

Colloidal Dispersions of Soft Matter

Chapter 4

OUTLINE:

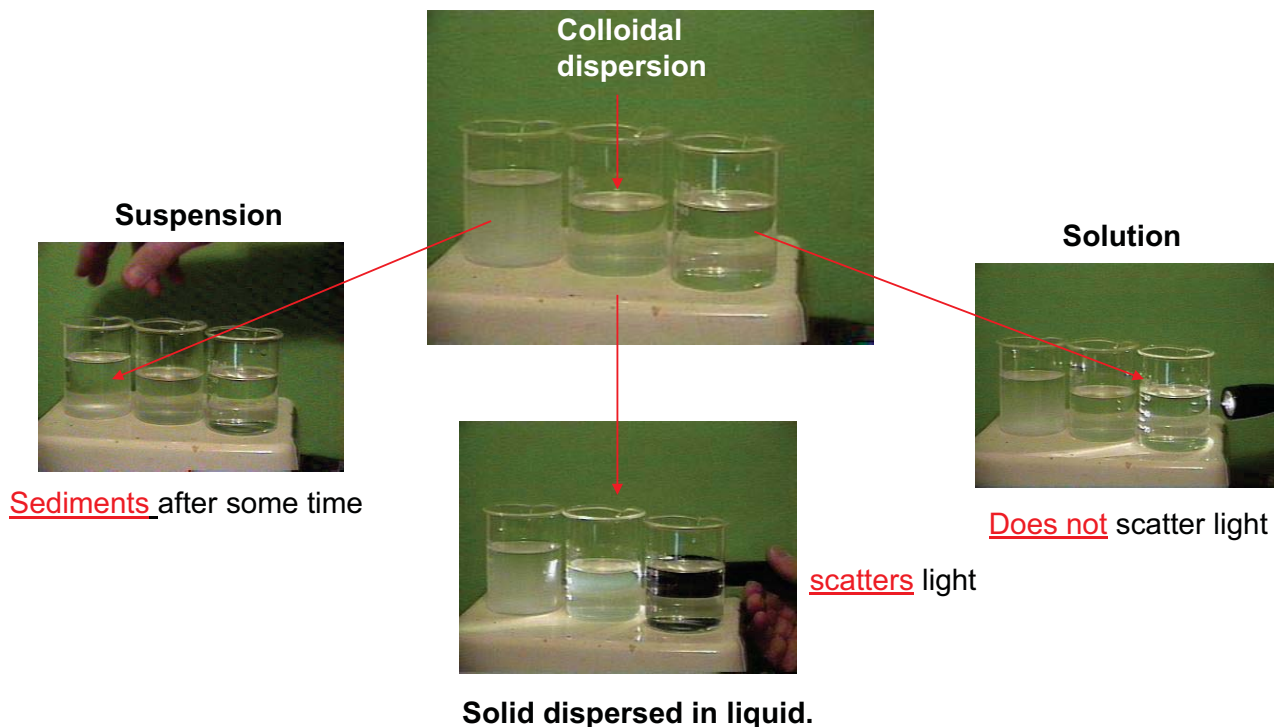
1. Introduction
2. Types of colloids
3. Particle motion
4. Forces that act between colloidal particles
5. Methods to stabilize colloids
6. Phase behaviour and stability of colloids



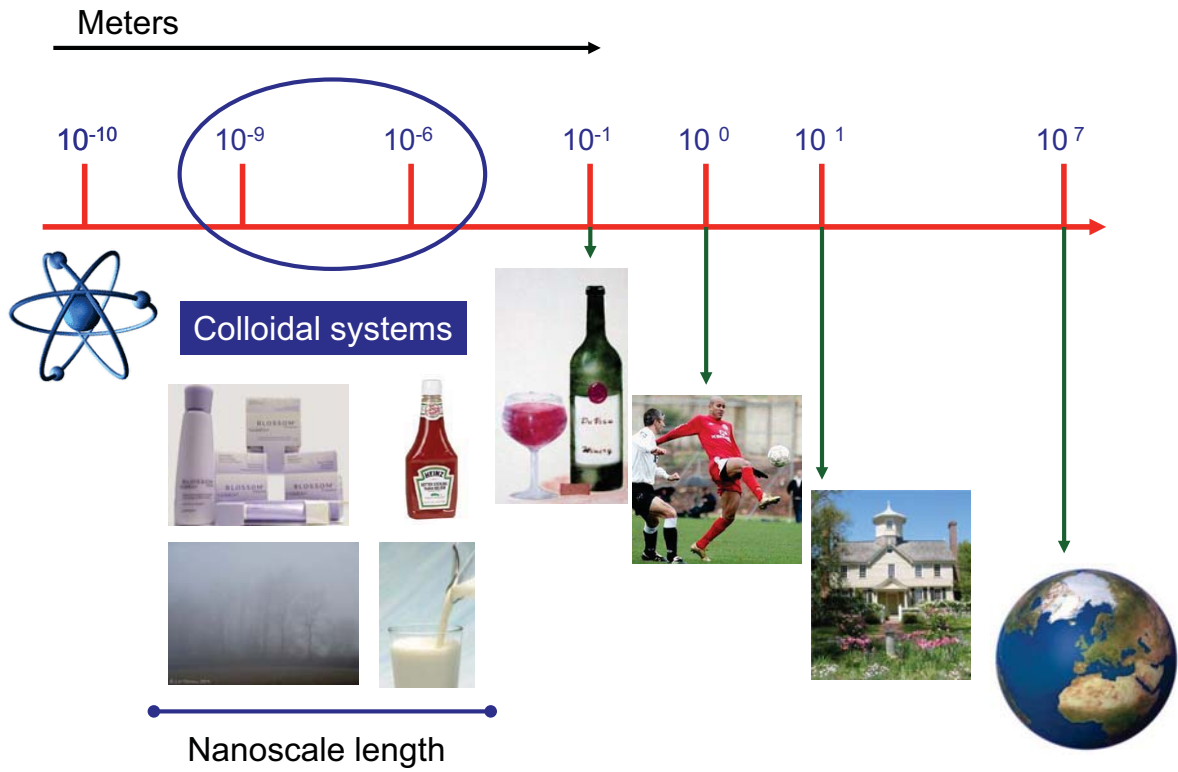
What are Colloidal Dispersions ?

Colloidal dispersions are heterogeneous systems.

A dispersed phase (solid, liquid or gas) in a dispersing medium (solid, liquid or gas).



Length Scale



Some Examples of Colloidal Dispersions

Biological colloids



Food colloids



Industrial colloids



Types of Colloidal Dispersions

Liquid in gas: Liquid aerosol



Solid in Gas: Solid aerosol



Gas in Liquid: Foam



Liquid in Liquid: Emulsion



Solid in Liquid: Sol



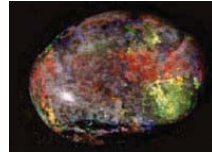
Gas in solid: solid foam



Liquid in Solid: Solid emulsion



Solid in Solid: Solid suspension



Characteristics of Colloidal Dispersions

1. High area of interface

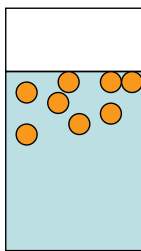
(1kg of polymer is dispersed in water in the form of spheres of 200nm or radius, giving 15000m² of interface between the water and the polymer)

2. Substantial interfacial energy (consequence of the high interfacial area)

Why do they not aggregate to form large clusters to reduce the interfacial energy?

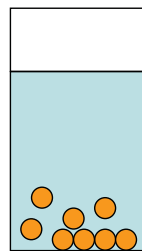
Understanding of stability of colloidal dispersions then forms the central issue.

The main driving force for destabilization: **Gravity**.

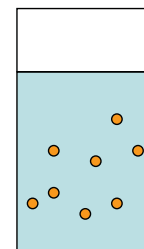


Dispersed phase is less dense: leads to **creaming**

Eg. Untreated full-cream milk



Dispersed phase is more dense: leads to **sedimentation**



Size of droplets reduced and dispersed.

Eg. Homogenized milk

Why decreasing size it remains dispersed in solution? -> $k_B T$

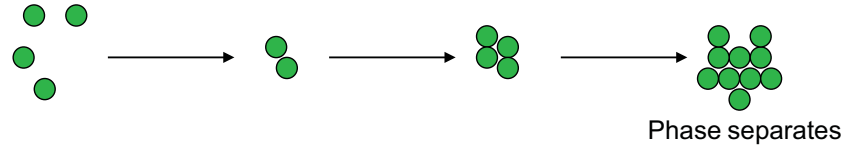




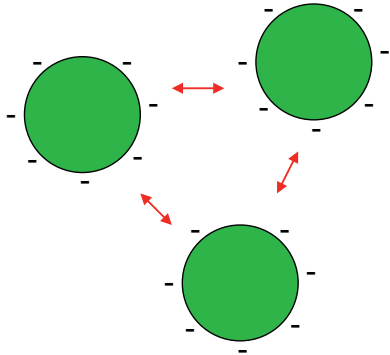
Robert Brown

Particle motion: Brownian motion

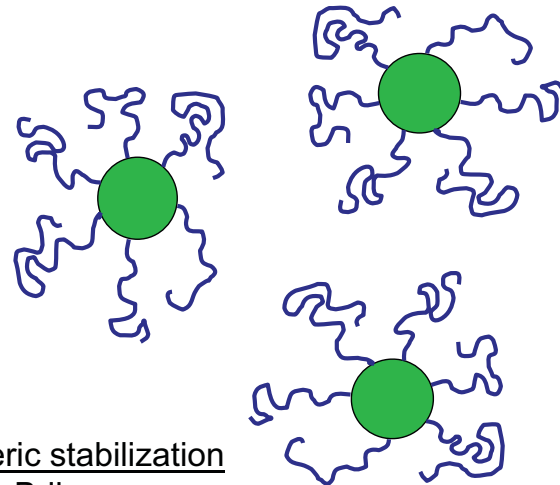
Particles are in random motion and they collide with each other.



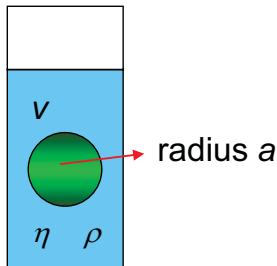
How to modify the forces that act between the particles?



Charge stabilization



Steric stabilization
Eg. Brij₇₀₀



Colloidal Particle in a Liquid

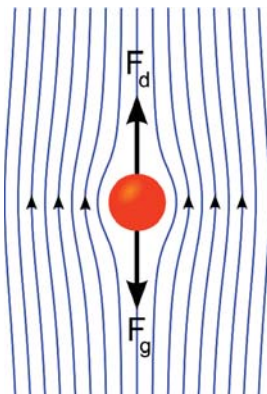
The drag is given by Reynold's number as:

$$R_e = \frac{\rho v a}{\eta} = \frac{\rho v}{\eta / a} \quad \text{Inertial forces/Viscous forces}$$

Relative importance of inertia and viscosity in the drag mechanism.

