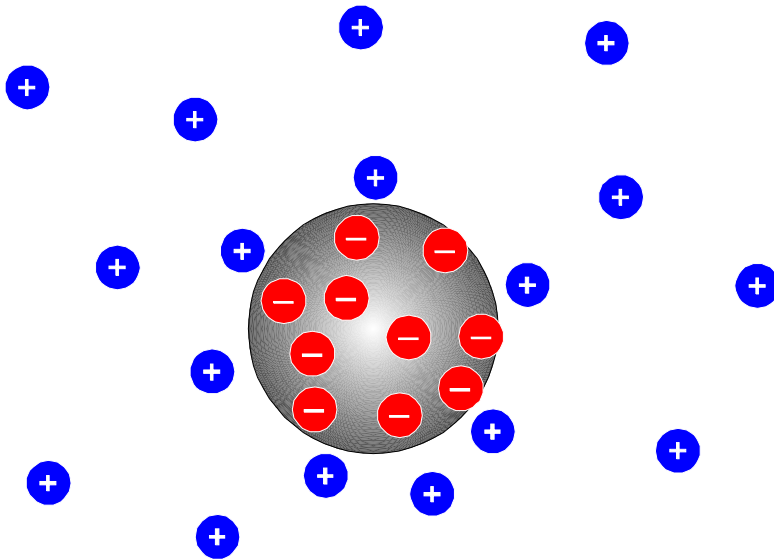


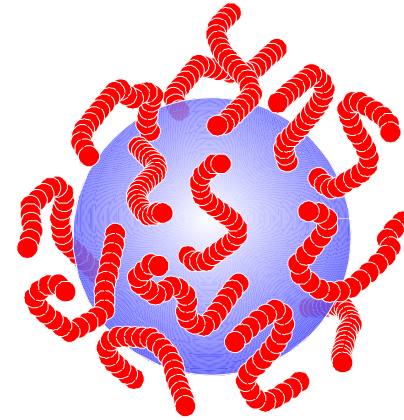
Interparticle Forces and Dispersion Stability

Lecture 3

Types of Colloidal Stabilization



Electrostatically stabilized

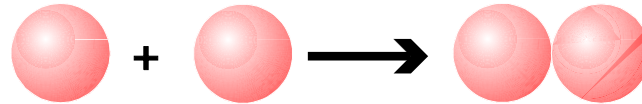


Sterically stabilized

All particles naturally attract each other.

Electrical charges or attached polymer layers screen the attraction.

Rate of Flocculation with Intermolecular Forces



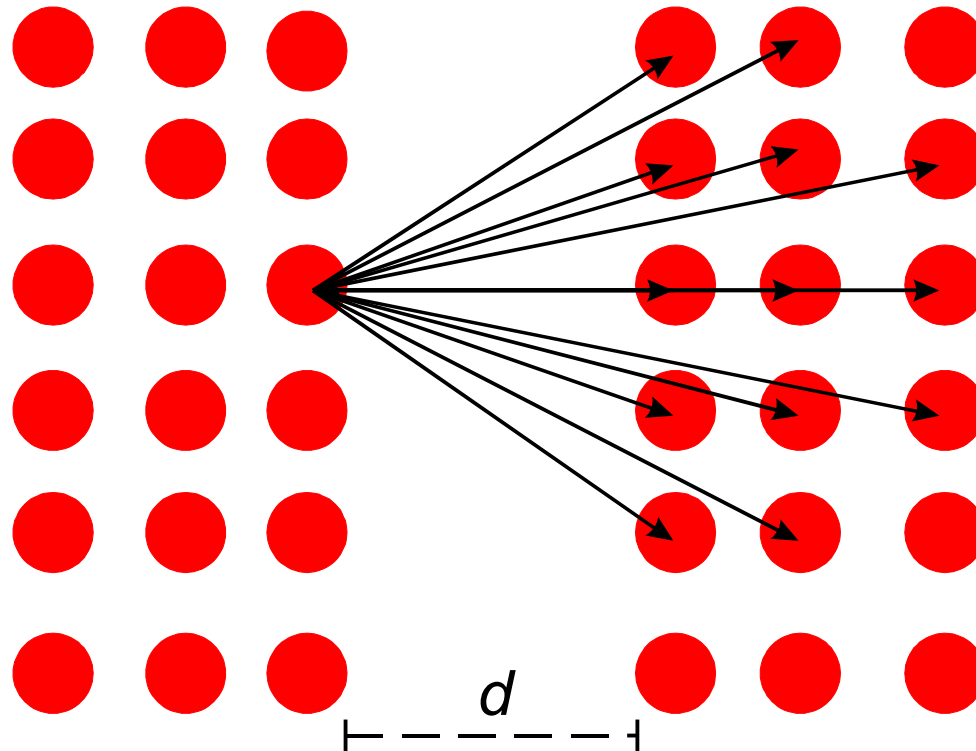
If we assume that particles collide directly along the line of their centers and take into account of any interparticle forces, then we find this second order rate has a characteristic time:

$$t_{1/2} = \frac{\eta\pi a^3 W}{\Phi kT}$$

$$W = 2a \int_{2a}^{\infty} \exp\left(\frac{U_{11}}{kT}\right) \frac{dr}{r^2}$$

W , which can be measured experimentally, is called the Stability Ratio.

