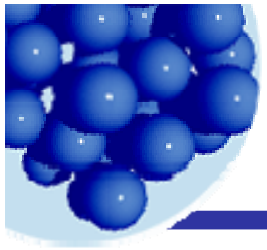


Steric stabilization – the role of polymers

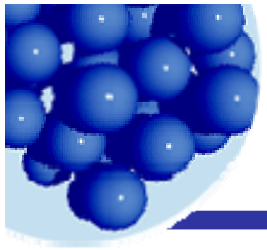
Dispersions in liquids: suspensions, emulsions, and foams

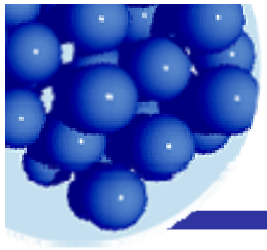
ACS National Meeting

March 21 – 22, 2009

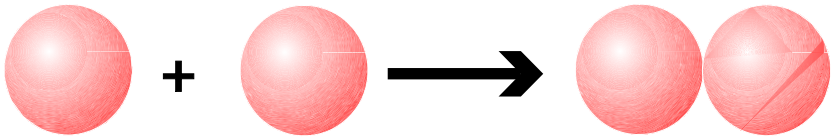
Salt Lake City

Ian Morrison© 2009





Rates of flocculation – Strength of interparticle forces



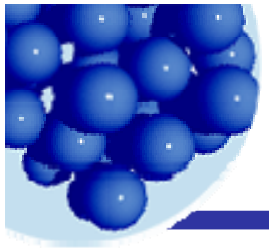
The time for half the particles to flocculate is:

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

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

The stability ratio depends on the interparticle forces:

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



Theories of dispersion energies

Using a perturbation theory to solve the Schroedinger equation for two atoms, London found:

$$U(r) = -\frac{\Lambda_{ab}}{r^6}$$

where $\Lambda_{ab} = \left(\frac{h\nu_a h\nu_b}{h\nu_a + h\nu_b} \right) \alpha_a \alpha_b$

ν is a characteristic frequency

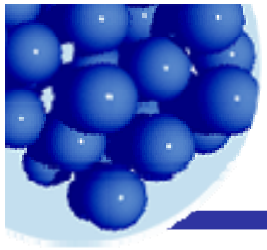
and α is polarizability

Casimir and Polder refined the theory to account for the finite speed of light, *c:*

$$U(r) = -\frac{23hc\alpha^2}{4\pi^2 r^7}$$

This “retardation” diminishes the attraction.

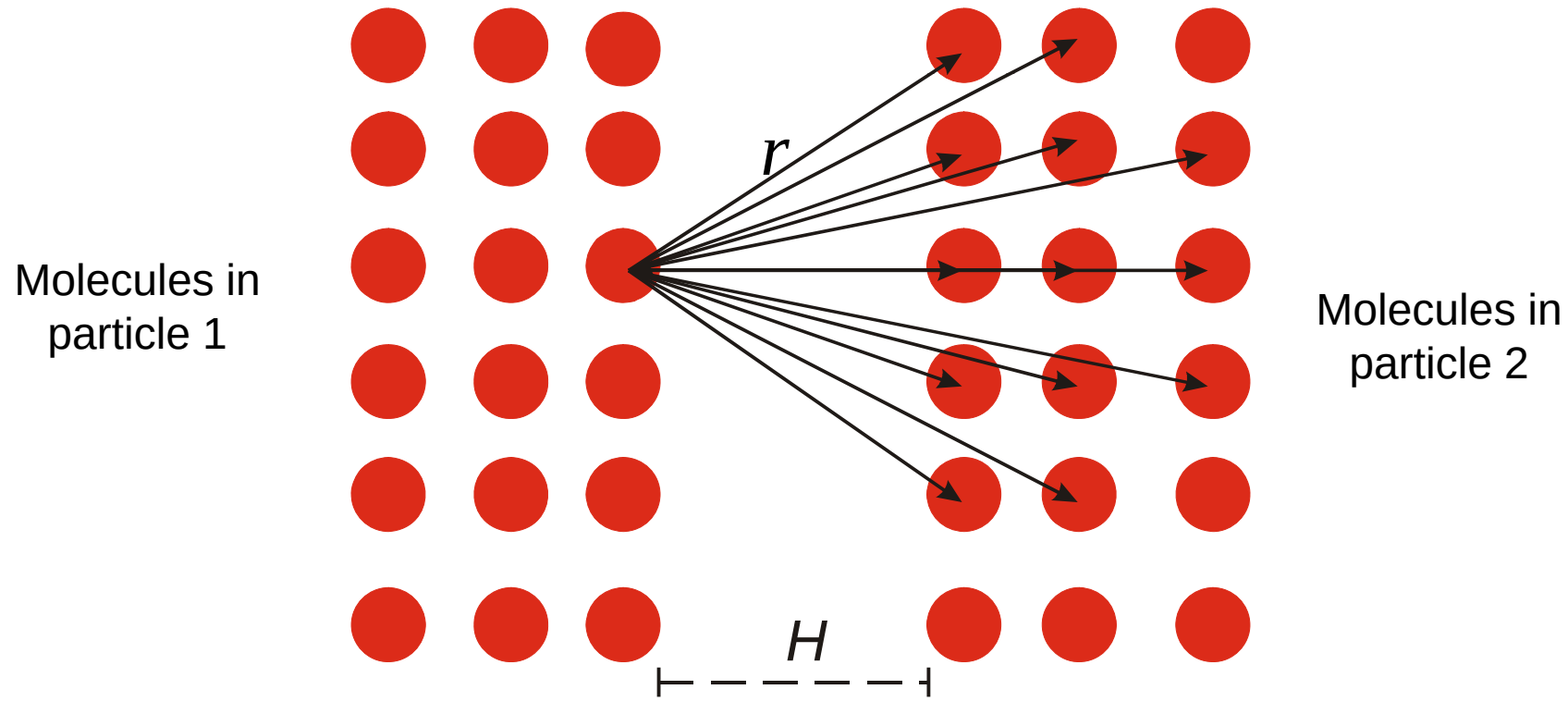
F. London, The general theory of molecular forces, *Trans. Faraday Soc*., *33*, 8, **1937**.
Casimir and Polder, *Phys. Rev*. 73, 360, **1948**.