For colloidal particles R_e is very low (viscous-force dominated regime)

The drag force F_s is given by Stoke's law as: $F_s = 6 \pi \eta a v$



If the difference in density between the sphere and the liquid is $\Delta\rho$, the gravitational force F_g is:

$$F_g = \frac{4}{3} \pi a^3 \Delta\rho g$$

When the drag force and the gravitational force is balanced, the terminal velocity is given by:

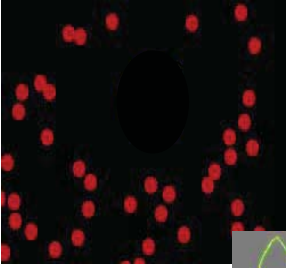
$$F_s = F_g \quad \longrightarrow$$

$$v_t = \frac{2a^2 \Delta\rho g}{9\eta}$$

This gives relevant kinetic energy for colloids?



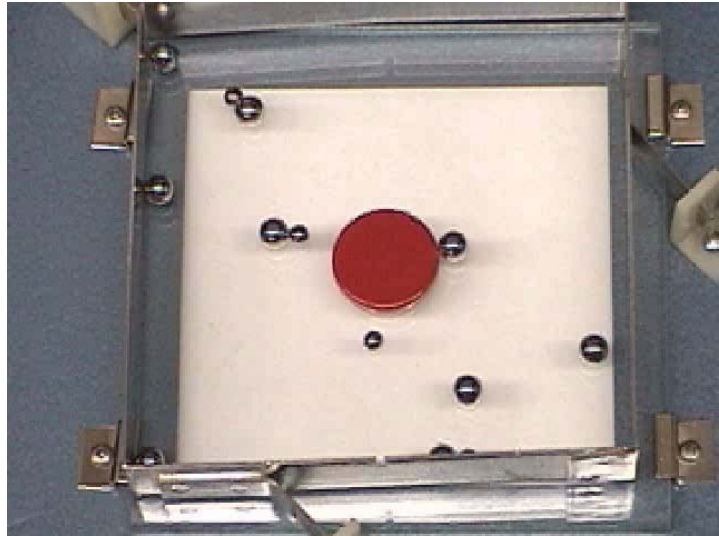
Brownian Motion and Einstein equation



Random motion of colloidal particles, polymers, micelles etc.

Colloidal particles as being constantly bombarded by the random impacts of the molecules of the solution

Random-walk



In a random walk the mean of the total displacement is always zero:

$$\langle \mathbf{R}(t) \rangle = 0$$

But the mean value of the square of the displacement is proportional to the number of steps, and thus the time:

$$\langle (\mathbf{R}(t))^2 \rangle = \alpha t \quad \text{How we can find } \alpha ?$$

Brownian Motion and Einstein equation

Equation of Motion:

$$m \frac{d^2 \mathbf{R}}{dt^2} + \xi \frac{d\mathbf{R}}{dt} = \vec{F}_{random}$$

Drag force proportional to the velocity

Re number is very low, so the Stokes law can be applied:

$$F_s = 6\pi\eta a v \rightarrow \xi = 6\pi\eta a$$

The movements for x, y and z directions are not correlated so, it is sufficient to obtain the results just for x:

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle \rightarrow \langle \mathbf{R}^2 \rangle = 3\langle x^2 \rangle$$

1D Equation of Motion:

$$m \frac{d^2 x}{dt^2} + \xi \frac{dx}{dt} = F_{random}$$

Brownian Motion and Einstein equation

Now:
$$\frac{d(x^2)}{dt} = 2x \frac{dx}{dt}$$

We multiply the 1D equation of motion by x :

$$m x \frac{d^2 x}{dt^2} + \xi x \frac{dx}{dt} = x F_{random} \rightarrow m x \frac{d^2 x}{dt^2} + \frac{\xi}{2} \frac{d(x^2)}{dt} = x F_{random}$$

Now:
$$\frac{d}{dt} \left(x \frac{dx}{dt} \right) = \left(\frac{dx}{dt} \right)^2 + x \frac{d^2 x}{dt^2} \rightarrow x \frac{d^2 x}{dt^2} = \frac{d}{dt} \left(x \frac{dx}{dt} \right) - \left(\frac{dx}{dt} \right)^2$$

Substituting:

$$m \frac{d}{dt} \left(x \frac{dx}{dt} \right) - m \left(\frac{dx}{dt} \right)^2 + \frac{\xi}{2} \frac{d(x^2)}{dt} = x F_{random}$$

Averaging we have:
$$m \frac{d}{dt} \left(\left\langle x \frac{dx}{dt} \right\rangle \right) - m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle + \frac{\xi}{2} \frac{d \langle (x^2) \rangle}{dt} = \langle x F_{random} \rangle$$

From the Theorem of equipartition of energy:
$$\frac{mv_x^2}{2} = \frac{k_B T}{2} \rightarrow m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle = k_B T$$

So,

$$\frac{\xi}{2} \frac{d \langle (x^2) \rangle}{dt} = m \left\langle \left(\frac{dx}{dt} \right)^2 \right\rangle \rightarrow \frac{\xi}{2} \frac{d \langle (x^2) \rangle}{dt} = k_B T \rightarrow \frac{d \langle (x^2) \rangle}{dt} = 2 \frac{k_B T}{\xi}$$

Integrating on t

$$\langle (x^2) \rangle = 2 \frac{k_B T}{\xi} t \rightarrow \langle (\mathbf{R}^2) \rangle = 6 \frac{k_B T}{\xi} t$$

Mean Displacement

$$\lambda_x = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

We can define the diffusion coefficient D :

$$D = \frac{k_B T}{\xi}$$

Stokes-Einstein equation:

$$D_{SE} = \frac{k_B T}{6\pi\eta a}$$

Using the Stokes equation, $\xi = 6\pi\eta a$

Using light scattering we can obtain the diffusion coefficient from the colloidal solution and calculate the particle size using this equation

Forces between colloidal particles.

1. Inter-atomic & Inter-particle forces.
2. van der Waals forces.
3. Electrical double layer forces.
4. Stabilization with grafted polymers.
5. Depletion interactions.

Inter-atomic & Inter-particle forces

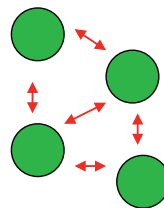
Acrylic polymer spheres of radius 100 nm.

Interfacial energy of each particle is 2×10^{-15} J.

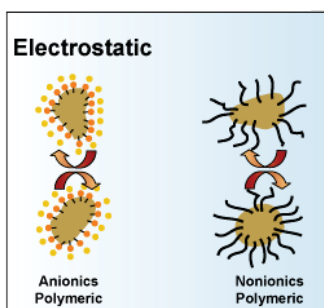


Larger than $k_B T$

Should lead to unstable product



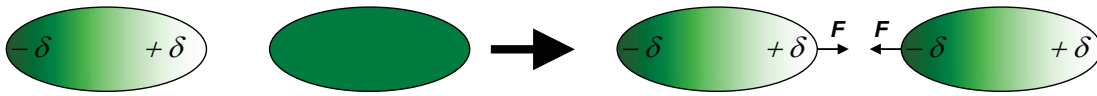
Steric stabilization
or
Charge stabilization



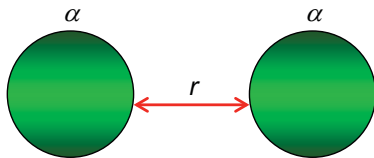
Free charges dissolved in the solvent prevents instability

van der Waals forces

These interactions arise between uncharged, weakly interacting atoms & molecules. Their origin can be understood using quantum mechanics and arises from the interaction between fluctuating dipoles in each atom. It is very weak $\sim k_B T$.



Spherical atom with radius a :



The potential $V(r)$ is:

$$V(r) = -\frac{3}{4} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\alpha^2}{r^6} \hbar\omega$$

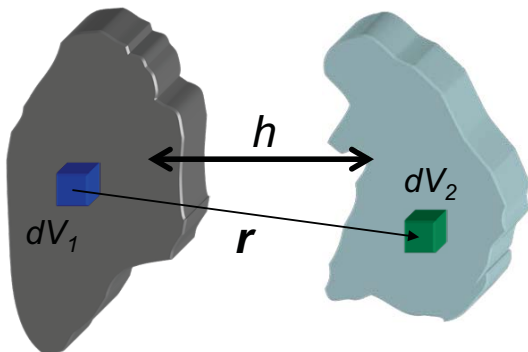
↓
Ionization energy

Interaction is not strongly directional.

Dispersion interactions between molecules on each particle causes attractive van der Waals forces in colloidal systems.

Effective interaction = Total potential = Sum of potentials between the pairs of molecules. i.e. Pair-wise additive and multi-body interaction is neglected.

Since we know the potential between the atoms ($-C/r^6$), the TOTAL POTENTIAL $U(h)$ between two macroscopic bodies as a function of their separation h can be calculated over a double integral over the volumes of each of the bodies:



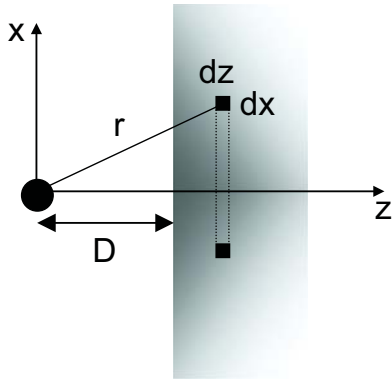
$$U(h) = \iint -\frac{C}{r^6} \rho_1 dV_1 \rho_2 dV_2$$

↓
Atomic number density of the volume element.

It depends on the shape and separation of the colloidal particles.