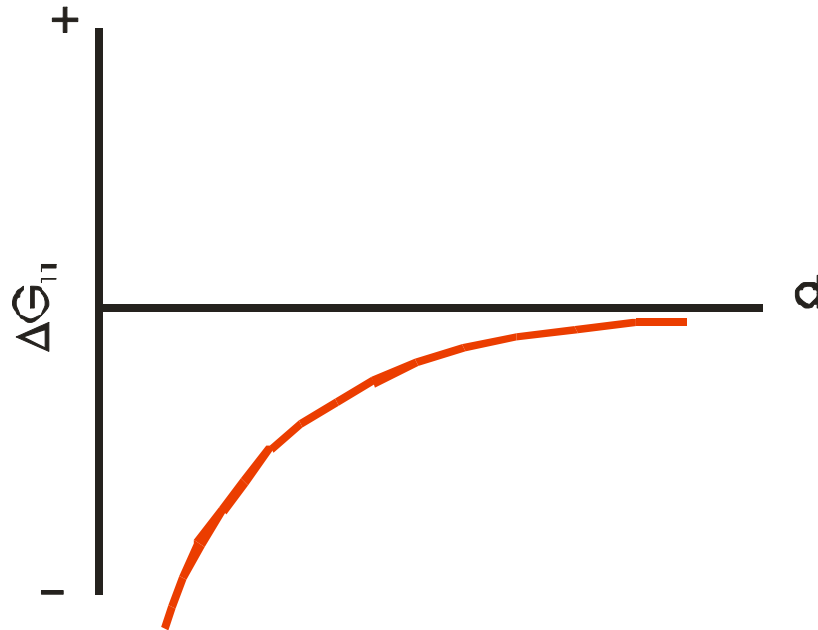
Hamaker model for the attraction between particles



Molecules in
particle 1

Molecules in
particle 2

Hamaker equations for dispersion force attraction



For two flat plates:

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

For two spheres:

$$\Delta G_{11} = \frac{-A_{11}a}{12d}$$

The A_{11} are the Hamaker constants.

Hamaker constants for some materials

Substance	A_{11} (10^{-20} J)				
Graphite	47.0	Polyvinyl acetate	8.91	Methyl ethyl ketone	4.53
Gold	45.3, 45.5, 37.6	Polyvinyl alcohol	8.84	Water	4.35, 3.7, 4.38
Silicon carbide	44	Natural rubber	8.58	Hexane	4.32
Rutile (TiO ₂)	43	Polybutadiene	8.20	Diethyl ether	4.30
Silver	39.8, 40.0	Polybutene-1	8.03	Acetone	4.20, 4.1
Germanium	29.9, 30.0	Quartz	7.93	Ethanol	4.2
Chromium	29.2	Polyethylene oxide	7.51	Ethyl acetate	4.17
Copper	28.4	Polyvinyl chloride	7.5	Polypropylene oxide	3.95
Diamond	28.4	Hydrocarbon (crystal)	7.1	Pentane	3.94, 3.8
Zirconia (<i>n</i> -ZrO ₂)	27	CaF ₂	7	PTFE	3.8
Silicon	25.5, 25.6	Potassium bromide	6.7	Liquid He	0.057
Metals (Au, Ag, Cu)	25 – 40	Hexadecane	6.31		
Iron oxide (Fe ₃ O ₄)	21	Fused quartz	6.3		
Selenium	16.2, 16.2	Polymethylmethacrylate	6.3		
Aluminum	15.4, 14, 15.5	Polydimethylsiloxane	6.27		
Cadmium sulfide	15.3	Potassium chloride	6.2		
Tellurium	14.0	Chlorobenzene	5.89		
Polyvinyl chloride	10.82	Dodecane	5.84, 5.0		
Magnesia	10.5, 10.6	Decane	5.45		
Polyisobutylene	10.10	Toluene	5.40		
Mica	10, 10.8	1,4-Dioxane	5.26		
Polyethylene	10.0	<i>n</i> -Hexadecane	5.1		
Polystyrene	9.80, 6.57, 6.5, 6.4, 7.81	Octane	5.02, 4.5		
		Benzene	5.0		
		<i>n</i> -Tetradecane	5.0		
		Cyclohexane	4.82, 5.2		
		Carbon tetrachloride	4.78, 5.5		

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:

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

Which leads to:

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

and

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

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:

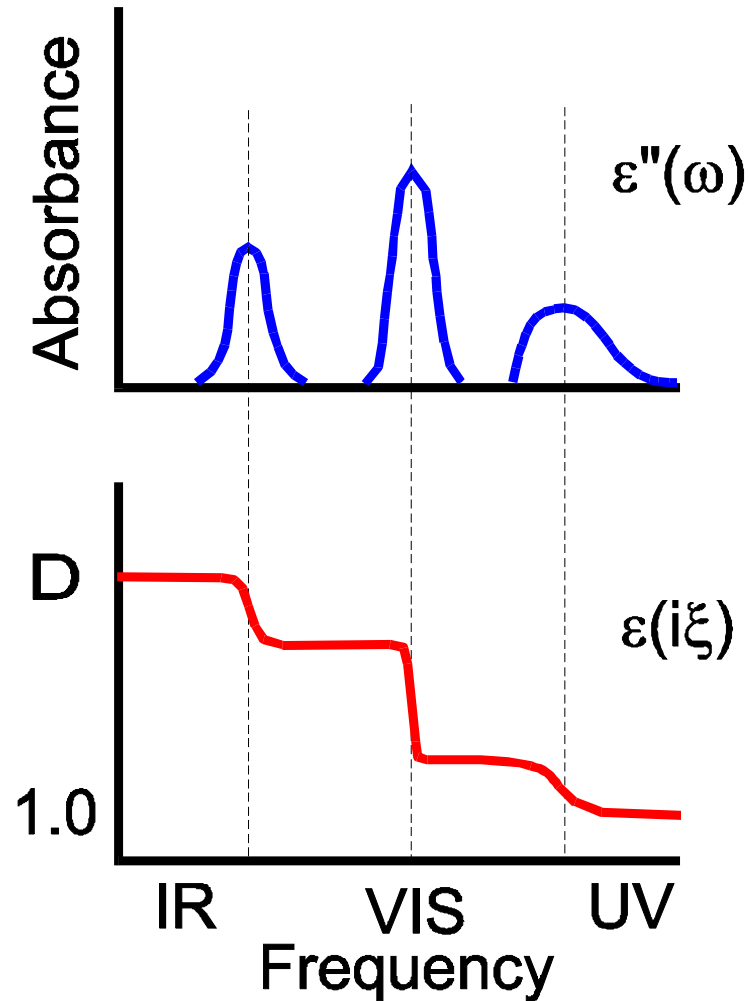
$$\Delta G_{123}^{nr} = -\frac{A_{123}^{nr}}{12\pi d^2}$$