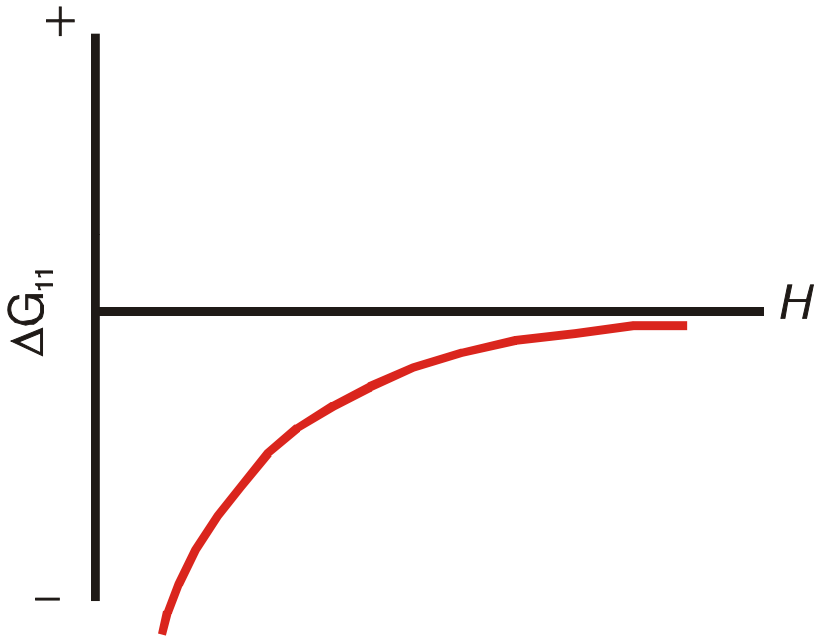
Hamaker model for the attraction between particles

The intermolecular attraction is due to London (dispersion) energies:

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



Hamaker equations for dispersion force attraction



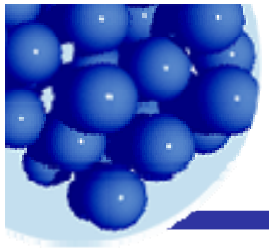
For two spheres (per pair):

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

For two flat plates (per unit area):

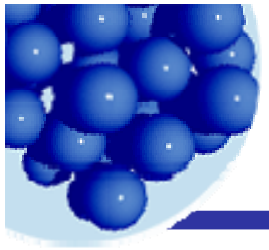
$$\Delta G_{11} = \frac{-A_{11}}{12\pi H^2}$$

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:

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

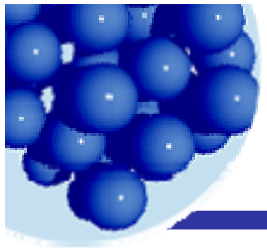
Introducing the approximation: $A_{12} \simeq \left[A_{11} A_{22} \right]^{1/2}$

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

Limitation of Hamaker theory:

all molecules act independently

Lifshitz theory:

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

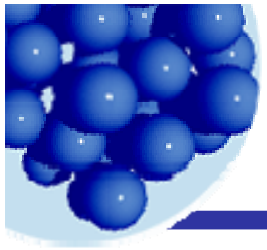
What describes the electronic fluctuations in the particle?