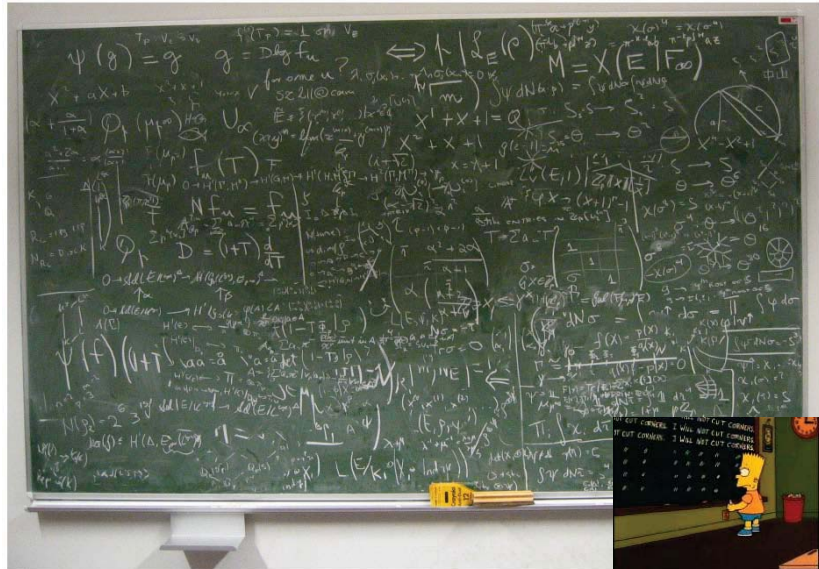
Single atom and semi-infinite Wall

Van der Waals Forces



$$dw(D) = -\frac{2\pi\rho dx dz C}{r^6} = -\frac{2\pi\rho dx dz C}{(z^2 + x^2)^3}$$

$$r = (z^2 + x^2)^{1/2}$$



Two flat infinite surfaces in vacuum.

Hamaker constant

$$U(h) = -\frac{A_H}{12\pi h^2}$$

$$A_H = \pi C \rho_1 \rho_2$$

For many materials $A_H \sim 10^{-19} \text{J}$

van der Waals interaction free energies between bodies of different geometries

| | |
|--|---|
| <p>Two atoms</p> <p>$w = -C/r^6$</p> | <p>Two spheres</p> <p>$W = -\frac{A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$</p> |
| <p>Atom-surface</p> <p>$w = -\pi C \rho / 6D^3$</p> | <p>Sphere-surface</p> <p>$W = -AR/6D$</p> |
| <p>Two parallel chain molecules</p> <p>$W = -3\pi CL/8\sigma^2 r^6$</p> | <p>Two cylinders</p> <p>$W = \frac{AL}{12\sqrt{2} D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$</p> |
| <p>Two crossed cylinders</p> <p>$W = -A/\sqrt{R_1 R_2} / 6D$</p> | <p>Two surfaces</p> <p>$W = -A/12\pi D^2$ per unit area</p> |

Two spherical particles in vacuum.

Derjaguin approximation $h \ll R$

$$U(h) = -\frac{A_H R}{12h}$$

$h \gg R$

$$U(h) = -\frac{16}{9} A_H \frac{R^6}{h^6}$$

A_H : the effective strength of van der Waals interaction between colloidal particles.

Hamaker constants (10^{-20} J)

| Material (M) | M air M | M water M |
|---------------------------|-----------|-------------|
| Alkanes | | |
| $n = 5$ | 3.75 | 0.336 |
| 6 | 4.07 | 0.360 |
| 7 | 4.32 | 0.386 |
| 8 | 4.50 | 0.410 |
| 9 | 4.66 | 0.435 |
| 10 | 4.82 | 0.462 |
| 11 | 4.88 | 0.471 |
| 12 | 5.04 | 0.502 |
| 13 | 5.05 | 0.504 |
| 14 | 5.10 | 0.514 |
| 15 | 5.16 | 0.526 |
| 16 | 5.23 | 0.540 |
| Fused quartz | 6.50 | 0.833 |
| Cryst. quartz | 8.83 | 1.70 |
| Water | 3.70 | 0 |
| Fused silica | 6.55 | 0.849 |
| Calcite | 10.1 | 2.23 |
| Calcium fluoride | 7.20 | 1.04 |
| Sapphire | 15.6 | 5.32 |
| Poly(methylmethacrylate) | 7.11 | 1.05 |
| Poly(vinylchloride) | 7.78 | 1.30 |
| Polystyrene | 6.58 | 0.950 |
| Poly(isoprene) | 5.99 | 0.743 |
| Poly(tetrafluoroethylene) | 3.80 | 0.333 |
| Mica (brown) | — | 1.98 |
| Mica (green) | — | 2.14 |

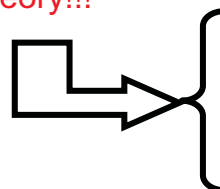
Limitations of this simple approach

1. The assumption of pairwise additivity of forces is strictly incorrect because the fluctuating dipoles in any pair of atoms is influenced by all the other atoms in the system and not only by the atoms in the pair
2. For larger separations (10nm and greater) the effects of finite speed of propagation of fields arising from the fluctuating dipoles become significant – **Casimir effect**

Retardation effect : r^{-6} \rightarrow r^{-7}

Two infinite sheets : h^{-2} \rightarrow h^{-3}

Quantum field Theory!!!



$$U(h) = -\frac{A_H}{12\pi h^2}$$

Lifshitz theory for the Hamaker constant A_H

Last time...

- Colloids ($10^{-9} - 10^{-6}$) – many peculiarities

- Brownian Motion

$$\langle (x^2) \rangle = 2 \frac{k_B T}{\xi} t \rightarrow \langle (\mathbf{R}^2) \rangle = 6 \frac{k_B T}{\xi} t$$



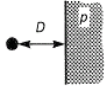
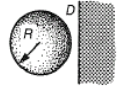
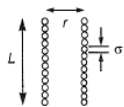
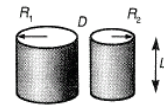
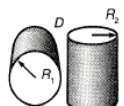
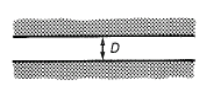
$$D_{SE} = \frac{k_B T}{6\pi\eta a} \quad \lambda_x = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

Last time...

- van der Waals Forces

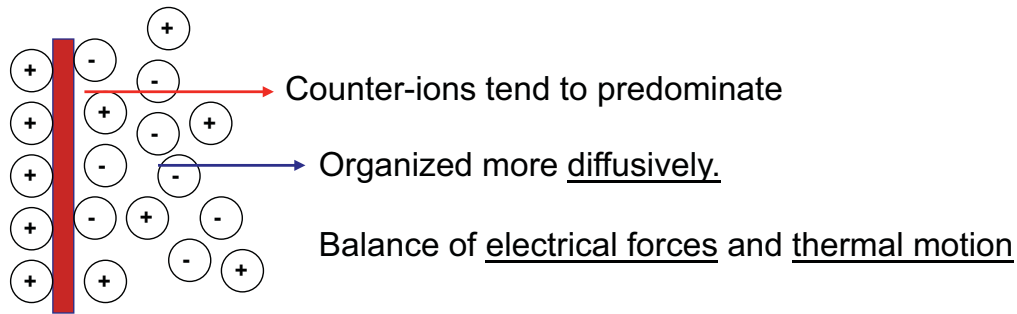
- Very weak for a single pair of atoms
- Additive character
- The net interaction depends on the geometry and shape of the bodies

van der Waals interaction free energies between bodies of different geometries

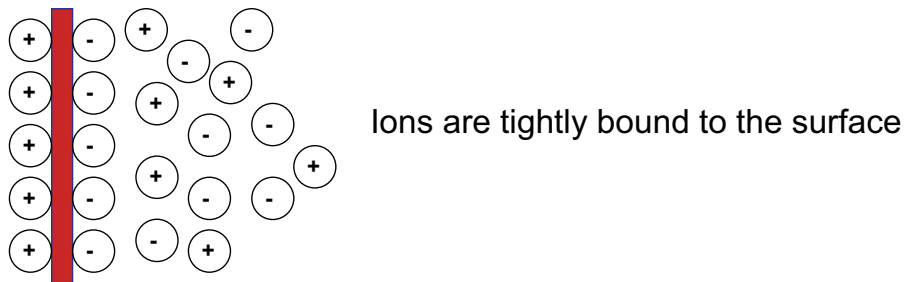
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| <p>Two crossed cylinders</p>  <p>$W = -A/\sqrt{R_1 R_2}/6D$</p> | <p>Two surfaces</p>  <p>$W = -A/12\pi D^2$ per unit area</p> |

Electrostatic double layer forces

A charged surface attracts counter-ions leading to the formation of an ionic atmosphere.



Diffuse double layer model

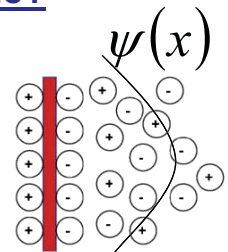


Stern model

How can we determine the concentration profile?

The density of the ions will be described by the Boltzmann equation

$$n(z) = n_0 \exp\left(\frac{-ze\psi(x)}{k_B T}\right)$$



The potential $\psi(x)$ can be determined by the Poisson Equation:

$$\nabla^2 \psi(\vec{x}) = -\frac{\rho}{\epsilon \epsilon_0} \quad \text{In 1D: } \rho(z) = -\epsilon \epsilon_0 \left(\frac{d^2 \psi}{dx^2}\right)$$

In the simplest case where the only ions present are the counterions needed to balance the charge on the surface, $\rho = ze$ and we obtain the Boltzmann-Poisson equation:

$$\frac{d^2 \psi(x)}{dx^2} = -\left(\frac{ze n_0}{\epsilon \epsilon_0}\right) \exp\left(\frac{-ze\psi(x)}{k_B T}\right)$$

The surface might be in contact with a univalent salt as, for example, sodium chloride and in this way we will have both positive and negative ions with concentrations n_+ and n_- to consider:

$$n_{\pm} = n_0 \exp\left(\mp \frac{ze\psi(x)}{k_B T}\right)$$

Typo in the Book !

The net charge density will be: $\rho = ze(n_+ - n_-)$ \longrightarrow $\left(\frac{d^2 \psi}{dx^2}\right) = -\frac{ze}{\epsilon \epsilon_0} (n_+ - n_-)$

How can we determine the concentration profile?

So,
$$\frac{d^2\psi(x)}{dx^2} = -\left(\frac{zen_0}{\epsilon\epsilon_0}\right)e^{\left(\frac{-ze\psi(x)}{k_B T}\right)} + \left(\frac{zen_0}{\epsilon\epsilon_0}\right)e^{\left(\frac{ze\psi(x)}{k_B T}\right)} = \left(\frac{zen_0}{\epsilon\epsilon_0}\right)\left(e^{\left(\frac{ze\psi(x)}{k_B T}\right)} - e^{\left(\frac{-ze\psi(x)}{k_B T}\right)}\right)$$

Now,
$$\sinh x = \frac{e^x - e^{-x}}{2} \longrightarrow 2 \sinh\left(\frac{ze\psi(x)}{k_B T}\right)$$

Which gives
$$\frac{d^2\psi(x)}{dx^2} = \frac{2zen_0}{\epsilon\epsilon_0} \sinh\left(\frac{ze\psi(x)}{k_B T}\right)$$

If the potential is small, $ze\psi(x) \ll k_B T$ (*Debye-Huckel approximation*)

$$\sinh x = x + \frac{1}{6}x^3 + \frac{1}{120}x^5 + \frac{1}{5040}x^7 + \dots \Rightarrow \sinh\left(\frac{ze\psi(x)}{k_B T}\right) \approx \frac{ze\psi(x)}{k_B T}$$

We will have,

$$\frac{d^2\psi(x)}{dx^2} = \left(\frac{2z^2e^2n_0}{k_B T \epsilon\epsilon_0}\right)\psi(x)$$

The solution is,

$$\psi(x) = \psi_0 \exp(-\kappa x) \quad \kappa = \left(\frac{2e^2n_0z^2}{\epsilon\epsilon_0 k_B T}\right)^{1/2}$$

The result can be generalized to a solvent with many different ions:

$$\kappa = \left(\frac{e^2 \sum_i c_i z_i^2}{\epsilon\epsilon_0 k_B T}\right)^{1/2}$$

The sum is over all the types of ions.