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

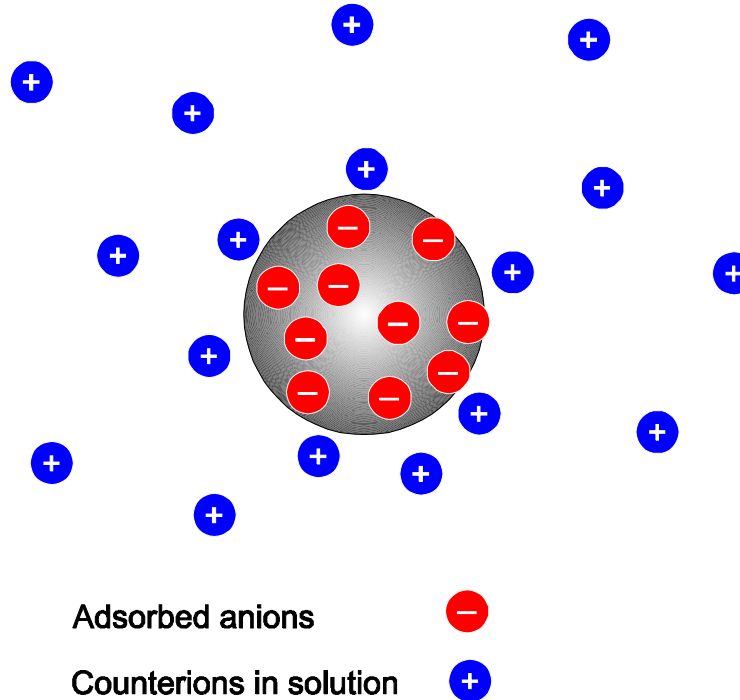
Lifshitz calculations

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.



Charged Particles in Suspension

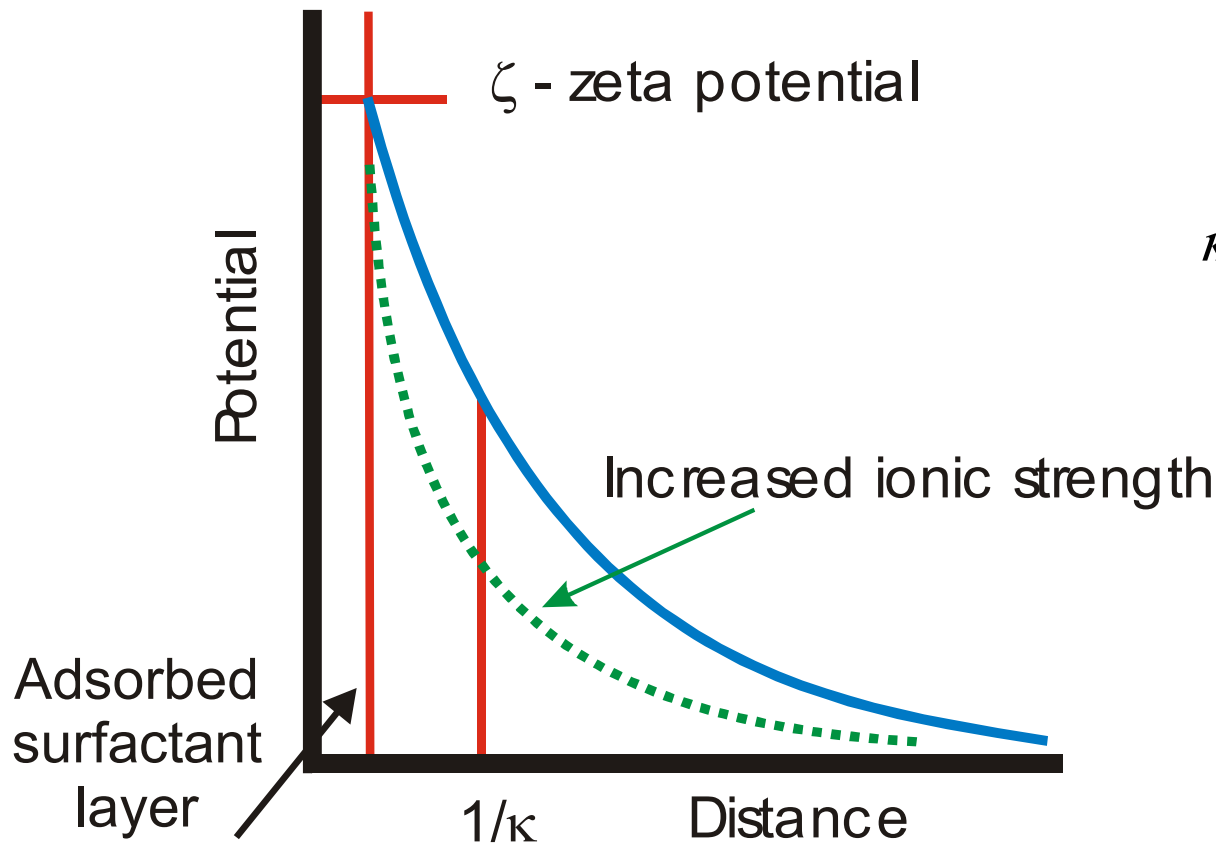


The electric potential at the surface of the particle is called the zeta potential.

The loosely held countercharges form the “electric double layer.”