the absorption spectra: uv-vis-ir

Result:

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

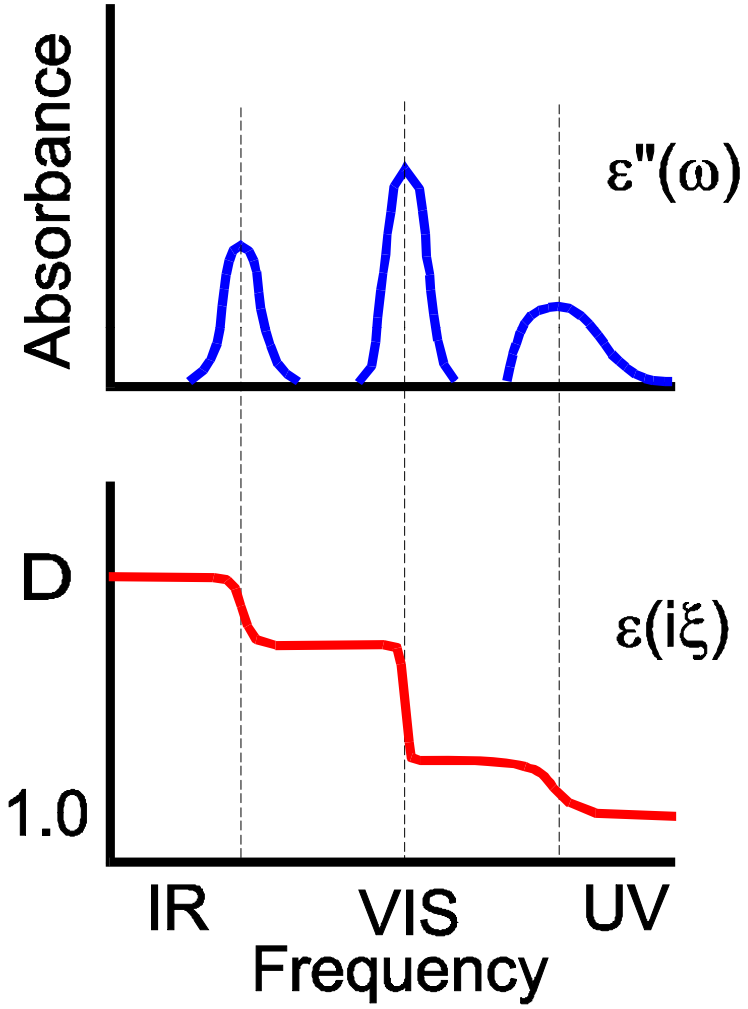
The Lifshitz constant depends on the absorption spectra of the particles.

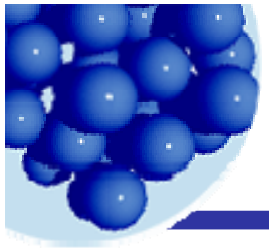


Data for Lifshitz calculations

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 calculations

The Lifshitz constant is a double summation of products of dielectric functions:

$$A_{123} = \frac{3kT}{2} \sum_{n=0}^{\infty}{}' \sum_{m=1}^{\infty} \frac{\left(\Delta_{12}\Delta_{32}\right)^m}{m^3}$$

The dielectric functions are differences in dielectric constants over a series of frequencies:

$$\Delta_{12} = \frac{\varepsilon_1(i\xi_n) - \varepsilon_2(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_2(i\xi_n)} \text{ and } \Delta_{32} = \frac{\varepsilon_3(i\xi_n) - \varepsilon_2(i\xi_n)}{\varepsilon_3(i\xi_n) + \varepsilon_2(i\xi_n)}$$

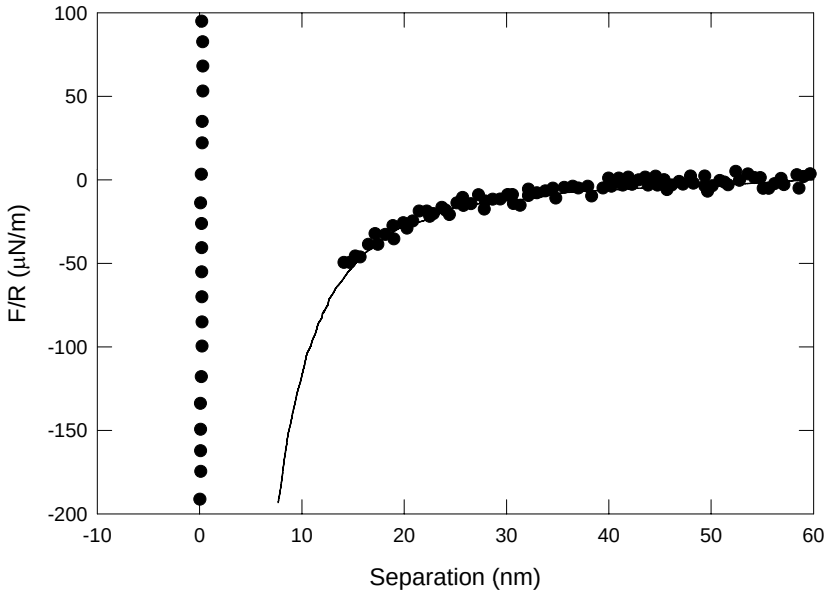
The frequencies are:

$$\xi_n = n\frac{4\pi^2 kT}{h}$$

where *k* is the Boltzmann constant, *T* is the absolute temperature, *h* is Planck's constant, and the prime on the summation indicates that the $n = 0$ term is given half weight. At 21°C, ξ_1 is 2.4×10^{14} rad/s, a frequency corresponding to a wavelength of light of about 1.2 *μ*m. As *n* increases, the value of ξ increases and the corresponding wavelength decreases, hence ξ takes on more values in the ultraviolet than in the infrared or visible.

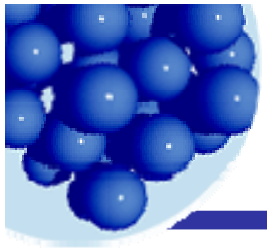
Lifshitz calculation vs measurement

Force - separation for TiO_2 at the PZC

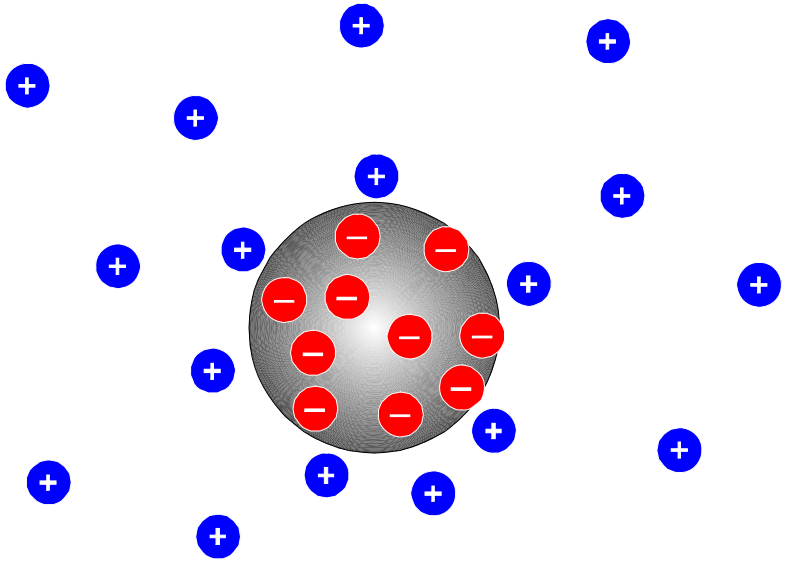


direction	ε(0)	ω_{IR}(rad/s)	C_{IR}	ω_{UV}(rad/s)	C_{UV}
perpendicular	86	1×10^{14}	80	7.49×10^{15}	4.77
parallel	170	1×10^{14}	163	7.24×10^{15}	6.01

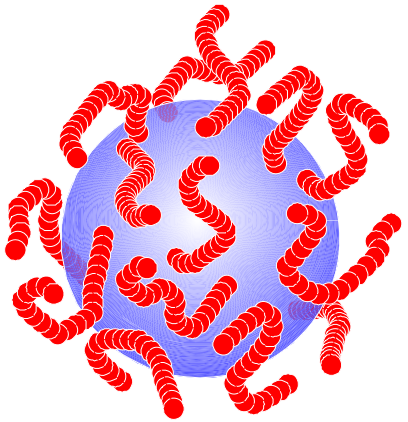
Larson, I.; et al
JACS, **1993**, *115*,11885-11890.



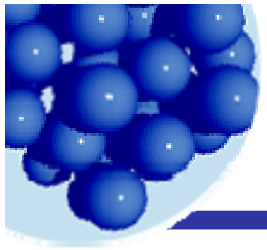
Colloidal stability requires a repulsion force:



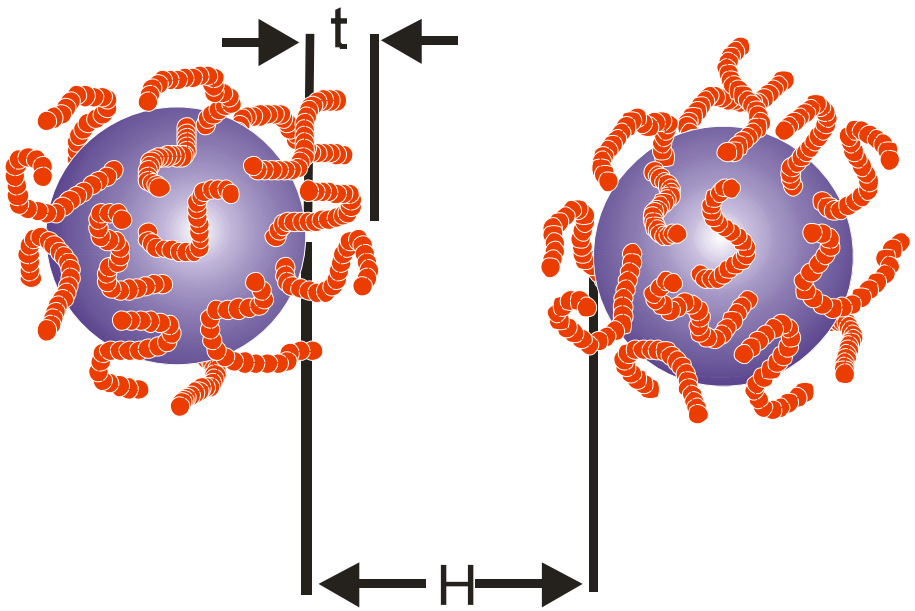
Electrostatically stabilized



Sterically stabilized



Steric stabilization

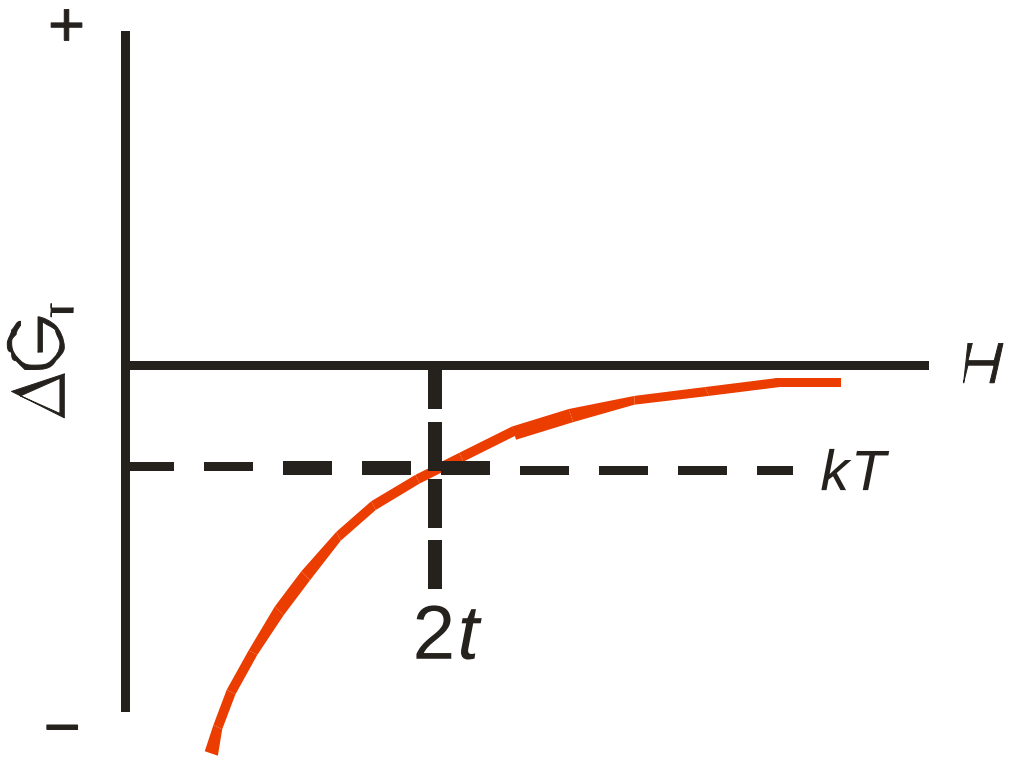


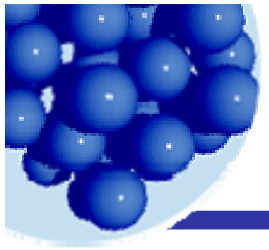
Work is required to push polymer layers into each other.