$1/\kappa$ is called the Debye screening length. Provides first estimate of (i) the distance beyond which Coulomb interactions can essentially be ignored and (ii) size of the region near a point charge where opposite-charge counterions can be found.

Typical Values:

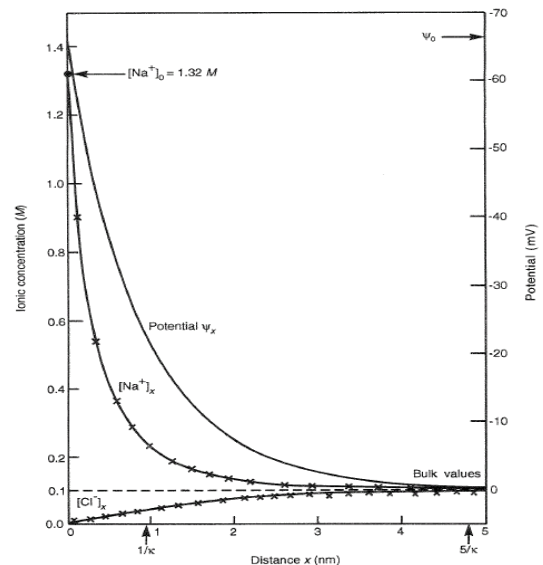
$$1/\kappa = \begin{cases} 0.304/\sqrt{[\text{NaCl}]} \text{ nm} & \text{for 1:1 electrolytes (e.g., NaCl)} \\ 0.176/\sqrt{[\text{CaCl}_2]} \text{ nm} & \text{for 2:1 and 1:2 electrolytes} \\ & \text{(e.g., CaCl}_2 \text{ and Na}_2\text{SO}_4\text{)} \\ 0.152/\sqrt{[\text{MgSO}_4]} \text{ nm} & \text{for 2:2 electrolytes (e.g., MgSO}_4\text{)} \end{cases}$$

0.1mM NaCl solution : $1/\kappa = 30.4 \text{ nm}$

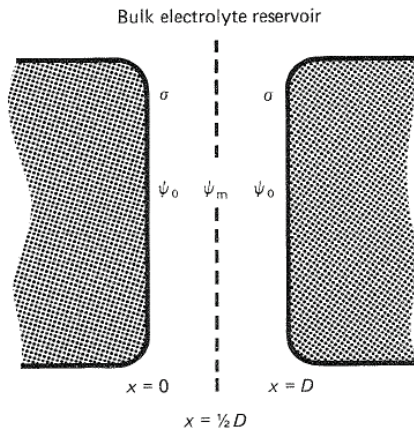
1.0mM NaCl solution : $1/\kappa = 9.6 \text{ nm}$

1.0M NaCl solution : $1/\kappa = 0.3 \text{ nm}$

Pure water, pH7: $1/\kappa = 960\text{nm} \sim 1 \mu\text{m}$



What happens when two equally charged plates are brought together?



In vacuum one would find a repulsion due to the electrostatic forces. However, in solution the attracted counterions will maintain the charge neutral.

Indeed, it will be the excess osmotic pressure of the counterions in the gap that will lead to the repulsive force. In the limit of **large separations** and **low surface potentials**, the pressure between the plates will be:

$$P = 64k_B T n_0 \tanh^2 \left(\frac{ze\psi_0}{4k_B T} \right) \exp(-\kappa D)$$

What about short separations? —————> DLVO theory (Derjaguin, Landau, Verwey, Overbeck)

The total interaction between the double layer MUST include van der Waals interactions:

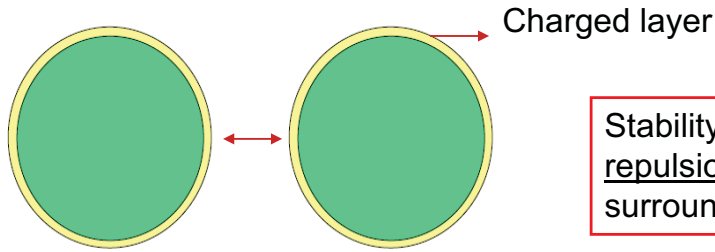
- Unlike the double layer interaction the van der Waals interaction potential is largely insensitive to the variation in electrolyte concentration and pH.
- van der Waals attraction must always exceed the double layer repulsion at small enough distances

Stabilizing Colloidal Systems

Stability surrounding the colloidal particle can be obtained by:

- With an electrical double layer (electrostatic or charge stabilization).
- With adsorbed or chemically attached polymeric molecules (steric stabilization).
- With free polymer in the dispersion medium (depletion stabilization).

Electrostatic or Charge Stabilization



Stability is provided by the mutual repulsion of electrical double layer that surrounds the particles.

Empirical observations on the dependence of electrical double layer
(Schulze-Harvey rule).

-- Double layer depends predominantly on the **ionic strength of the dispersion medium** and less predominantly on the valence of the co-ion, concentration of the sol, and nature of the sol.

The ionic strength of the dispersion medium can be expressed as:
$$I = \frac{1}{2} \sum_i z_i^2 c_i$$

Valence of ions i Molar concentration of the ions

For a 1:1 electrolyte, I is proportional to the concentration. Let us then represent ionic strength by the concentration c .

At low ionic strength (electrolyte $c = 10^{-3}$ M): thickness of double layer is about 5 – 10 nm (same order as VDW attraction). This explains the charge stabilization in dispersions of low ionic strength.

At high ionic strength ($c > 10^{-1}$ M): thickness of the double layer is less than 1 nm. The range of double layer repulsion is usually insufficient to counterbalance the VDW attraction. This explains the coagulation of the dispersion with increasing ionic strength.



Demerits of charge stabilization:

- Great sensitivity to ionic strength of the dispersion medium.
- Works only in polar liquids that can dissolve the electrolytes.
- Most effective only in low concentrations.

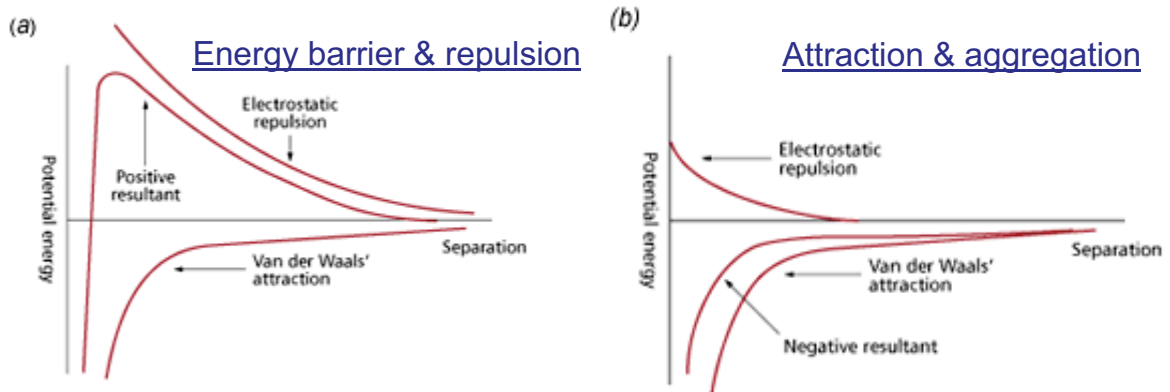


Still widely used due to simplicity and low cost price.

Potential Energy curves

As particles approach each other the electrical force **increase exponentially**.

The attractive forces increase as an **inverse power of separation**.



Forces between molecules are a balance of repulsive (short distance) + attractive (larger length scale)

The Lennard-Jones potential:
$$V(r) = 4\epsilon \left[\underbrace{\left(\frac{r_0}{r}\right)^{12}}_{\text{Repulsive}} - \underbrace{\left(\frac{r_0}{r}\right)^6}_{\text{Attractive}} \right]$$

DLVO Theory: Derjaguin-Landau-Verwey-Overbeek theory.

Useful tool for understanding the stability of colloids.

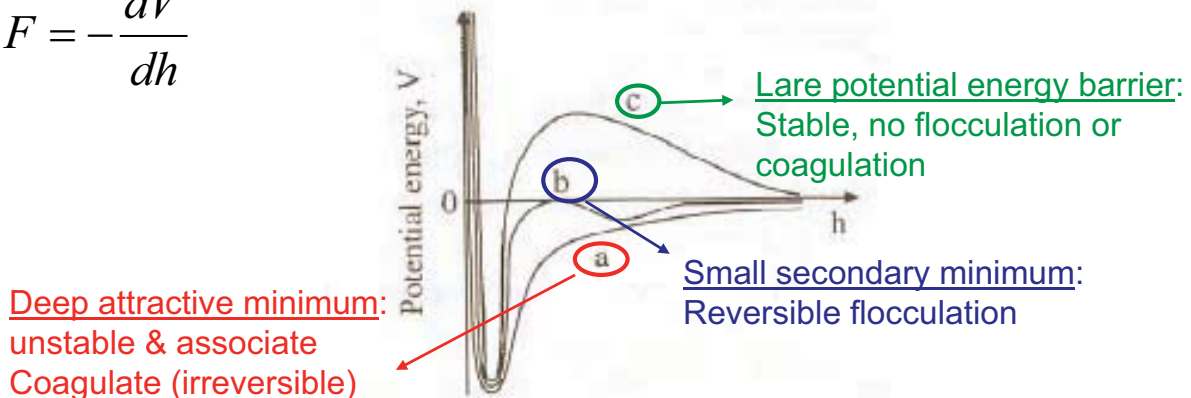
Allows for forces between electrical double layer (repulsive) and long range VDW forces (attractive)

Total interaction = sum of (Attractive interactions + Repulsive interactions).