Stern's model for a charged particle

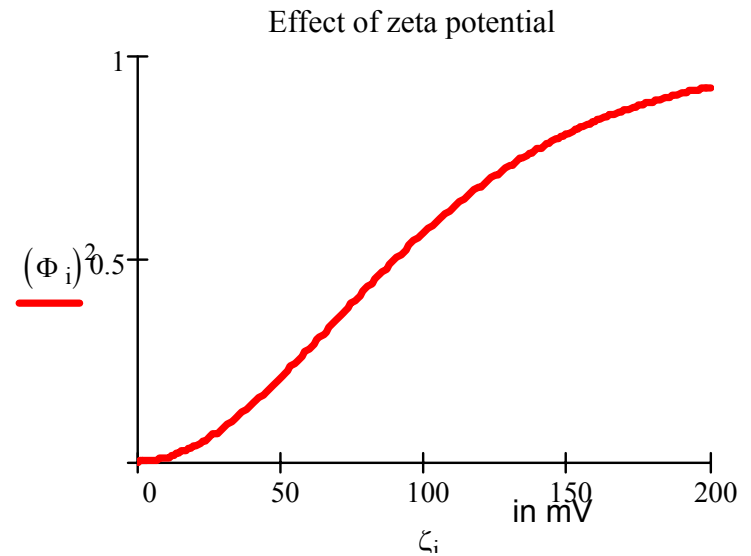
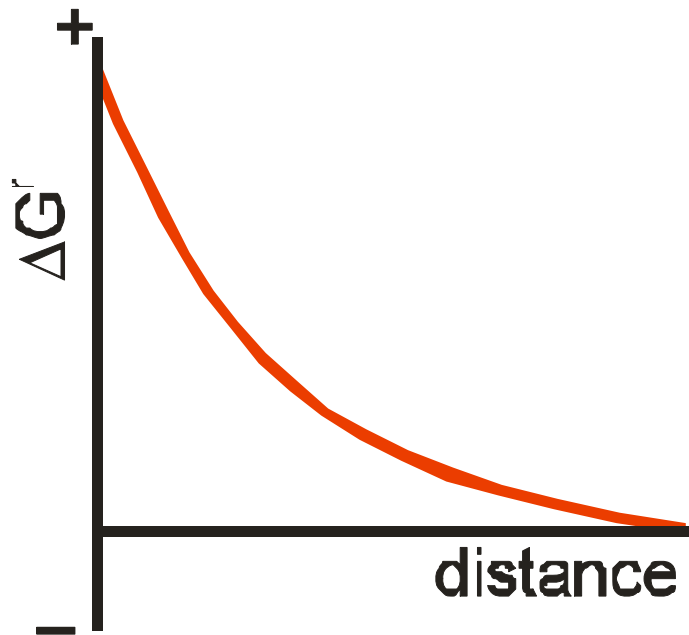
$$\text{Potential} = \zeta \exp(-\kappa d)$$



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

The electrostatic repulsion between spheres

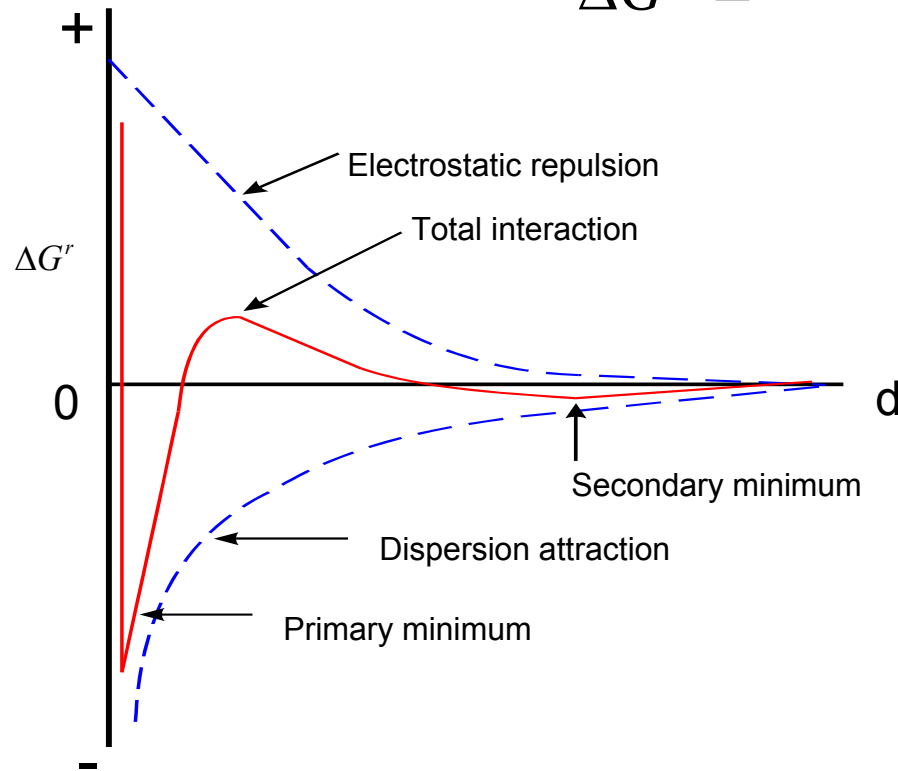
$$\Delta G^r = \frac{64n_0kT\pi a\Phi^2}{\kappa^2} \exp(-\kappa d)$$



Electrostatic stability of dispersions*

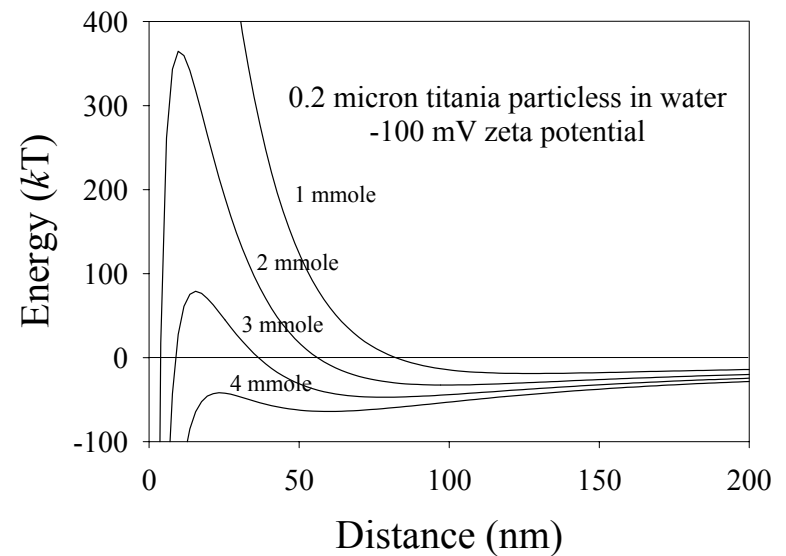
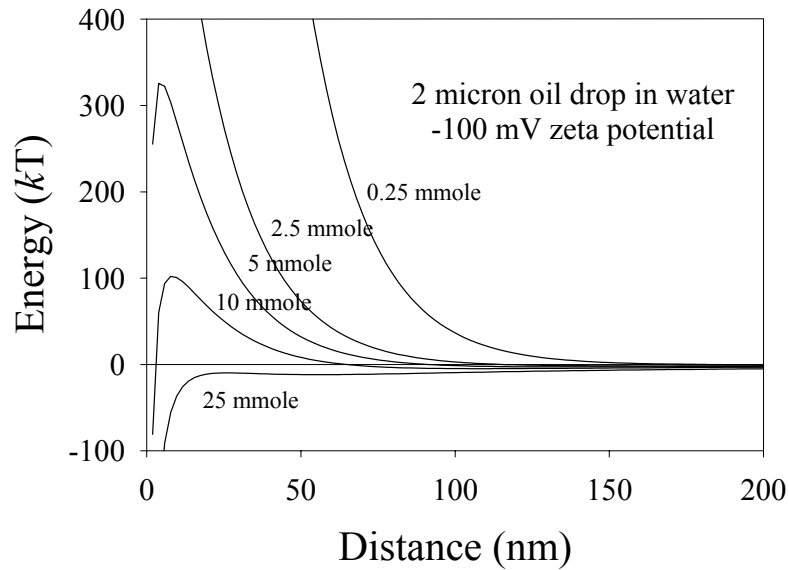
The total interaction between two spheres is the sum of the electrostatic repulsion and the dispersion attraction:

$$\Delta G^T = \frac{64n_0kT\pi a\Phi^2}{\kappa^2} \exp(-\kappa d) - \frac{A_{121}a}{12d}$$



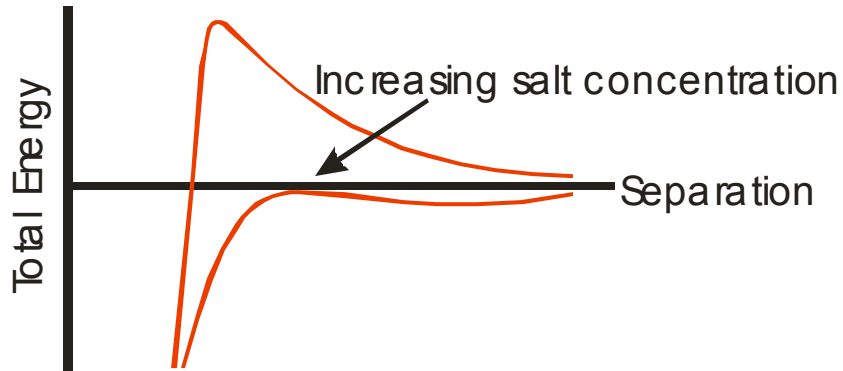
*DLVO theory

Stability of dispersions as a function of electrolyte concentration



Critical coagulation concentration

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



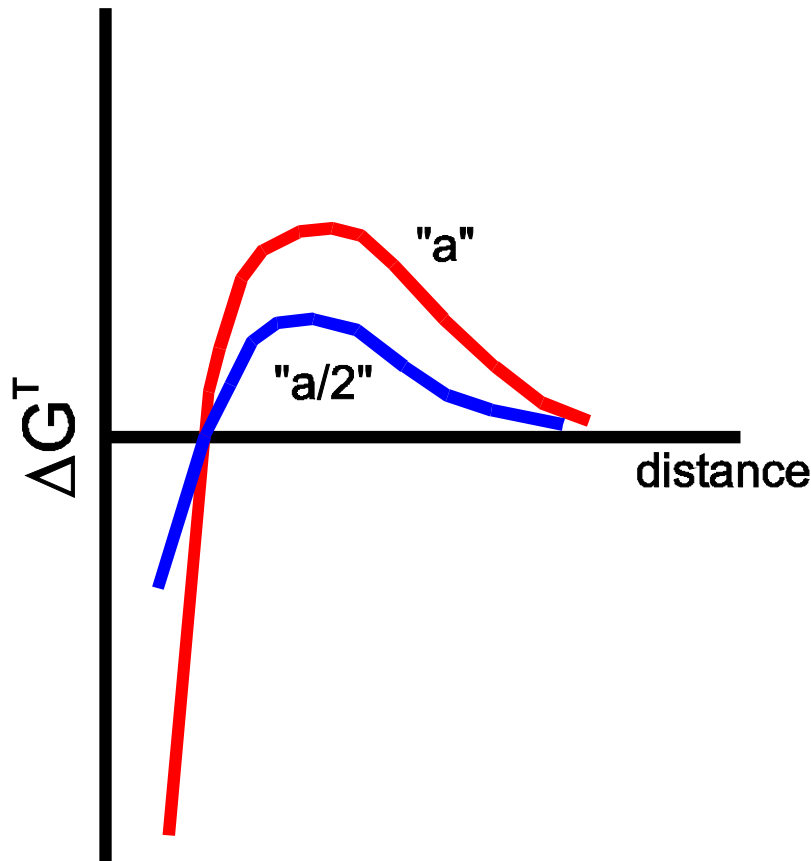
$$\Delta G^t = 0 \quad \text{and} \quad \frac{d\Delta G^t}{dH_0} = 0$$

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

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

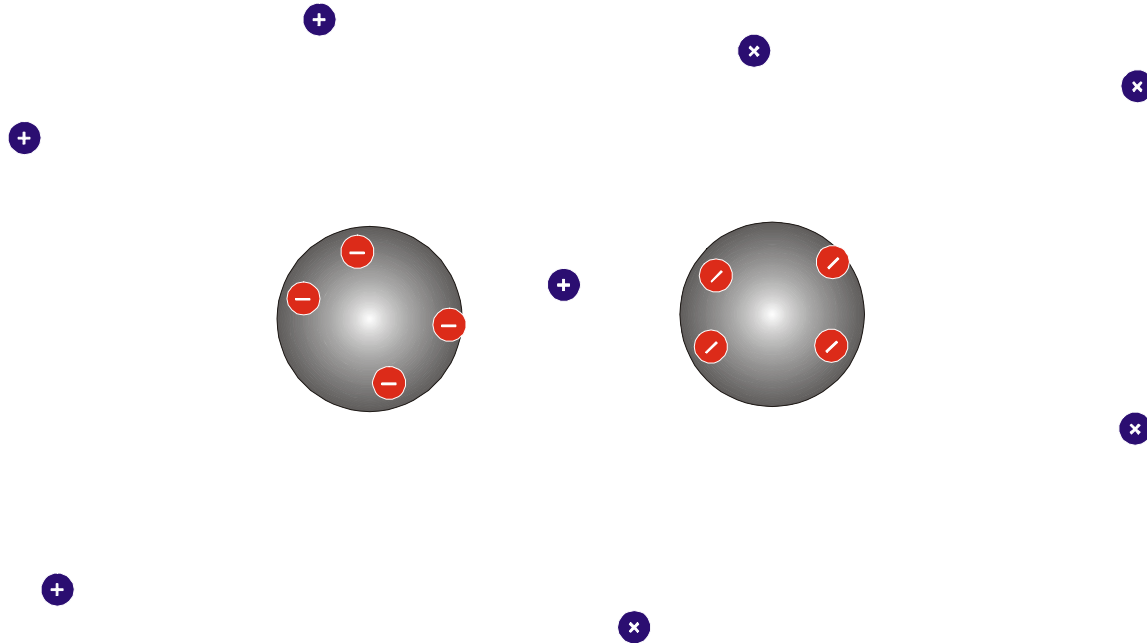
Particle size effect in electrostatic stabilization