When $H < 2t$ then $\Delta G \gg 0$

Dispersion attraction between spheres

$$\Delta G_{121} = \frac{-A_{121} d}{24H}$$





Criterion for Steric Stabilization (1st order)

The kinetic energy must be greater than the attractive energy: $$kT > \frac{A_{121}d}{24H}$$

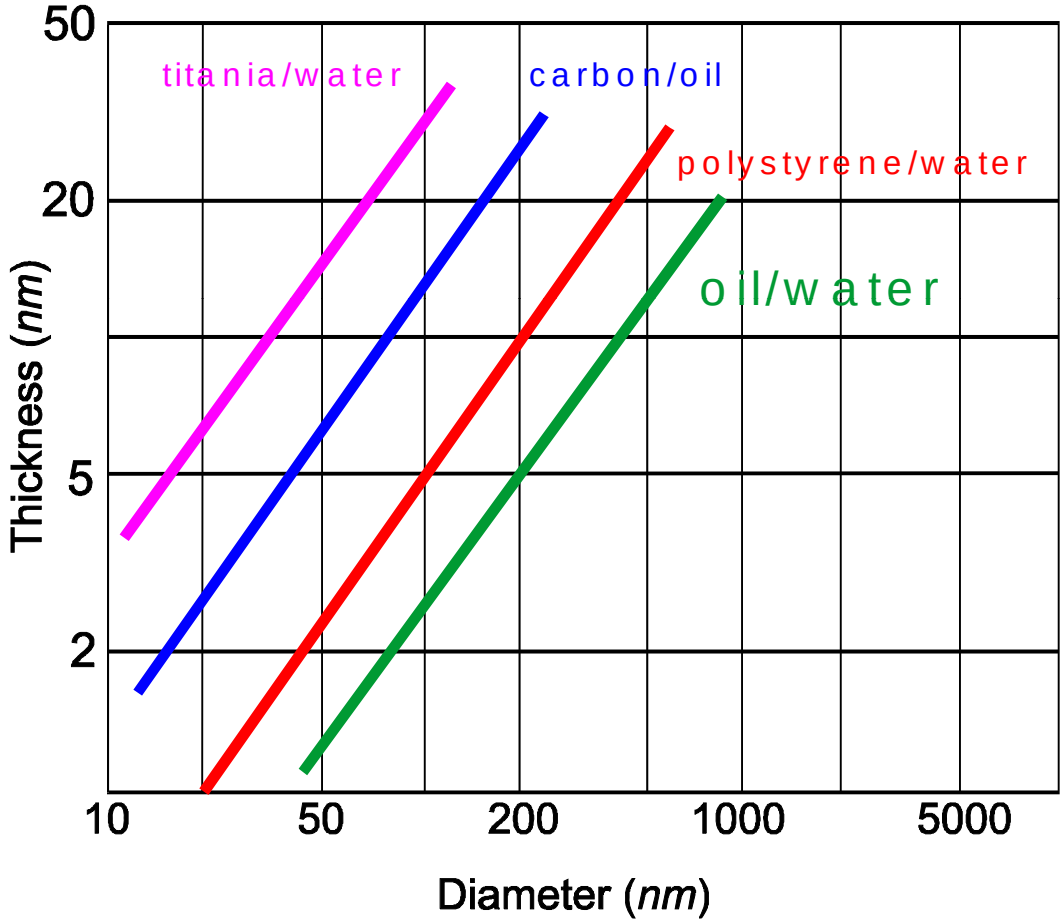
Especially when the polymer layers just touch: $$kT > \frac{A_{121}d}{48t}$$

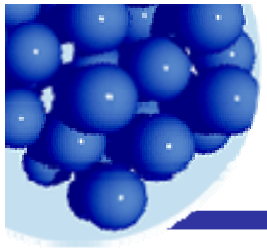
or $$t > \frac{A_{121}}{48kT}d$$

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 for steric stabilization





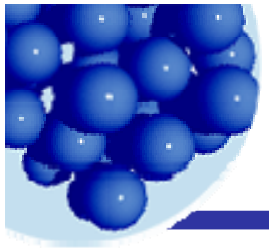
A simple theory for polymer “thickness”

A reasonable assumption is that the surface coating has a thickness equal to the radius of gyration.

Radius of gyration 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



The Size of polymers in solution

A polymer forms a random coil in solution. The polymer increases the viscosity of the solution in a manner approximately dependent on molecular size.

This polymer size can be calculated from the intrinsic viscosity:

$$\left\langle r^2 \right\rangle^{1/2} = \left(\frac{2}{5} \frac{MW}{N_0} [\eta] \right)^{1/3}$$

Where *MW* is molecular weight and N_0 is Avogadro's number.