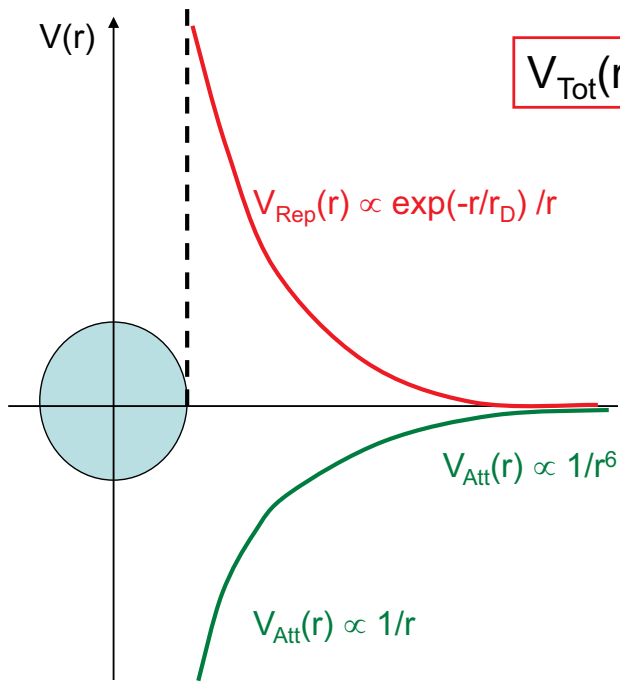
$$V_{Tot}(r) = V_{Att}(r) + V_{Rep}(r)$$

Force = negative gradient of V with respect to distance h of the colloidal particles.

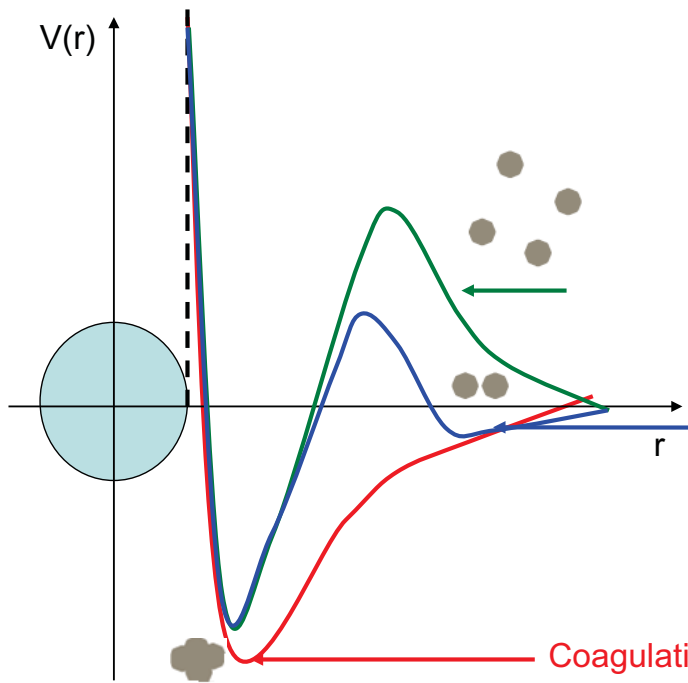
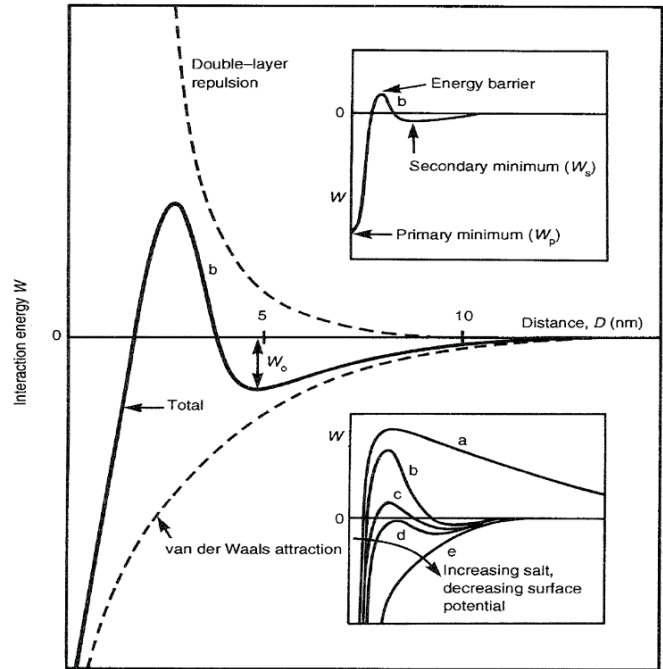
$$F = -\frac{dV}{dh}$$



DLVO Theory: Derjaguin-Landau-Verwey-Overbeek theory.



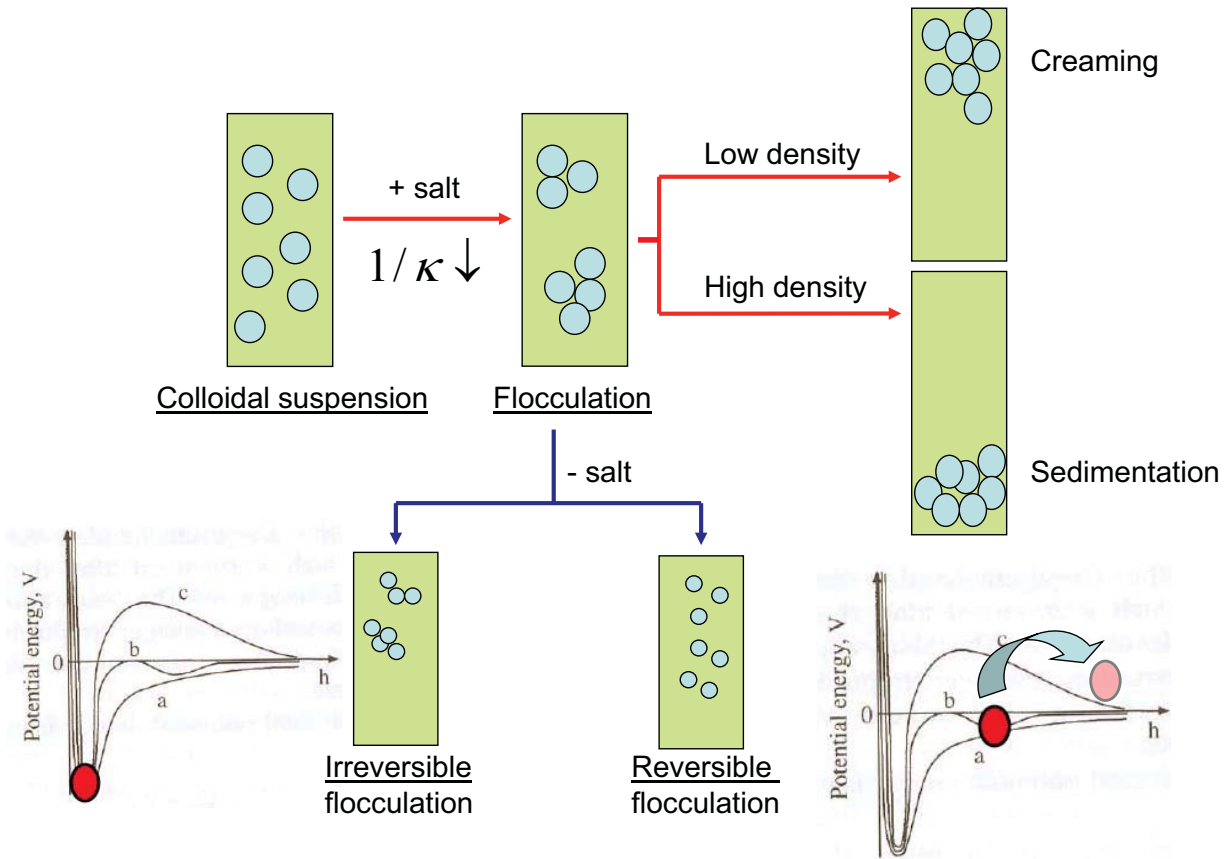
$$V_{\text{Tot}}(r) = V_{\text{Rep}}(r) + V_{\text{Att}}(r)$$



$$\text{SALT concentration } C > C > C$$

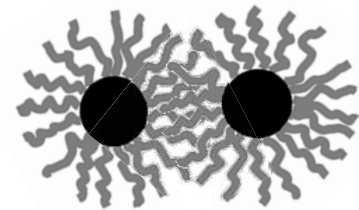
The system is unstable at high and intermediate salt concentration

Simple Experiment

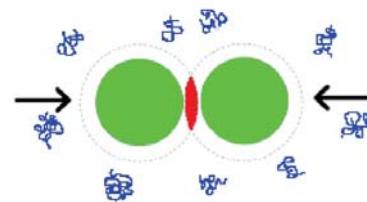


Stabilization using polymers

Steric stabilization

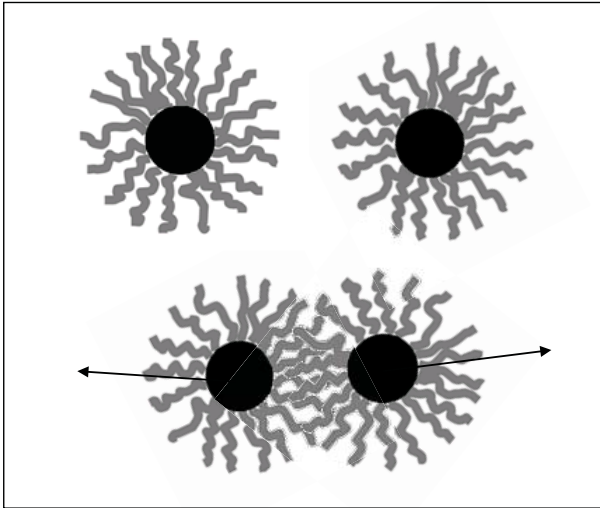


Depletion stabilization



Steric Stabilization

I like the lady but can't trust the snake



For a polymer to be effective at stabilizing the colloid the solvent must be a good solvent.

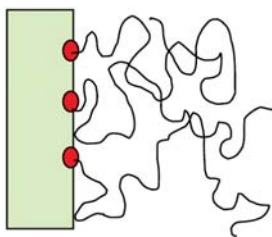
The range of interaction is governed by the distance from the surface that the polymer chains extend.

For polymers with molecular weight > 10,000 D, the chain dimensions are comparable to, or in excess of, the range of VDW attraction.

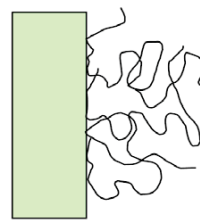
Limited interpenetration of chains leads to effective repulsion.

Steric stabilization

Achieved by attaching (grafting or chemisorption) macromolecules to the surface of the particles.