$$\Delta G^T = \frac{64n_0kT\pi a\Phi^2}{\kappa^2} \exp(-\kappa d) - \frac{A_{121}a}{12d}$$



The larger the particles, the more stable the dispersion!

Electrostatic repulsion in nonpolar liquids



The dielectric constant is low, so that particles repel each other strongly.

The ion concentration is low, so the electrical double layers are very thick.

Therefore repulsion is simple Coulombic repulsion.

Electrostatic stability in nonpolar liquids

$$\Delta G^{total} = \frac{4\pi D\epsilon_0 a^2 \zeta^2}{d + 2a} - \frac{Aa}{12d}$$

$$\text{Stability ratio} = W = 2a \int_{2a}^{\infty} \exp\left(\frac{\Delta G^{total}}{kT}\right) \frac{dr}{r^2}$$

The integral can be calculated approximately:

$$W \cong \left(\frac{Ak^2T^2}{3072D^3\epsilon_0^3a^3\zeta^6}\right)^{1/4} \exp\left(\frac{2\pi D\epsilon_0 a\zeta^2}{kT}\right)$$

A reasonable criterion for stable dispersions is:

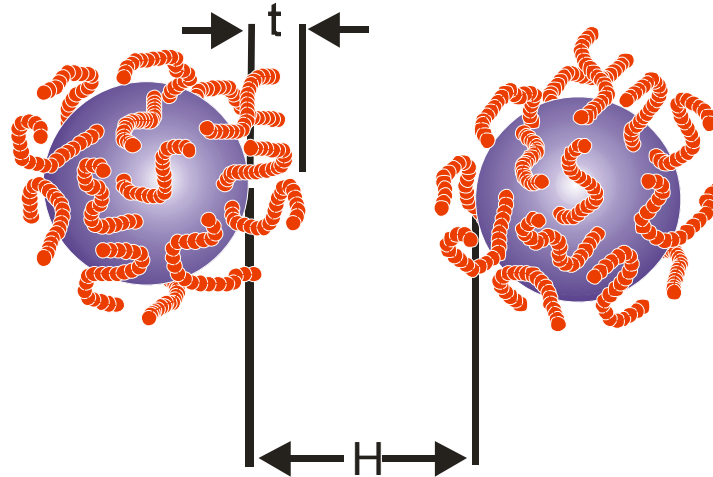
$$\zeta^2 \geq \frac{10^3}{Da} \text{ with } \zeta \text{ in } mV \text{ and } a \text{ in } \mu m$$

Zeta potential to stabilize dispersions in nonpolar liquids

Radius (μm)	Zeta Potential (mV)
0.01	224
0.05	100
0.1	71
0.3	41
0.5	32
0.75	26
1.0	22
5.0	10

Steric stabilization

Criterion for Steric Stabilization



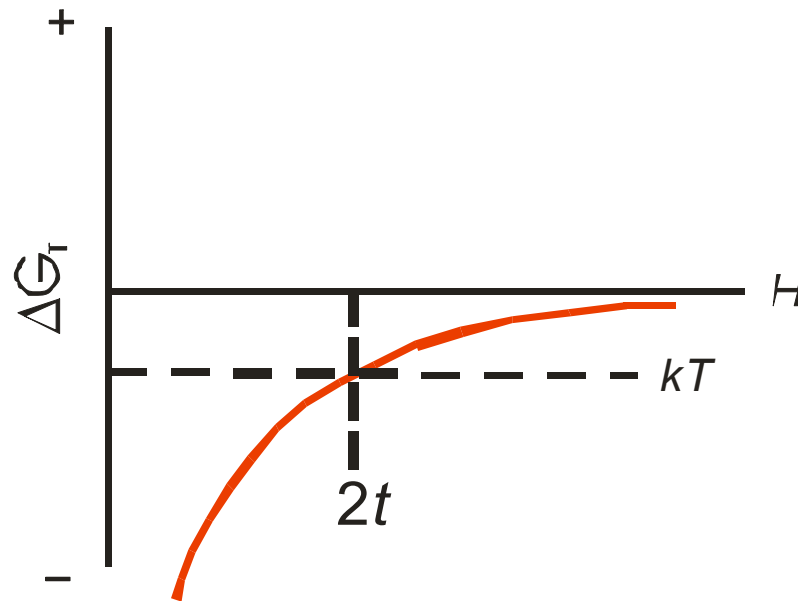
Work is required to push the particles closer together than their polymer layers keep them apart.