The intrinsic viscosity is gotten by:

$$[\eta] = \lim_{c \to 0} \frac{1}{c} \left(\frac{\eta_{solution}}{\eta_{solvent}} - 1 \right)$$

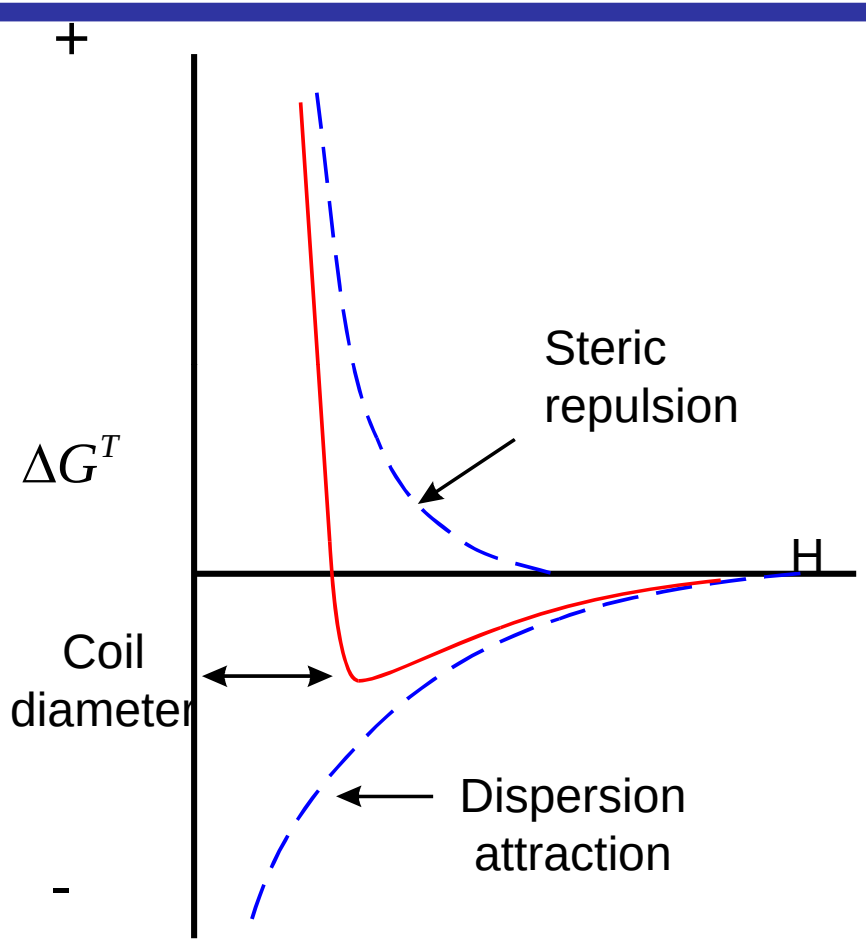
or $$[\eta] = \frac{1}{c^*}$$

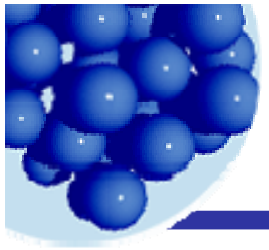
where c^* is the concentration where the viscosity is not linear in concentration.

or $$R_g = \frac{l\sqrt{n}}{\sqrt{6}}$$

where *l* is the "Kuhn" length.

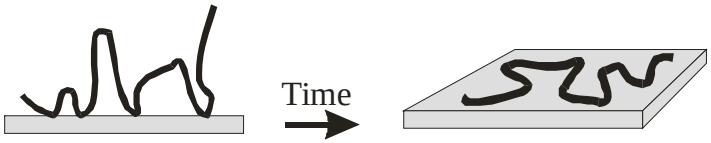
Steric stabilization – a better model



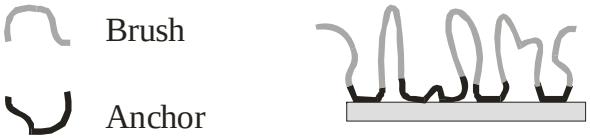


Configurations of adsorbed polymers

Homopolymers

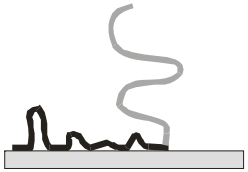


Random copolymers



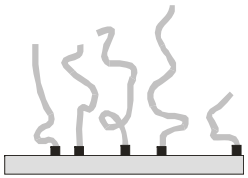
Block copolymers

Two or three segments are common.