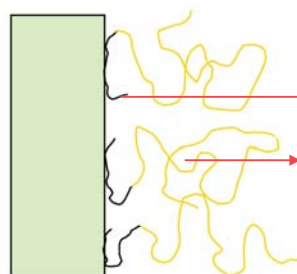


Chemical adsorption
(grafted polymers)



Physical adsorption
(homopolymers)

Requires a good solvent
& a bad surface.



Anchor group

Soluble group

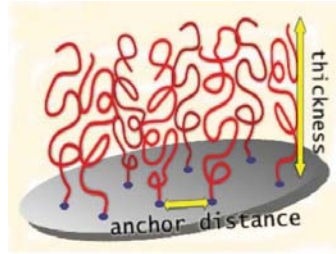
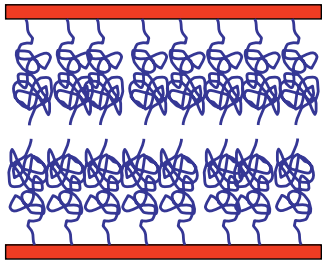
Physical adsorption
(block polymers)

• Best steric stabilizers

- No dependence on ionic strength.
- Organic/aqueous solvents.
- Wide range of concentration.

Morphologies of Grafted Polymer Layers: Effect of Solvent

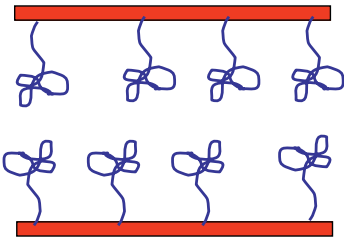
Good solvent



Stretched away from grafting point.

- Local density of segments increase.
- Osmotic tendency (from medium).
- Repulsion.

High grafting density: polymer brushes



Less stretched conformation.

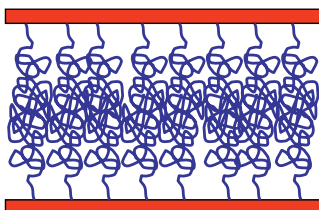


- Local density of segments decrease.
- Conformation increase.
- Entropy increase.
- Attraction.

Low grafting density: polymer mushrooms

Morphologies of Grafted Polymer Layers: Effect of Solvent

Poor solvent



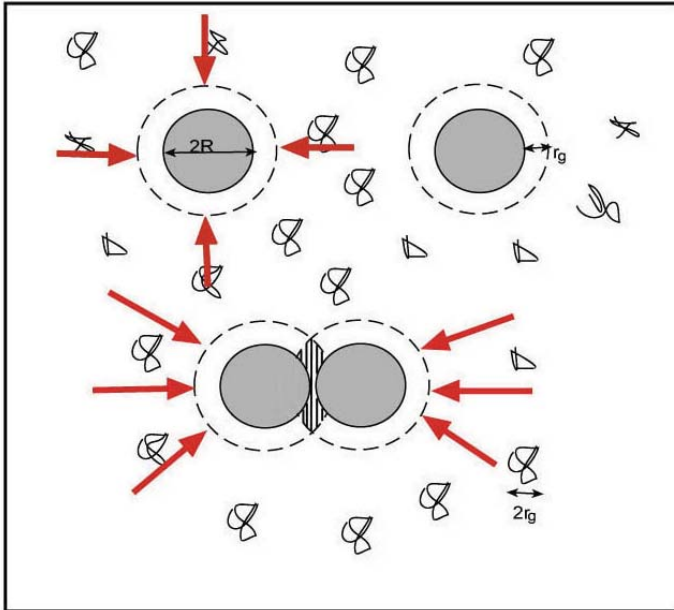
- Chains avoid contact with solvent.
- Approaches through intervening polymer layer.
- Attraction.

Effective at intermediate length-scale (flocculation).
Short distance: repulsion is dominant.

Importance of solvent quality

Depletion Interactions

- Free non-adsorbing polymer in a good solvent.
- Polymer chains are excluded from the region between the particles.
- Occurs when the R_g of the polymer is greater than the interparticle separation.



Leads to osmotic compression (net flow of polymer between colloid particles into the bulk solution).

Attractive potential.

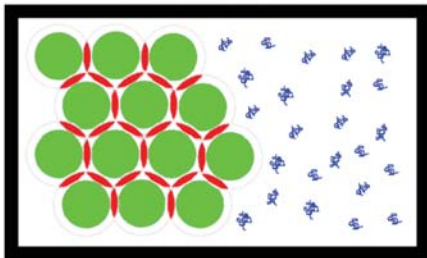
$$v(r) = -\pi V_o(r)$$

The range and strength can be varied: varying M_w & concentration.

To fuse biological cells in aqueous solution using poly(ethylene glycol).

This is used in protein crystallography to induce protein crystallization

Depletion Interactions

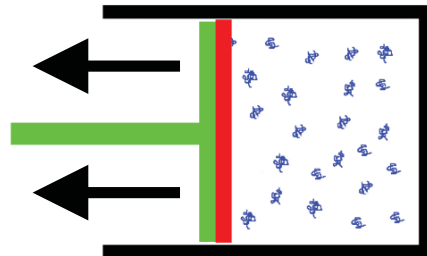


It can be understood as the increasing of volume. The osmotic pressure P_{osm} is given by the ideal gas expression:

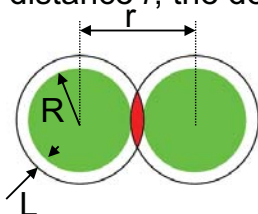
$$P_{osm} = \frac{N}{V} k_B T$$

The net interaction potential between the particles, F_{dep} is simply

$$F_{dep} = -P_{osm} V_{dep}$$



For two spherical particles with radius R and depletion zones L separated at a distance r , the depletion volume is:



$$V_{dep} = \frac{4\pi}{3} (a + L)^3 \left(1 - \frac{3r}{4(a + L)} + \frac{r^3}{16(a + L)^3} \right)$$

Typo in the book!

Stability and phase behavior of colloids

- There are many ways to tune the interaction between colloidal particles from repulsive to attractive:
 - **Add salt** to an electrostatically stabilized colloid, reducing the Debye screening length and decreasing the magnitude of the electrostatic repulsion relative to the van der Waals attraction
 - **Add poor solvent** to a polymerically stabilized colloid: the resulting attractive polymer/polymer interactions will lead to a net attraction between the colloid particles
 - **Physically or chemically remove** grafted polymer chains from the surface of the colloidal particles
 - **Add non-adsorbing polymer** to cause an increase of the size of the depletion interaction

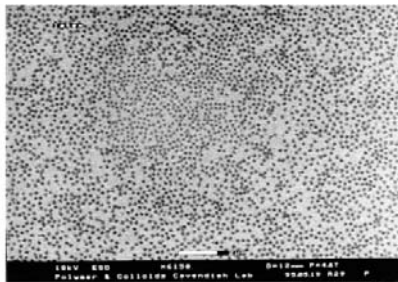


Figure 1. Core-shell latex (15% w/w) at 1.8 °C, 4.6 r. Polymer latices are in Brownian motion. Although there are some small regions of aggregation, overall there are no significant areas of aggregation.

Crystallisation of hard-sphere colloids

$$V(r) = \begin{cases} \infty & , r \leq R \\ 0 & , r > R \end{cases}$$

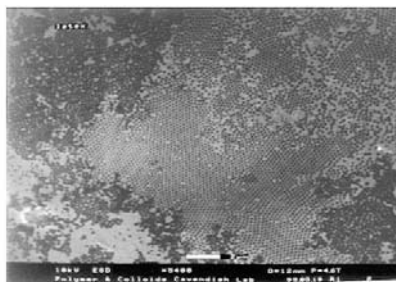
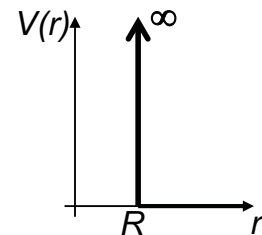


Figure 2. Sample as Figure 1. As evaporation of water proceeds, the polymer latices exhibit partial ordering.

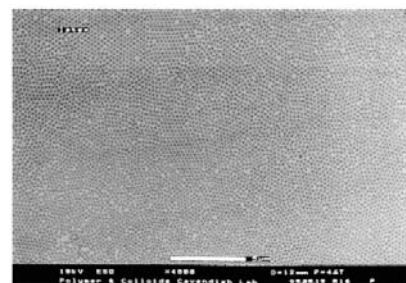


Figure 3. Sample as Figure 1. At late stages, when the particle concentration is high, the polymer latices mainly exhibit a honeycomb packing structure (for hexagonal arrangement).

Langmuir 1996, 12, 6250–6256

Morphology of Core-Shell Polymer Latices during Drying

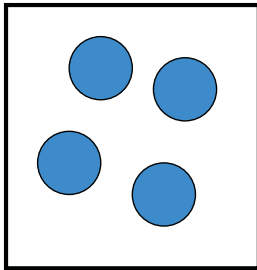
Chaobin He and Athene M. Donald*

Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, U.K.

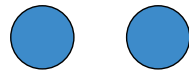
Received April 29, 1996. In Final Form: August 23, 1996⁹

Understanding Colloidal Crystallization

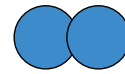
The Hard-Sphere Model



Assembly of **perfect spheres** that interact through a **potential**.



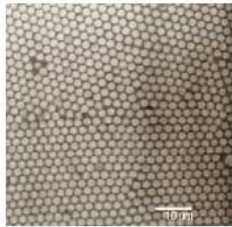
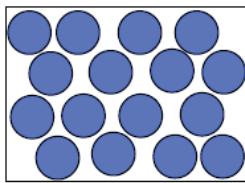
Potential = 0



Potential = ∞

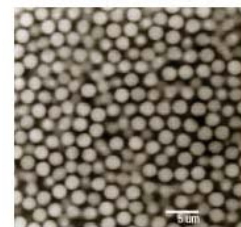
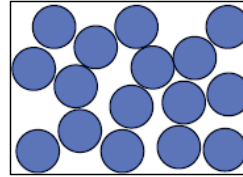
What happens on packing ?

Regular close-packed structure



Maximum density at $\phi = 0.74$

Random close-packed structure



Maximum density at $\phi = 0.63$

At high ϕ simple packing constraints force the spheres to a close-packed crystalline structure.

Crystallisation of hard-sphere colloids

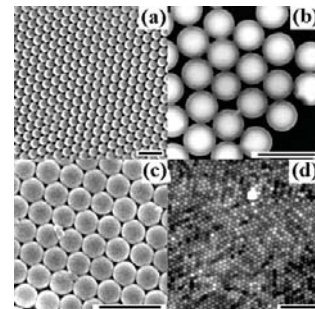
Volume Fractions:

Perfect Close-packed structure : 0.7404

Random Close packing : 0.63

However, crystals appear at much lower volume fraction. At a volume fraction of 0.494 there is an abrupt transition to a crystal with a volume fraction of 0.545 : **WHY?**

→ Entropy!