In thermodynamic terms, this is:

$$\text{w h e n } H \leq 2 t \text{ t h e n } \Delta G_T \gg 0$$

Dispersion Attractive Energies 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:

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

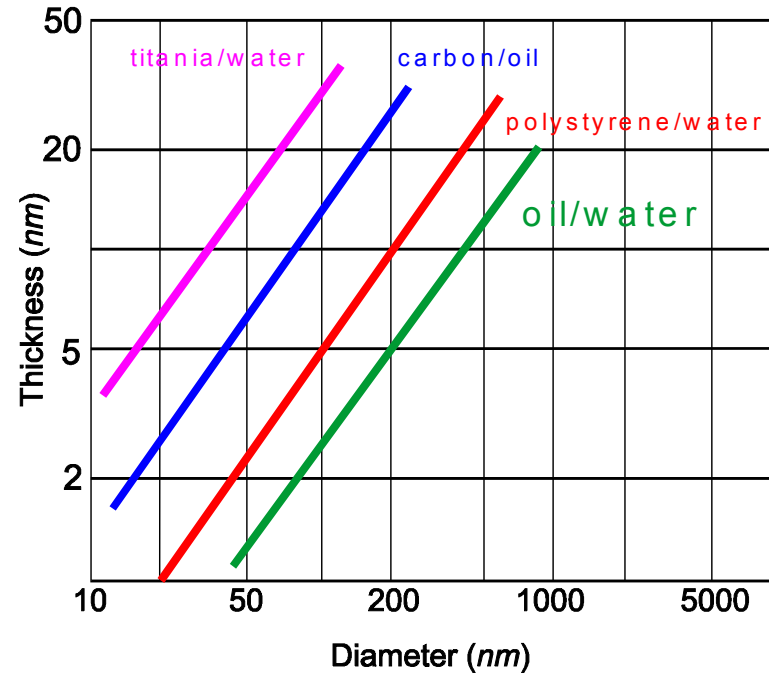
Therefore the polymer layer thickness around each particle, t , as a function of diameter must be greater than:

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

For example:

	$A_{121} (x 10^{20}) \text{ J}$	$A_{121}/48kT$
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 Layer Thickness Necessary for Steric Stabilization

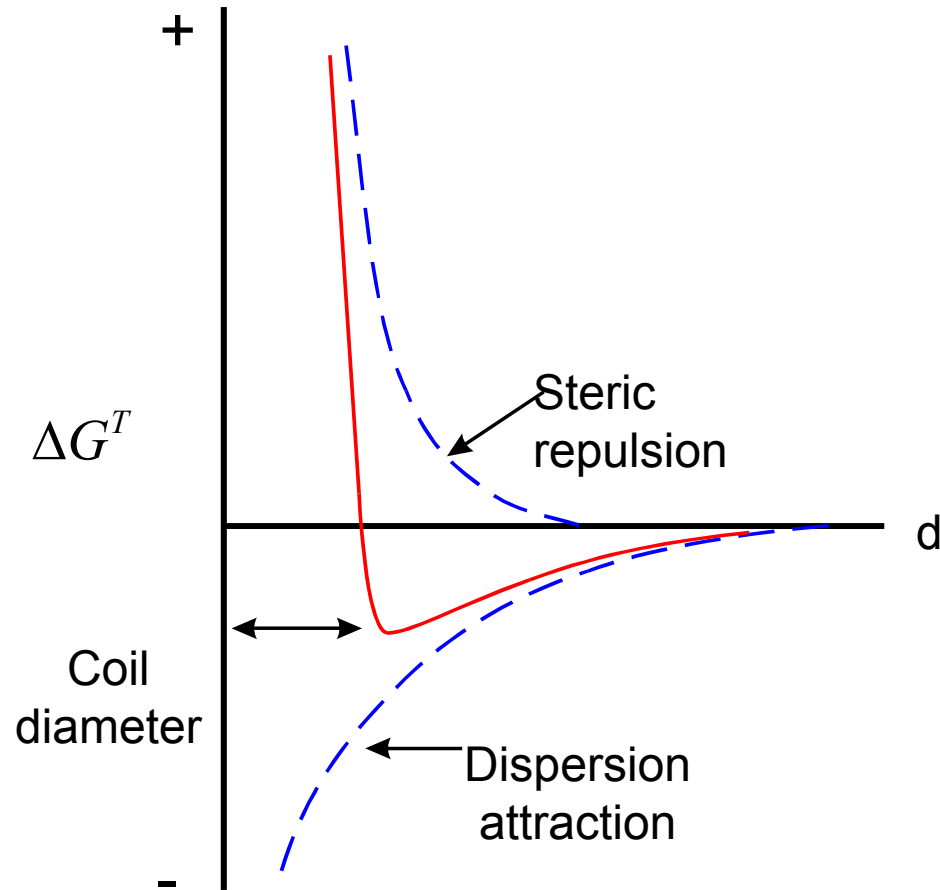


A Simple Theory for Polymer “Size” in Solution

Typical dimensions of polymer chains of different molecular weights

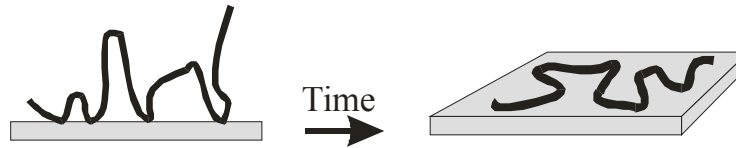
Molecular weight	Radius of gyration (nm) $\langle r^2 \rangle^{1/2}$
1,000	2
10,000	6
100,000	20
1,000,000	60

Steric Stabilization for 2 Spheres



Possible Configurations of Adsorbed Polymers

Homopolymers



Random copolymers



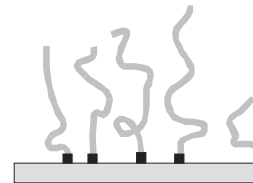
Block copolymers

Two or three segments are common.