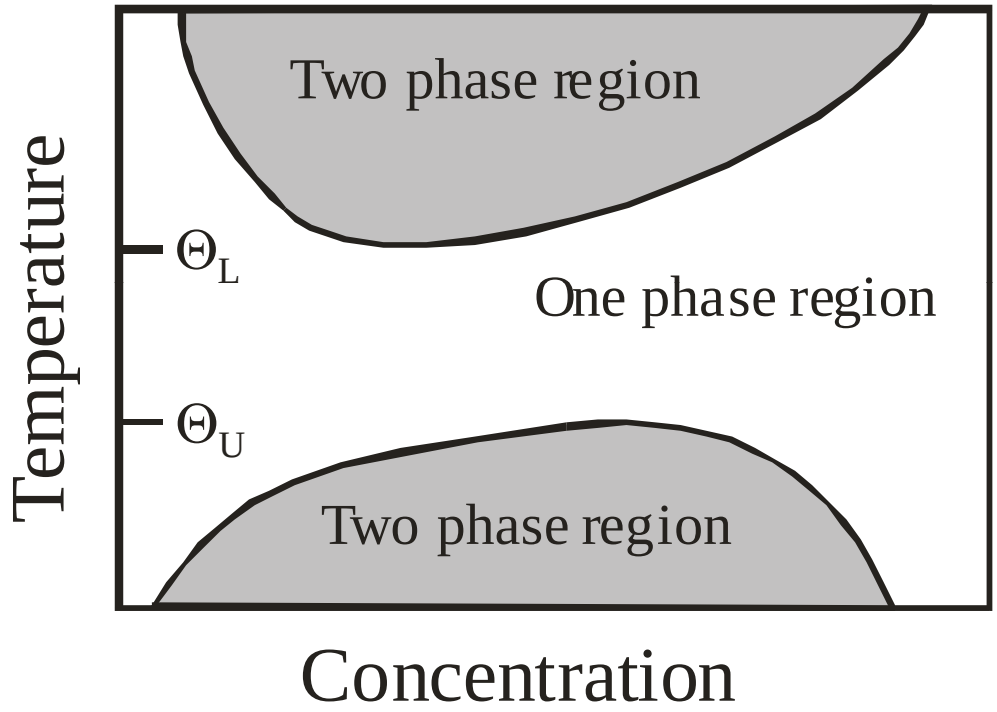


Grafted polymers

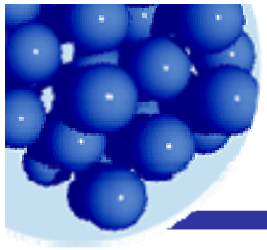
Polymers may be attached to or grown from the surface.



Polymers in solution - Phase Diagrams



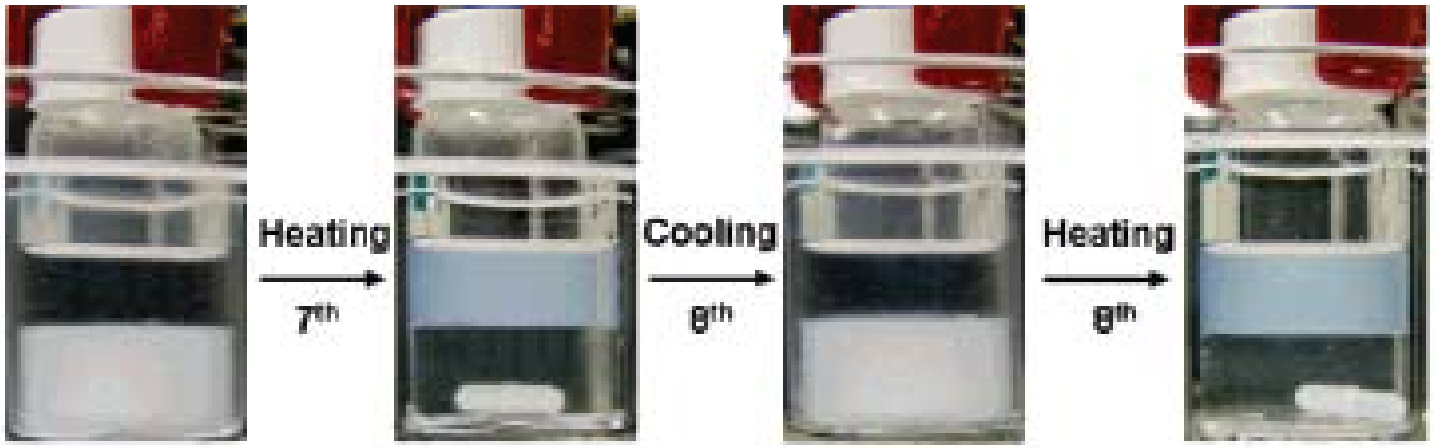
Sterically stabilized dispersions are stable when the polymer is soluble – the one phase regions.



Steric stabilization!

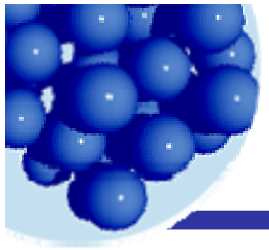
Ethylacetate

Aqueous



141 *nm* silica particles- with grafted polymer.
Pictures were taken at 0 C and 60 C.
The particles phase-transfer with the change in polymer solubility.

Langmuir **2007,** *23,* 2208−2217

Temperature-Induced Transport of Thermosensitive Hairy Hybrid Nanoparticles between Aqueous and Organic Phases

Dejin Li and Bin Zhao*