Perfect gas: $S_{ideal} = k_B \ln \left(a \frac{V}{N} \right)$

If the gas atoms have a finite volume b:

$$S = k_B \ln \left(a \frac{(V - Nb)}{N} \right)$$

We can rewrite it as: $S = S_{ideal} + k_B \ln \left(1 - \frac{bN}{V} \right)$

If $bN \ll V$, we use

$$\log(1 - x) = -x - \frac{1}{2}x^2 - \frac{1}{3}x^3 + \dots$$

$$S = S_{ideal} - k_B \left(\frac{N}{V} \right) b$$

The free energy is: $F = F_{ideal} + k_B T \left(\frac{N}{V} \right) b$

There is an effective repulsion between the atoms which might causes the particle to arrange themselves on a crystal lattice

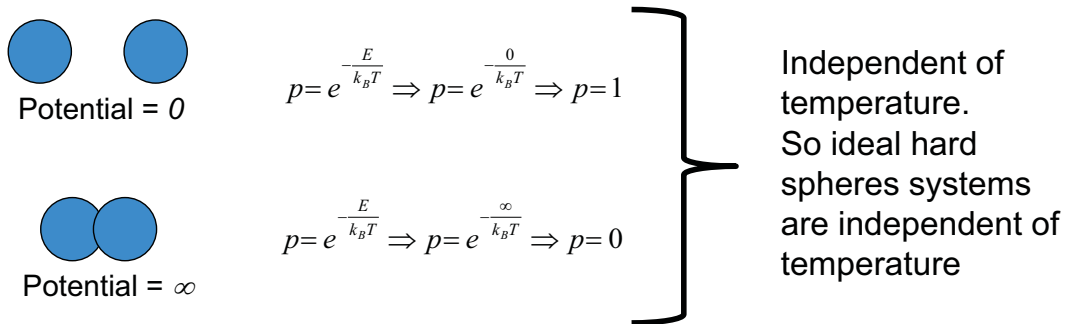


In reality the problem is much more complicated because multibody interaction must be included in the calculation (or simulation)!

What about temperature in Hard sphere crystallization

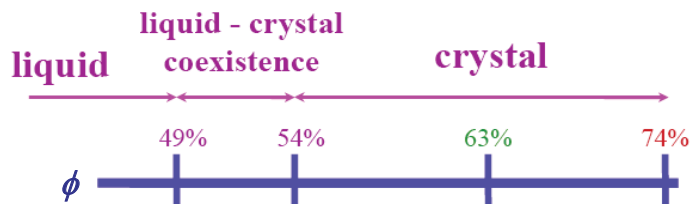
The probability of an configuration is proportional to the Boltzman factor for the particular energy E of that state.

For hard sphere interactions we have only two situations:



In real systems is not possible to have infinitely abrupt hard sphere potentials and the. The width of the potential will change with temperature.

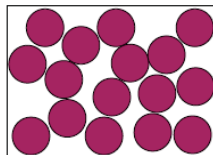
Crystals appear at a much lower volume fraction of spheres.



Sphere suspension with an intermediate volume fraction will separate into two coexisting phases.

Molecular Packing Entropy drives the crystallization.

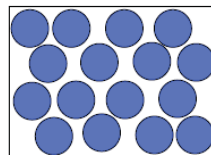
Disordered



- Higher Translational entropy
- Lower fluctuation entropy (locally, some particles might be jammed)

Maximum packing at $\phi = 0.63$

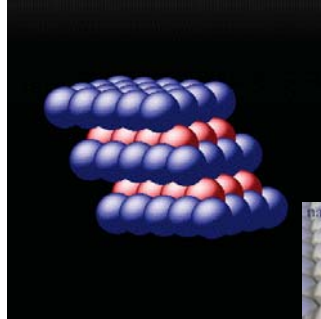
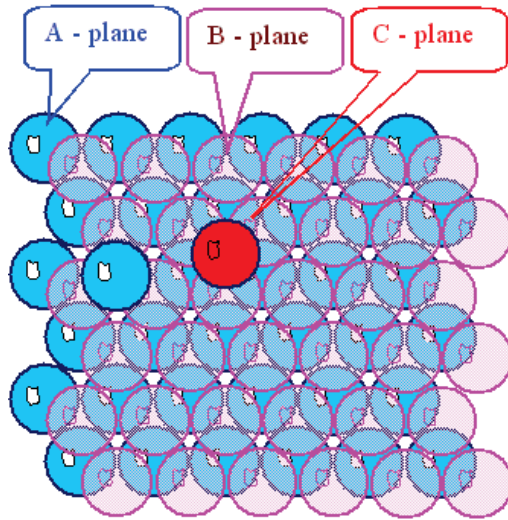
Ordered



- Lower Translational entropy (long-range)
- Higher fluctuation entropy (locally, each particle has more space to explore)

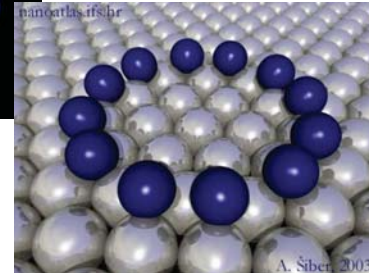
Maximum packing at $\phi = 0.74$

Single-Close Packed Layer

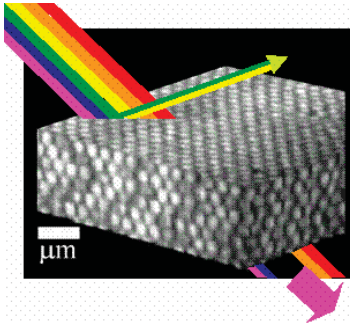


HCP: **abababab**

FCC: **abcabcabc**



Face-centered cubic (FCC) & Hexagonal close packed structures.

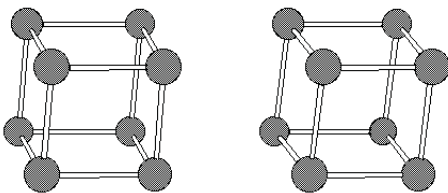


Mainly HCP structures with large **stacking faults** (photonic bandgap materials).

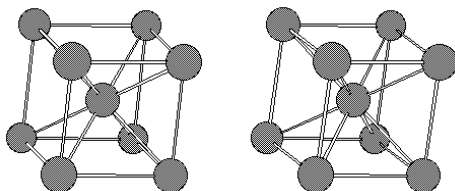
Crystal structure should be largely **defect free** for such effects.

Packing of spheres

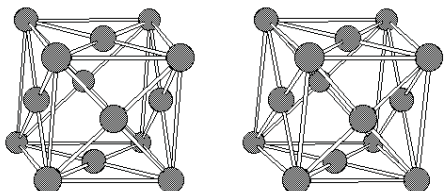
Simple Cubic (SC) : $\phi=0.52$



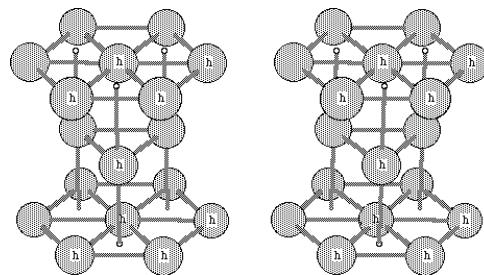
Body Centered Cubic (BCC): $\phi=0.68$



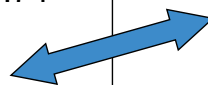
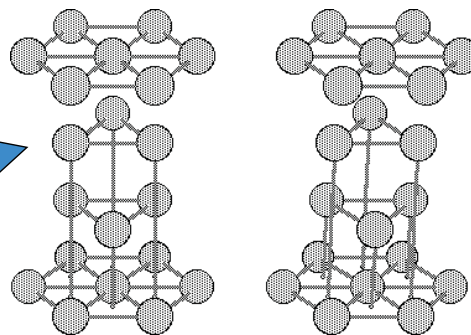
Face Centered Cubic (FCC): $\phi=0.74$



HCP coordination : $\phi=0.74$



Cubic Closest Packing : $\phi=0.74$



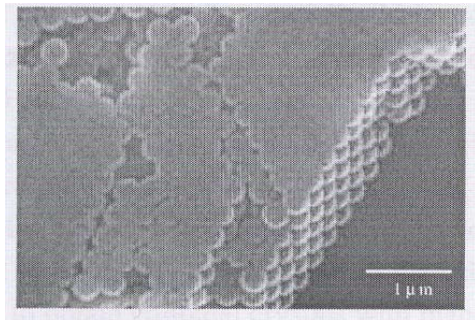
Self-assembly of Monodispersed Colloidal Particles

Sedimentation in a gravitational field

Commonly used technique of making colloidal crystals.

Efficient and simple method to get multilayer assemblies.

SEM image of colloidal crystals (multi layer structure) of polystyrene particles.



Demerit:

Limitation in size range. particles < 300 nm deposit very slowly.

Particles > 550 nm deposit too fast

Poor periodicity & uneven surface topology.

Slow sedimentation on a template: *Colloidal epitaxy*.

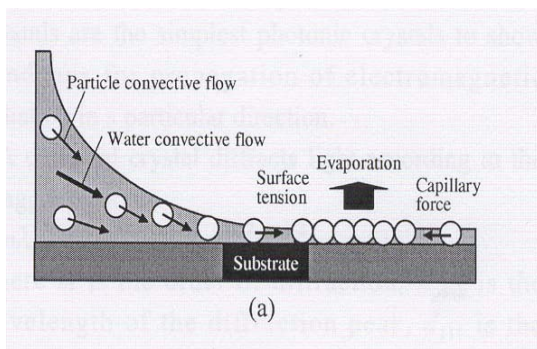
Leads to tailoring of lattice structure, orientation and size of the crystals.