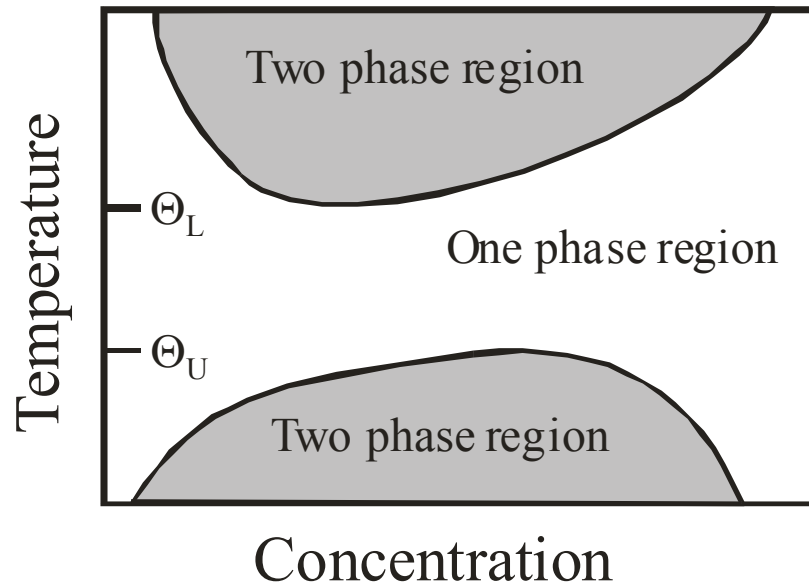


Grafted polymers

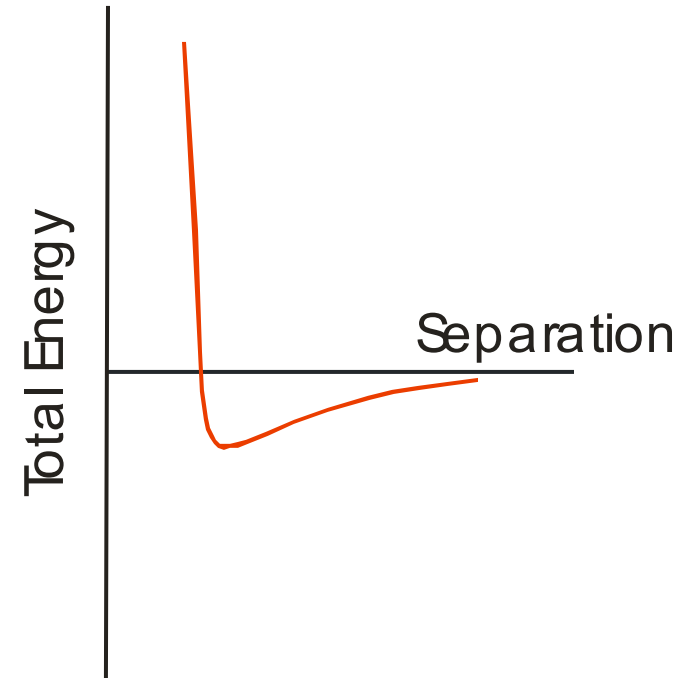
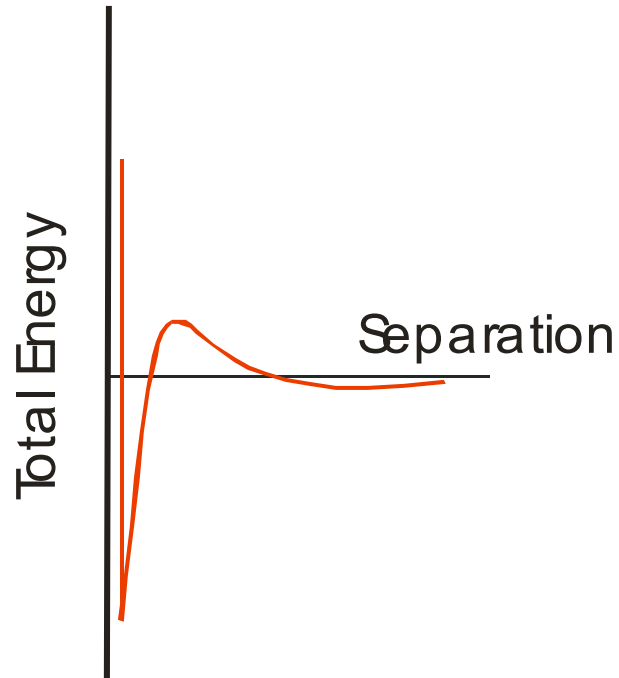
Polymers may be attached to or grown from the surface.



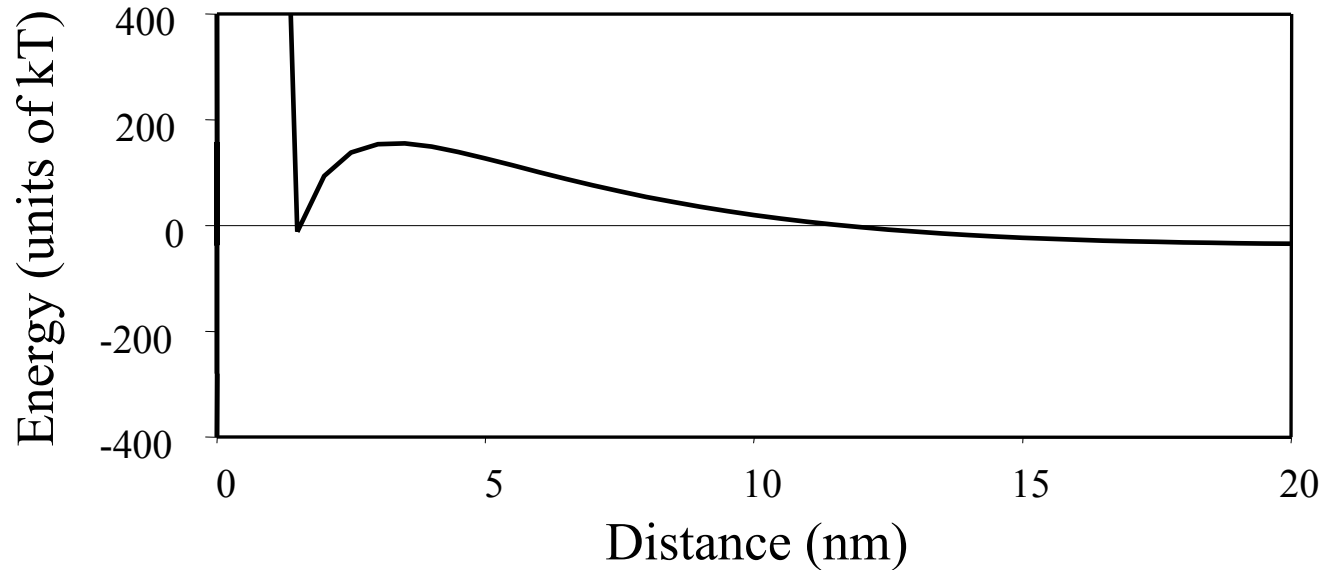
Polymer Solution Phase Diagram



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.