Self-assembly of Monodispersed Colloidal Particles

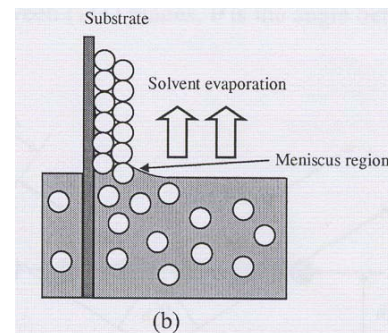
Solvent Evaporation

Self-assembly driven by **capillary forces**

Gives quality colloidal crystals (due to **directional crystallization** in the meniscus)



Driven by surface tension and capillary force in horizontal plane (Nagayama 1995)



Driven by interaction between particles and substrate in vertical plane (Jiang & Colvin 1999)

Limitation:

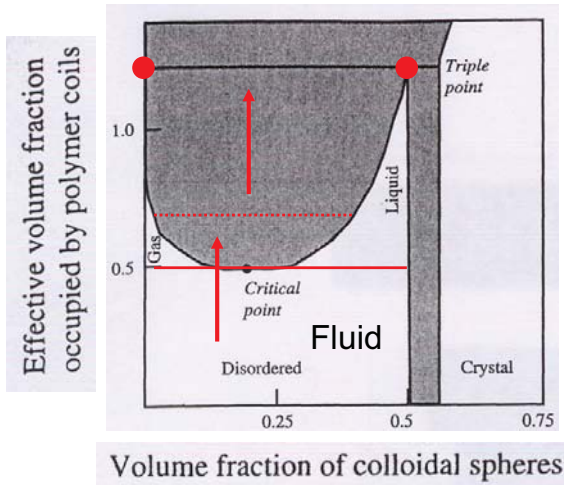
Long evaporation time & deposition limited to smaller colloidal particles

Sedimentation rate faster than evaporation rate: particles depart from meniscus (*Termination of process*)

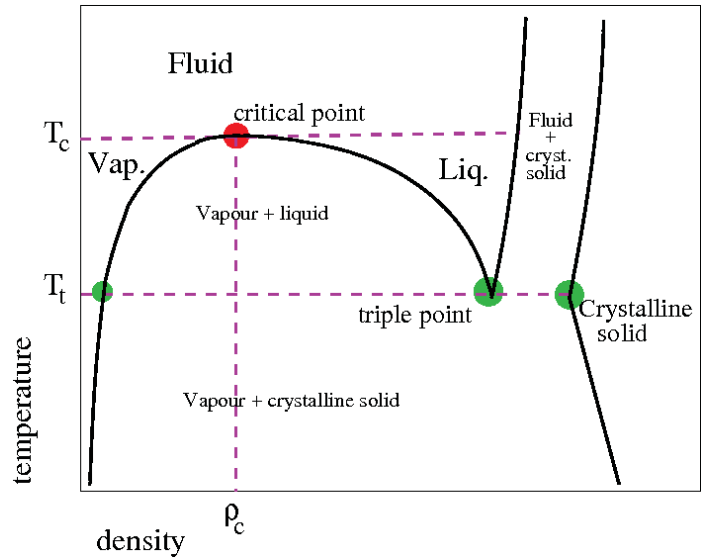
Colloids with weak attractions

- ✓ **Attractive interactions** leads to a disordered, condensed phase.
- ✓ Adding a **non-adsorbing polymer** creates a **weak attractive** part of the potential.
- ✓ The magnitude depends on the **volume fraction** of the polymer added.

Amount of added polymer as a function of particle concentration.



Calculated phase diagram for a colloid of hard sphere with added non-adsorbing polymer to the solution.



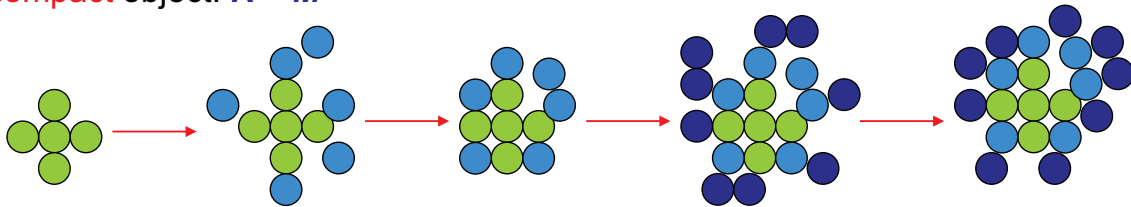
Colloids with Strong Attractions

Depending on the **depth of the attractive potential** we can have two situations:

- Attractive well \sim few $k_B T$: the phase transition is reversible and also equilibrium is easily reached

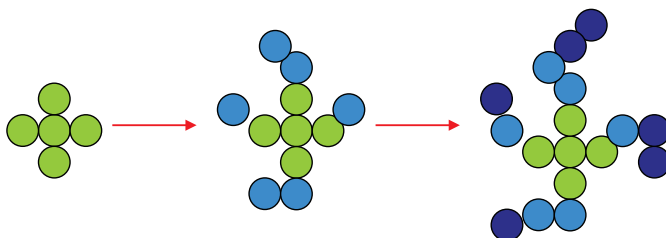
Aggregation with rearrangement leads to compact aggregates

3-D **compact** object: $R \sim M^{1/3}$



- Attractive well $\gg k_B T$: it is more and more difficult to reach equilibrium. If two particles come into contact and stick they take longer and longer to unstick.

Aggregation without rearrangement leads to fractal aggregates



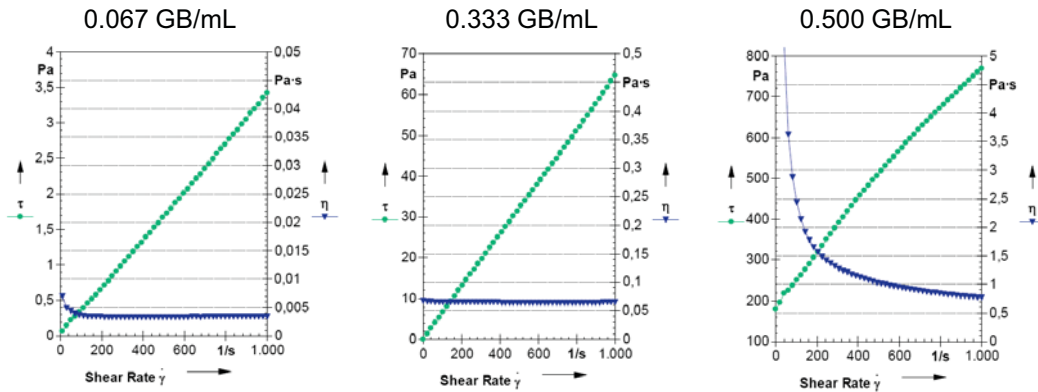
For a **fractal** object: $R \sim M^{1/d_f}$

Flow in concentrated dispersions



Adding particles to a liquid we might expect:

- Increasing in Viscosity
 - Pronounced non-Newtonian effects in flow (ex. Shear thinning)
- } gummy bear Solution !!!



For a **very dilute** suspension of hard spherical particles at volume fraction ϕ it can be shown that the viscosity is Newtonian with a viscosity η related to the viscosity of the dispersing liquid η_0 (*Einstein*)

$$\eta = \eta_0(1 + 2.5\phi)$$

For higher volume fractions the viscosity might depend on higher powers of the volume fraction or on the shear rate.

Dependence on shear rate:

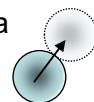
- If the shear rate is **large** then the structure of the system of the dispersion is perturbed by the flow.
- If the shear rate is **low**, then the Brownian motion will restore the arrangement of the particles to their normal rest state.

Dimensionless analysis: at which shear rate it might be expected to the flow to perturb the structure of the dispersion?



A characteristic time for the diffusion is given by the time taken for a sphere to diffuse a distance equal to its on size:

$$\tau_D = a^2 / D_{SE} = \frac{6\pi\eta_0 a^3}{k_B T}$$



The shear rate $\dot{\gamma}$ has dimensions of inverse time so, the characteristic time corresponding to this shear rate τ_{shear} is given by

$$\tau_{shear} = \dot{\gamma}^{-1}$$

The ratio of these two characteristic times τ_D / τ_{shear} is the dimensionless number called **Peclet number**

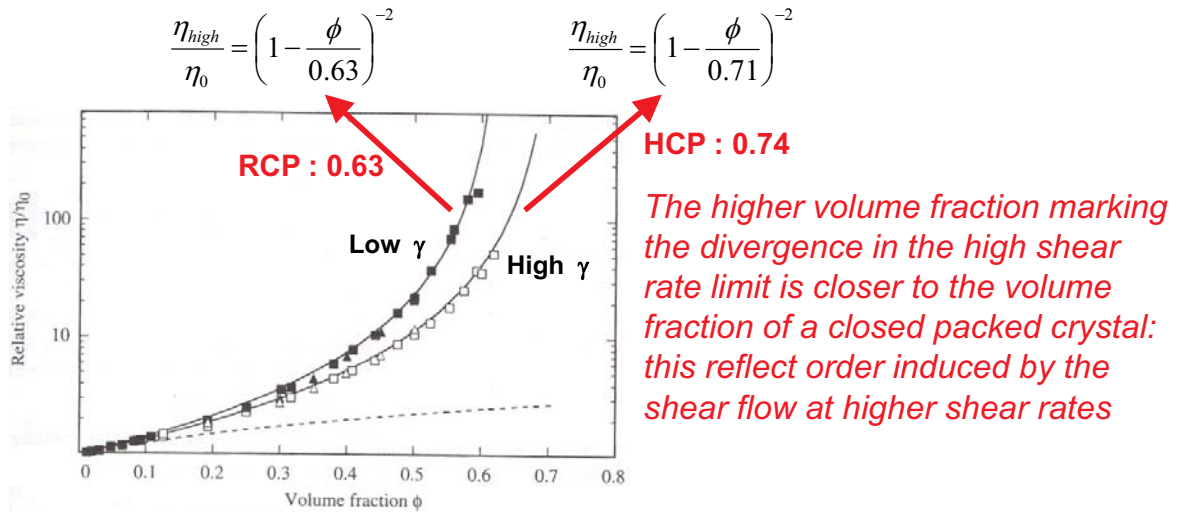
$$Pe = \frac{6\pi\eta_0 a^3 \dot{\gamma}}{k_B T}$$

Relative importance of shear and Brownian motion

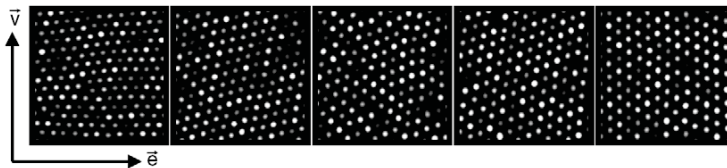
$Pe \ll 1$: Brownian motion able to maintain the dispersion on the unperturbed state

$Pe \gg 1$: Brownian motion is unable to restore the structure of the rest configuration on the timescale set by the shear rate

Example: Packing of hard spheres induced by shear rate



Example: HCP conformation induced by shear rate.



$$Pe \approx 2$$

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Confocal microscopy of colloidal dispersions in shear flow using a counter-rotating cone-plate shear cell
 Didi Derks, Hans Wisman, Alfons van Blaaderen and Arnout Imhof

Summary of Chapter 4

1. Types of colloids
2. Particle motion, Terminal velocity
3. Forces that act between colloidal particles
4. Methods to stabilize colloids: electrostatic, steric, depletion, Bridging flocculation etc.
5. DLVO theory
6. Colloids with attractive interactions
7. Flow in concentrated dispersions